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Arise, awake and stop not till the goal is reached.

- Swami Vivekananda

Abstract

The field of organic electronics, till recently a mere research topic, is currently making rapid strides and tremendous progress into entering the mainstream electronics industry with several applications and products such as OLED televisions, curved displays, wearable devices, flexible solar cells, etc. already having been commercialized. A major component in these devices, especially for photovoltaic applications, is a transparent conductor used as one of the electrodes, which in most commercial applications are highly doped wide bandgap semiconducting oxides also called Transparent Conducting Oxides (TCOs). However, TCOs exhibit inherent disadvantages such as limited supply, brittle mechanical properties, expensive processing that present major barriers for the more widespread economic use in applications such as flexible transparent conductors, owing to which suitable alternative materials are being sought. In this context we present two approaches in realizing alternative TCs using metal-polymer hybrid materials, with high figures of merit that are easily processable, reasonably inexpensive and mechanically robust as well.

In this context, our first approach employs laminated metal-polymer photonic bandgap structures to effectively tune optical and electrical properties by an appropriate design of the material stack, factoring in the effect of the materials involved, the number of layers and layer properties. We have found that in the case of a four-bilayer Au/polystyrene (Au|PS) laminate structure, an enhancement in optical transmittance of $\sim 500\%$ in comparison to a monolithic Au film of equivalent thickness, can be achieved. The high conductivity ($\sim 10^6 \Omega^{-1}\text{cm}^{-1}$) of the metallic component, Au in this case, also ensures planar conductivity; metallic inclusions in the dielectric polymer layer can in principle give rise to out-of-plane conductivity as well enabling a fully functional TC. Such materials also have immense potential for

several other applications owing to the sensitivity of this resonant tunneling effect, such as optical filters, optical power limiters, antireflection coatings, electrochromic devices, to name a few.

Our second approach to realizing an alternative flexible TC is based on random networks of Ag-NWs and their composites with various polymers that are electrically conducting or insulating. While considered a highly promising material system with a potential to replace commercially used TCOs like ITO, the high variability in films of Ag-NWs fabricated from solutions is however a major issue for scalability and reproducibility. This variability can in turn be attributed partly to NW dispersion instability, which can be addressed by the use of polymer additives and modified solution chemistries. In preparing such composites, considerable attention has been given to the use of conducting polymers like PEDOT:PSS which can contribute to charge transport as well. We present here a systematic approach to obtaining quantifiably uniform, highly transparent and conducting films in a reproducible manner, with composites of Ag-NWs with both conducting (PEDOT:PSS) and non-conducting polymers (like PSS and PVA), demonstrating the effectiveness of such an approach. While Ag-NW films spun cast from solution show good electrical conductivity ($\sim 2\text{-}50\ \Omega/\square$) and high transparency ($\sim 70\text{-}90\%$), they also show high variability ($\sim 15\text{-}20\%$ in R_{Sheet} and NW coverage) and poor reproducibility. Ag-NW/polymer composites, on the other hand, show similar electrical and optical properties with high figures of merit but with lower variability and greater uniformity ($<5\%$ variation in R_{Sheet} and NW coverage). The composite films also show remarkable retention of electrical conductivity even after several cycles of mechanical flexing, further justifying the use of polymer-stabilized networks and paving the way for greater control and ease in processing transparent, conducting and flexible films for novel devices.

The Ag-NWs based TCs were also incorporated in organic solar cell devices to test for their efficacy in an application and their performances were compared to that of control cell devices having ITO as the TC electrode. We found that performances of Ag-NW/polymer composites, particularly those of PEDOT:PSS were comparable to ITO-based solar cells, with power conversion efficiencies $\sim 3\%$, thus demonstrating the effectiveness in using these TCs in potential commercial applications such as solar cells, OLEDs, displays, etc.

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*Sudarshan Narayanan, August 2014
Pittsburgh, PA*

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List of Abbreviations

0D	Zero-dimensional
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AAO	Anodic Aluminum Oxide
AFM	Atomic Force Microscope
AM	Air Mass coefficient
ATO	Aluminum-doped Tin Oxide
AZO	Aluminum-doped Zinc Oxide
BHJ	Bulk Heterojunction
CIGS	$\text{Cu}(\text{In}_x\text{Ga}_{1-x}\text{Se}_2)$ (Copper Indium Gallium Selenide)
CIS	Copper Indium Selenide
CNT	Carbon Nanotube
CVD	Chemical Vapor Deposition
DC	Direct Current
DI	De-ionized
DLS	Dynamic Light Scattering
DLVO	Derjaguin-Landau and Verwey-Overbeek
DMF	N,N-Dimethyl Formamide
DMSO	Dimethyl Sulfoxide
DOS	Density of States

ECL	Electron Channel Layer
EG	Ethylene Glycol
EM	Electromagnetic
FF	Fill Factor
FoM	Figure of Merit
FTO	Fluorine-doped Tin Oxide
FZO	Fluorine-doped Zinc Oxide
HFA	Hexafluoroacetone
HMDS	Hexamethyldisilazane
HOMO	Highest Occupied Molecular Orbital
HTL	Hole Transport Layer
I-V	Current - Voltage
IPA	Isopropyl Alcohol
ITO	Indium Tin Oxide
IZO	Zinc-doped Indium Oxide
J-V	Current (density) - Voltage
LCD	Liquid Crystal Display
LED	Light Emitting Diode
LUMO	Lowest Unoccupied Molecular Orbital
m-SWNT	Metallic Single-walled Carbon Nanotube
NREL	National Renewable Energy Laboratory
NW	Nanowire
OLED	Organic Light Emitting Diode
OPV	Organic Photovoltaic
OSC	Organic Solar Cell
P3AT	poly(3-alkyl thiophene)
P3HT	poly(3-hexyl thiophene)

PAA	poly(acrylic acid)
PANi	poly-aniline
PBG	Photonic Bandgap
PCBM	[6,6] phenyl-C ₆₁ -butyric acid methyl ester
PCE	Power Conversion Efficiency
PEDOT:PSS	poly(ethylene dioxythiophene):poly(styrene sulfonate)
PEM	Plane-wave Expansion Method
PET	poly(ethylene terephthalate)
PF	poly-fluorine
PPV	poly(phenylene vinylene
PPy	poly-pyrrole
PS	polystyrene
PT	polythiophene
PV	Photovoltaic
PVA	poly(vinyl alcohol)
PVD	Physical Vapor Deposition
PVP	poly(vinyl pyrrolidone)
RF	Radio Frequency
SCDF	Spherical Contact Distribution Function
SEM	Scanning Electron Microscope
SWNT	Single-walled Carbon Nanotube
TC	Transparent Conductor
TCO	Transparent Conducting Oxide
TE	Transverse Electric
TEM	Transmission Electron Microscope
THF	Tetrahydrofuran
TM	Transverse Magnetic

TMM	Transfer Matrix Method
UHV	Ultra-high Vacuum
UV	Ultra Violet
VASE	Variable Angle Spectroscopic Ellipsometry
VDW	Van der Waals
VLS	Vapor Liquid Solid
ZP	Zeta Potential

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Chapter 1

Introduction

Transparent conductors are becoming ubiquitous in a host of civil and military applications, including transparent electrical contacts in solar cells, antireflection coatings, heated glass for aircraft and automobile windows, heat reflecting mirrors for glass and incandescent bulbs, electrochromic devices and smart windows, electrodes for LCD displays, and photovoltaics. However, finding abundant materials with optimal electrical and optical properties and that can be produced economically is a particular challenge. Furthermore, many of the examples listed above are conductive only in the plane of the film or coating, whereas electrical contacts for device applications require uniform electrical conductivity in all directions.

The design of most transparent conductors usually involves selecting materials with reasonable combinations of optical transmission in the visible region and electrical conductivity; this process involves compromising one property for the other. In addition, the materials have to be carefully processed at optimal conditions to minimize microstructural defects and impurities.

1.1 Transparent conducting materials

Research on transparent conductors began as early as in 1907 when Badeker reported the coexistence of electrical conductivity and optical transparency in a film of CdO [1]. In the succeeding century a variety of materials have been found to be both optically transparent and electrically conductive; the different types of transparent conductors can be categorized as follows:

- **Ultra-thin metal films:** Very thin films of metals, especially Au, Ag and Cu are fairly transparent through the visible region since their skin depths, related to the optical extinction coefficients, are of the order of a few tens of nanometers [2, 3]. However, metal films, with plasma absorption frequencies due to interband transitions typically inside the visible region, are quite absorbing and reflecting.
- **Wide-bandgap oxide-based semiconductors:** Some oxides with bandgaps > 3 eV allow for transmission of light over the visible spectrum. However, such wide bandgap materials are either insulating (at room temperature) or mildly semiconducting (at higher temperatures). Hence, for a combination of optical transmittance and electrical conductivity to occur, one has to degenerately dope these materials to increase the free carrier density. This can be brought about either by introducing electron-donating impurities or through native stoichiometric point defects, namely oxygen vacancies [4]. With high electrical conductivity and optical transmittance, these oxides are the most widely used materials for commercial applications. Despite the advantages of high electrical conductivity and low optical absorption, transparent conducting oxides (TCOs) are typically associated with expensive instrumentation for processing, native defects, and diminishing supply of raw materials. Moreover, their brittle nature makes them unsuitable for applications demanding mechanical flexibility.

- **Conjugated polymers:** Discovered to possess (semi)conducting properties, conjugated polymers are used in OLEDs and are being developed for other organic electronic devices such as photovoltaic cells. Although they cannot compare in performance with their inorganic counterparts, they have been quickly absorbed for use in applications where high-speed performance is not an important criterion. Now, a variety of conjugated polymers, such as derivatives of polypyrrole and polythiophene [5, 6], are being investigated as transparent conductors. Very high transmittances and conductivities of the order of $\sigma \sim 10^2 - 10^3 \text{ S cm}^{-1}$ have been achieved. Environmental, thermal and chemical instabilities however limit their use in even mildly harsh environments.
- **Novel nanostructured materials:** A large body of current work in this area is dedicated to the study of novel materials like graphene, carbon nanotubes, metal nanowires, etc [7–11]. These new materials aim to serve as alternatives to conventional transparent conductors in certain niche applications which would demand mechanical flexibility, biocompatibility, inexpensive solution processing and thermal and chemical stabilities.
- **Photonic bandgap structures:** By utilizing the well-known physics of photonic crystals, interference effects in a periodic structure consisting of alternating layers having different dielectric functions can yield enhanced reflectance or transmittance over a tunable range of optical frequencies [12, 13]. While extensive work has been conducted on such structures for tuning the reflectance and transmittance, there are few reports in the literature that employ these structures to engineer films that are both optically transparent and electrically conductive.

This research study focuses on exploring alternative pathways to flexible, transparent conductors. The *first* approach to obtaining transparent conductors is based on

photonic bandgap structures, wherein layering of materials of varying dielectric properties in an appropriate manner has an effect on the optical and electrical properties of the structure. The *second* approach is based on random networks of silver nanowires and hybrid films of silver nano wires and a conducting polymer. These materials have the advantage of being easy to process and have the potential for scale-up.

1.2 Scope and outline of this thesis

1.2.1 Research objectives and hypotheses

The objective of this research work is to understand the role of microstructure in facilitating the fabrication of electrically conducting thin films that are highly transparent, easily processable and mechanically robust as well, by the use of metal-polymer hybrid material systems based on two approaches - (a) Laminated metal-polymer structures and (b) Metal-nanowire networks and their polymer composites. This work also endeavors to outline and verify factors that enable enhancement in performance of the chosen TCs and also improvements in technological relevance, i.e. the suitability for process scale-up and application to devices. To engineer materials capable of replacing commercial transparent conductors like ITO, a systematic study of the optical and electronic properties of such structures along with an insight into the nature of defects, film fabrication and processing methodologies, etc. and their influences on device performance is required.

Laminated metal-polymer structures as transparent conductors:

The aim of the proposed research is to provide an understanding of both the materials and structural relationships that will facilitate the application of the concept of ‘optical resonant tunneling’ to the fabrication of transparent and conducting (along

all directions) materials. The primary hypotheses that were tested are:

1. The optical absorption in metals can be significantly reduced by utilizing the favorable effects of optical resonant tunneling in metallodielectric composites, wherein light incident on such a structure can be localized within the dielectric layer, and hence away from the absorbing metal. A transparent dielectric layer can thus enable the realization of a structure that can transmit more light than a monolithic metal layer.
2. In the specific case of a laminated metallodielectric structure, there is an optimum configuration (pertaining to number of layer repeats, layer configuration - thicknesses and sequence) enabling demonstration of this effect, that will depend on the optical properties of the metal chosen. Although the applicability of the approach to polymeric (rigid or flexible) dielectric layers may appear to be a straightforward extension of previous work, it has never been demonstrated and it will provide the basis for the subsequent extension to flexible transparent conductors with high in-plane and out-of-plane conductivity.
3. The choice of metal can significantly alter the optical properties of the structure in consideration. Based on the characteristic absorption frequencies of different metals, the use of Ag is more suitable than Au to demonstrate increased transparencies over the visible wavelength spectrum.

Metal-nanowire/conducting-polymer composites as transparent conductors:

This project aims to establish improved processing pathways to Ag nanowire (NW)-based networked structures with solution-processed Ag-NW films. In particular, it is hypothesized that:

1. Addition of a polymer to Ag-NW dispersions will stabilize them and improve processability and facilitate more uniformly networked structures with reduced percolation thresholds and higher figure-of-merits (FoM).
2. The use of a conducting polymer (like PEDOT:PSS) will not only improve NW dispersion but also result in reduced sheet resistances in the composite film owing to the presence of alternate pathways for charge transport, especially at lower network densities. This effects further reduction in percolation thresholds and increase in FoMs, in addition to reducing surface roughness of the Ag-NW films, all factors critical to improved device performances.
3. When applied as a TC in photovoltaic devices such as organic solar cells, improvements in morphology of Ag-NW networks by the embedding of polymers will translate to improvements in device performance; by carefully tuning the fabrication process and the materials used, cell efficiencies comparable to that of ITO-based devices can be achieved.

1.2.2 Structure of thesis

The structure of this thesis is as follows -

Chapter 1 provides a generic introduction to the field of “transparent conductors”, continuing on to lay out the scope of this thesis along with the premise for the choice of materials considered here.

Chapter 2 describes the materials used as transparent conductors in greater detail, enumerating some of the limitations of TCOs with regards to processing, cost and flexibility and alternative material choices therein. Subsequently, concepts pertaining to optical resonant tunneling in laminated metallodielectric structures and transparent conducting silver-nanowire networks are also discussed, along with factors

that are key to improving processing of the same. Thereafter, a brief description of principles of photovoltaic energy conversion and organic solar cells is provided.

Chapter 3 describes the instrumentation employed in this work along with details of material-specific fabrication and characterization methods.

Chapter 4 presents results of our investigation of the applicability of optically resonant Au-polystyrene (Au|PS) laminate structures as potential TCs that are easy to process and mechanically robust. A systematic study of the factors relevant to tuning the structure in terms of number of layers, thickness of layers, optical properties, etc. for optimal performance is provided.

Chapter 5 reports on the use of solution-processed Ag-NWs as TC materials and the improvements achieved in dispersion, uniformity, electro-optical performance and mechanical resilience in the same, brought about by the incorporation of polymer additives.

Chapter 6 subsequently demonstrates the application of these approaches in realizing photovoltaic devices (solar cells, in particular) based on organic active materials, delivering performances comparable to that of ITO-employing solar cells.

Chapter 7 summarizes the results presented in this work whilst providing an outlook for potential directions for future research.

1.3 References

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Chapter 2

Background

2.1 Transparent conducting oxides

Transparent conducting oxides (TCOs) are a class of wide-bandgap oxides that have of late been extensively used for commercial transparent conducting applications. Possessing bandgaps of > 3 eV, these are known to be fairly transparent throughout the visible spectrum. In addition to being used for PV and other photovoltaic device applications TCOs are also considered for use as diffusion barriers[1], as light traps[2], as layers controlling contact work function and even as an interface between organic and other materials [3]. Since transparent conductors find use in a wide range of commercial applications such as lighting, displays, photovoltaics, touch panels, smart windows, EMI shielding, and anti-static coatings, to name a few, the transmittance and sheet resistance requirements correspondingly vary in a manner specific to the application. Table 2.1 provides a list of some common applications and corresponding transmittance and sheet resistance requirements therein. TCOs, in particular ITO, fulfill requirements for most applications because of the versatility in tunability of their electrical and optical properties.

The choice of a TCO appropriate for a particular application can be determined

2. Background

Table 2.1: Typical application-specific requirements for TC electrodes.

Application	% T range	% R_{Sheet} range $\Omega/\square$	Ref.
Touch screens	86-90	300-1000	[4, 5]
Displays	87-90	30-80	[4]
OLEDs	≥ 90	≤ 10	[5–7]
Solar cells	75-90	≤ 10	[5–8]
Antistatic coatings	≥ 90	≥ 1000	[5, 9]
Electrochromic cells	≥ 80	≤ 10	[10]
EMI shielding	≥ 70	≤ 10	[9, 11]

by considering a quantity known as the figure of merit [9], defined as the ratio of the electrical conductivity of the film to its optical absorption coefficient. Other critical factors include physical, chemical and thermal stabilities, work function, band structure, plasma resonance frequencies, ease of deposition, and cost of processing. To be made conductive they need to be degenerately doped as well.

Tin-doped indium oxide

Most TCOs are based on one of three different oxides – indium oxide, tin oxide or zinc oxide, of which, tin-doped indium oxide (ITO) is by far the most widely used TCO in displays, and as transparent contacts in solar cells, photodiodes, and LEDs. Commonly composed of 10% SnO_2 , ITO possesses the same structure as indium oxide, with Sn^{4+} substituting for some of the In^{3+} atoms. ITO is typically deposited using sputtering or electron beam evaporation techniques [10] at elevated substrate temperatures ($T_S \sim 250 - 400^\circ\text{C}$). The presence of oxygen vacancies increases its conductivity; the oxygen vacancies, in addition to the substitution of In^{3+} with an electron donating Sn^{4+} , makes ITO an n-type material. We have deposited ITO films on glass substrates having transmittance, $T > 90\%$, resistivities, $\rho \sim 10^{-5} \Omega\text{cm}$), and with measured energy band gaps of $\sim 3.5 - 4 \text{ eV}$ (See Table 2.2), consistent with

published literature [12], where highly transparent films ($> 95\%$) with low resistivities ($\rho \sim 7.2 \times 10^{-5} \Omega\text{cm}$) and large carrier concentrations ($N_e \sim 10^{21} \text{ cm}^{-3}$) have been reported [13].

Zinc oxide

Zinc oxide (ZnO) is another oxide that is very commonly used in PV window and display applications. Doped (typically with Al) ZnO thin films have been shown to have a resistivity as low as $\sim 2 \times 10^{-4} \Omega \text{ cm}$ and transmittances $> 95\%$. In comparison to ITO, ZnO films have an order of magnitude higher resistivity. However, in terms of cost, chemical and thermal stability, and to an extent, mechanical flexibility as well, ZnO films offer significant advantages over ITO. As with ITO, a high degree of control over oxygen pressure during sputtering is required for good quality ZnO films (that would have high crystallinity, fewer defects, and smoother film surfaces) owing to the easy reactivity of Al with oxygen [3]. While sputtering still remains the predominant method of depositing ZnO films, these can also be obtained by solution-processing [14] or even by electrolytic deposition [15], thus making ZnO more versatile and less expensive in terms of processing.

Tin oxide

Tin oxide (SnO_2), usually doped with F or Sb is considered as the TCO most suitable for large-area depositions, purely because of both the raw materials and processing being inexpensive. In contrast to both ITO and ZnO, tin oxide possesses the advantage of being easily deposited through chemical methods rather than PVD processes. Spray pyrolysis from chlorides (SnCl_2) and other organometallic precursors with low decomposition temperatures have yielded films with resistivities $\sim 6 \times 10^{-4} \Omega \text{ cm}$. Both F- and Sb-doped films (denoted as FTO and ATO, respectively) show similar properties and are often considered as a viable and inexpensive alternative to ITO for flexible applications [3].

Table 2.2 summarizes some important properties of In-, Zn-, and Sn-based TCOs. The table includes the common deposition methods and temperatures, as well as the figures of merit, electrical properties, and typical applications.

2.2 Limitations of TCOs

- Although ITO is considered to have the best combination of electrical conductivity and optical transmittance, it is not the best in either of these properties alone (Refer to table 2.2). High contact resistance with active layers in devices also limits their performance and hence efficiencies.
- High process temperatures, expensive equipment and instrumentation apparatus with fairly high maintenance requirements are disadvantages for large scale batch processing.
- These films are usually quite brittle and therefore not suitable for flexible contacts/electrodes. It does not form a low-resistance contact to all semiconductors either. Moreover, they are *n*-type as-grown and obtaining *p*-type material is difficult [9].
- Limited supply, large demand and thus increasing raw-materials costs, of late, for indium is a major concern for the future outlook for many technologies that rely on ITO as a transparent conductor [16].

Contact resistance

Despite their extensive use in devices manufactured commercially, TCOs do suffer from high interfacial/contact resistance to metal contacts as well as active layers in optoelectronic devices, like a-Si, CdTe, CIGS and even polymer-based materials like

^aData on cost of commercial product not available.

2. Background

Table 2.2: Summary of TCO properties (Sources: [3, 9])

Material Properties	Type of TCO		
	Indium based	Zinc based	Tin based
Dopants	Sn (ITO), Zn (IZO)	F (FZO), Al (AZO) , In, Ga	F (FTO), Sb (ATO)
Typical deposition methods	DC/RF sputtering	DC/RF sputtering, sol-gel methods	DC/RF sputtering, spray pyrolysis
Deposition temperatures	250-400°C	300-500°C	450-650°C
Sheet resistance ($\Omega/\square$)	$\sim 6 - 10$	$\sim 5 - 20$	$\sim 8 - 20$
Resistivity ($\Omega \text{ cm}$)	$1 - 3 \times 10^{-4}$	$4 - 5 \times 10^{-4}$	$\sim 6 \times 10^{-4}$
Figure of Merit (σ/α)	4 (ITO)	7 (FZO)	3 (FTO)
Work function (eV)	4-4.8 (ITO)	4.2 (FZO)	4.9 (FTO)
Typical applications	Displays, OLEDs	PVs, displays	Energy-efficient windows, PVs
Cost ($\$/m^2$)	$\sim 15 - 65$ [17]	$\sim 20-30$ [18]	– ^a

PEDOT:PSS, to name a few. According to a report [19], the interfacial regions in solar cells govern their performance to a great extent and hence have to be carefully controlled. The maximum permissible value for contact resistance is $\sim 10^{-2} \Omega \text{ cm}^2$; higher resistances lead to increased parasitic losses in the device, thereby limiting its efficiency.

In this regard, there have been some studies that have looked into contact resistances of conventional TCOs like ITO and ZnO with *p*- and *n*-type amorphous Si (a-Si:H) films, since a-Si:H is used as an active layer for high-efficiency solar cells currently. Guse *et al.* reported contact resistances of $\sim 0.5 - 4 \Omega \text{ cm}^2$ for SnO_2 based TCOs with *p*-type a-Si:H [20, 21] which is above the ideal permissible limit. The primary reason for increased contact resistances is the transformation of the electrical contact between an as-deposited ITO (or any other TCO) layer and the Si layer from an Ohmic one

to a Schottky one, on annealing [22]. Thermal annealing of oxide films is usually a necessary step in TCO processing to obtain films with sufficient conductivities, and results in improved crystallinity and also migration and substitution of the dopant atoms at the lattice sites. However, thermal annealing in the presence of an interfacial layer of Si (as in this case) leads to diffusion of In atoms (in ITO) towards Si and that of dopant atoms from Si towards ITO, where the amount of diffusion has been shown to be independent of the annealing temperature [23, 24]. Similarly, diffusion of In into organic layers has also been reported to play a role in increasing interfacial resistance and hence limit the efficiency of organic optoelectronic devices [25, 26].

2.3 TCO alternatives

It has been suggested that ITO and some of the TCOs will retain their dominance over the transparent conductors market, especially in applications like rigid flat-panel displays and high-performance capacitive touch screens where emphasis on optimum transparency and conductivity outweigh cost concerns [16]. However, for applications that require flexibility, as in the case of flexible, printable electronics and displays, owing to limitations of TCOs, including that of ITO as earlier mentioned, there has been increasing interest in alternatives that are not only easy and inexpensive to process, but also readily available and non-brittle [27].

Over the past few years significant advances have been made in recognizing the potential for various candidate materials, prominent ones among which include carbon nanotube (CNT) films, graphene (mono- and multi-layered films), metal gratings and even random networks of metal nanowires (Figure 2.1) [28]. In addition to these, some polymer alternatives, often referred to as *conducting polymers*, have also been identified and evaluated for this purpose, like poly(ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) [29], and also other polymers

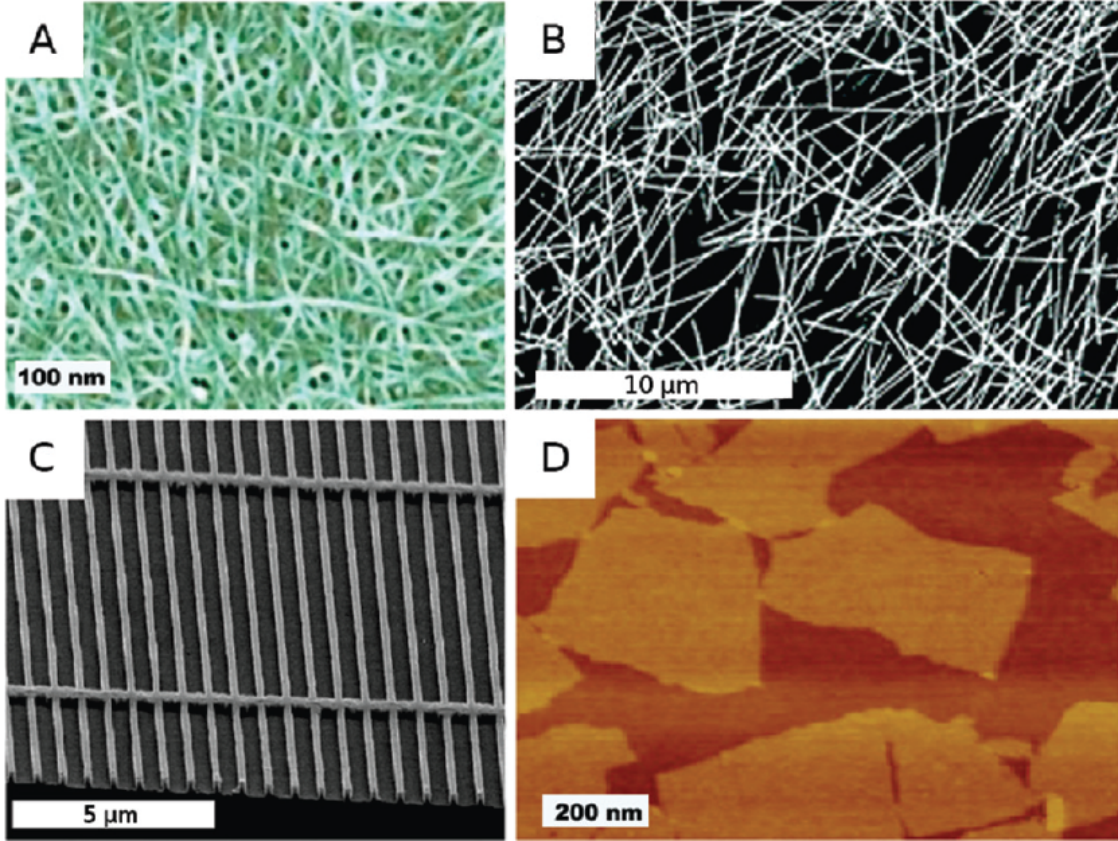


Figure 2.1: Candidate materials for transparent conductors. (A) Scanning electron micrograph (SEM) of a CNT film; (B) SEM of Ag-NW network; (C) SEM of Au NW grating and (D) atomic force microscope (AFM) image of solution-processed graphene films. Reprinted with permission from [28]. ©2010 American Chemical Society.

based on poly-pyrrole (PPy), poly-fluorine (PF), poly-aniline (PANi) [30–32]. However, polymeric materials fall short when compared to the other alternatives in terms of electrical conductivities, optical transmittances and even thermal stabilities, as a result of which composites of the former set of TCO alternatives with conducting polymers are also being studied.

2.3.1 Material systems and challenges therein

Metal nanowire (mostly that of Ag) networks have been shown to have sheet resistances (R_{sh}) of $\sim 16 \Omega/\text{sq}$ while being $> 85\%$ transparent (at $\lambda = 550 \text{ nm}$). To achieve equivalently low R_{sh} values, CNTs have to be $> 100 \text{ nm}$ thick, but higher thicknesses yield lower transparencies ($\sim 60\%$) [28]. While conducting polymers like

2. Background

PEDOT:PSS can achieve R_{sh} of $\sim 100 \Omega/\text{sq}$ at 80% transparency [33], graphene films grown by CVD processes have demonstrated resistances of $\sim 200 \Omega/\text{sq}$ with $T = 85\%$, and those obtained by solution processing have much higher resistance values ($\sim 400\text{--}500 \Omega/\text{sq}$) for similar transmittances. Although even a 7 nm thick graphene film should theoretically have an R_{sh} of $< 10 \Omega/\text{sq}$, the high density of grain boundaries associated with small grain sizes for the graphene flakes and defects therein, renders the resulting film highly resistive [28, 34, 35]. Multilayer structures using ITO and metals like Au and Ag have also been observed to not only increase electrical conductivity but also optical transmittance by way of utilizing optical interference effects brought about by the use of such structures [36, 37]. While sheet resistance for these structures are 1-2 orders of magnitude lower than that of a sole ITO layer, the presence of a metal increases optical absorption in the visible spectrum thereby decreasing the overall transmittance of the structure.

The material systems discussed above offer, among others, some significant advantages over conventional TCOs –

- ◇ Mechanical flexibility, which is relevant for use in flexible devices and displays
- ◇ Versatility/ease of processing; solution-based methods enable roll-to-roll processing and even printing
- ◇ Less expensive than ITO and even other TCOs.
- ◇ Abundantly available raw materials

Despite these advantages, none of the alternatives have been studied sufficiently well that they can replace ITO completely within the manufacturing process. The reliability and reproducibility of these films over repeated processing steps having consistently high transmittance and conductivity, comparable to that of ITO, is still

a factor that will determine the possibility of complete adoption of any of these materials as a replacement. Here it is also worth mentioning that in lieu of diverse requirements for devices and applications with respect to the TC properties, different materials may be deemed fit to take up the role; no one material can replace ITO in its entirety [16]. Some of the above material systems are discussed in more detail and specific challenges pertaining to each of these are also briefly discussed below.

Carbon-derived transparent conductors

1. **Carbon nanotubes:** CNTs are composed of carbon, one of the most abundant materials available on earth. They are essentially long hollow structures having walls that are formed with monolayer sheets of graphite. Rolling these nanotubes at specific and discrete angles and the radius of the tubes thus formed determine their properties, i.e. whether they turn out to be metallic or semiconducting. With the entire last decade spent in studying the properties of CNTs, they are currently the most mature material system possessing ample potential to replace ITO in several different applications.

Challenges: For TC applications however, metallic single-walled CNTs (m-SWNTs) are required which are difficult to synthesize in a selective manner [38]. Also, as mentioned before, films thicker than 100 nm have to be fabricated in order to obtain low sheet resistances, which in turn affect their optical transmittance [28]. Being a networked system, percolation plays an important role in determining critical network densities necessary for conduction [39]. The use of surfactants to stabilize CNTs in dispersion also tend to increase nanotube-junction resistances [40].

2. **Graphene:** This material too is composed of carbon and is essentially a monolayer of graphite which is known to be a very good conductor of electricity.

A CNT too is in essence, a graphene sheet rolled into a tube, with the manner of rolling determining its electrical conductivity. As mentioned earlier, in principle a film containing even a few sheets of graphene stacked one over the other would be highly conductive with very high transmittance. Graphene films can be obtained by several methods, the most common ones being: (a) heating SiC at elevated temperatures to reduce it to graphene [41]; (b) reduction of alkanes and other organic materials in a CVD chamber over lattice matching substrates; (c) exfoliation of graphitic oxide by a high temperature annealing step and (d) liquid-exfoliation using functionalized graphene followed subsequently by annealing [42].

Challenges: The CVD-processed graphene films have excellent properties while solution processed ones are more resistive. Regardless, the presence of large grain boundaries along small-sized grains, as well as defects in these graphene flakes significantly reduce the number of inter-flake tunneling probabilities, leading to sheet resistances that are very high in comparison to ITO and even to other nanomaterials. Morphological differences from one film to another also renders the fabrication process less repeatable/ reproducible. Yet another factor that limits conductivity of graphene is the incommensurate stacking of layers. Monolayers of graphene, while being highly conductive, are extremely difficult to fabricate, and as in the case of CNTs, multilayered sheets are obtained during processing. Weak inter-sheet interactions resulting from a large inter-sheet distance (as in the case of bulk graphite) thus affects conductivity [34, 35].

3. **Conducting polymers:** These are typically derived from conjugated polymeric systems as mentioned before, with PEDOT:PSS, a poly-thiophene derivative, being one of the most widely studied polymer for use as a

transparent conductor. While PEDOT:PSS films with sheet resistances between 50–100 Ω/sq have been obtained, pushing the limits of conductivity beyond this is still a challenge. Depending on how the films are processed, what chemical additives are used to treat the film, the conductivity of PEDOT:PSS can vary by several orders of magnitude.

Challenges: Since electrical conduction is dominated by charge hopping between polymer chains, a major challenge with conjugated polymeric systems is the anisotropy of charge transport that is very closely associated with the morphology, ordering and arrangement of polymer chains. In the case of PEDOT:PSS, another dimension that has to be factored into is the separation between the two components, PEDOT and PSS (as will be discussed in a later section) [29].

One-dimensional photonic bandgap structures

As mentioned before, one-dimensional multilayer structures having alternate metal and ITO layers have been fabricated that have good transmittance with improved conductivity as well. More effective use of optical interference effects can be obtained by careful design of metallodielectric multilayer stacks so as to concentrate a larger fraction of incident light inside the non-absorbing layer, as demonstrated by Scalora *et al.*, through what is known as optical resonant tunneling [11]. In these, while an enhancement in transmittance can be achieved by such structuring, out-of-plane or transverse conductance is not possible because of the presence of insulating dielectric layers.

Challenges: Two primary challenges can be identified with existing demonstrations of the optical resonant tunneling approach. First, all material systems studied to date correspond to brittle materials that do not lend themselves

to the application in the area of *plastic electronics* – one of the key application areas for ITO replacement materials. Second, in all reported studies the choice of materials renders the layered stacks lateral conductors but insulators in transverse direction. It is necessary to develop alternative fabrication strategies that will overcome these limitations and thus facilitate flexible transparent conducting composite materials with (approximately) isotropic conductivity.

Metal nanowire (NW) networks

Research on film coatings from networks of metal nanowires is fast gaining ground, as they are amenable to both easy processing and scaling. With sheet resistances of $\sim 10 \Omega/\text{sq}$ for $> 85\%$ transmittances, metallic nanowires, specifically those of Ag have demonstrated properties that are on par with what ITO films can achieve. Just as in the case of CNTs, these nanowires can also be easily flexed without compromising their performance. Nevertheless, there are several challenges with these systems that still limit their use in high-performance and high-efficiency photovoltaic devices.

Challenges: Electrical conduction in these networks depend on the existence of a percolating path/channel to conduct electrons. This very condition limits the simultaneous increase in electrical conductivity and optical transmittance, since a reduction in the thickness/density of the films/conducting units (nanowires), causes a dramatic increase in the sheet resistance, effecting a marked deviation from bulk-like behavior [34, 43, 44]. Meanwhile, at higher nanowire concentrations aggregation effects for solution-processed films hamper their reproducibility and attainable transmittance. Another limitation for solution-synthesized nanowires is the presence of a thin native poly(vinyl pyrrolidone) (PVP) coating that impedes effective contact between nanowires. Over and above, high surface roughness in these films often leads to current leakage in organic photovoltaic (OPV) devices [45].

2.3.2 Alternative approaches towards microstructured transparent conductors

Despite the several challenges and limitations even with the alternative material systems discussed above, it is evident that there is enormous potential in each of these, to replace ITO for most applications. However, to optimize the performance of these materials, rather than seeking newer materials, it is necessary to outline novel strategies that enhance functionality of these very materials so as to not only push them beyond current transparent conductor requirements but also evaluate their applicability and relevance in other functional devices. In this regard we discuss here in greater detail two approaches that we understand to have the ability to compete well with existing technologies –

- Optical resonant tunneling in laminated metal-polymer structures for transparent conductors and other applications
- Networked metal nanowire-polymer composites for flexible, transparent and conducting devices

2.4 Laminated metal-polymer structures

2.4.1 One-dimensional photonic bandgap structures (PBGs)

Whilst literature abounds with reports on ways to tune the electronic and optical properties of materials, only more recently has the control of optical properties of materials through structures known as photonic crystals been explored [46, 47]. These structures respond to incident light in a unique manner, exhibiting the presence of a photonic bandgap (PBG) in addition to tunable transmittance or reflectance, thereby encouraging their use in optical devices like optical limiters and switches, optical diodes and transistors, etc [11].

2. Background

In crystalline materials, electrons propagate as waves that are governed by periodicity in the atomic potential arising from a periodic arrangement of atoms in the crystal. By analogy, light waves can also propagate through a photonic crystal with a periodic dielectric structure. Hence, just as the periodic lattice prohibits the propagation of electron waves of certain energies (wavelengths) leading to the formation of an electronic energy bandgap, a periodic dielectric function (or index of refraction) forbids propagation of light in certain directions and for certain ranges of wavelengths, analogously called the photonic bandgap (PBG) [47].

One-dimensional PBG materials are layered, periodic structures comprising materials with different dielectric functions and hence optical constants. The structure is similar to that of a stacked Fabry-Perot etalon or a Fiber Bragg Grating. In these structures, interference of multiply reflected light between two highly reflecting surfaces, leads to either a transmission minimum or a maximum, which depends on conditions determined by the wavelength of light, angle of incident light and the distance between the reflecting surfaces (Figure 2.2).

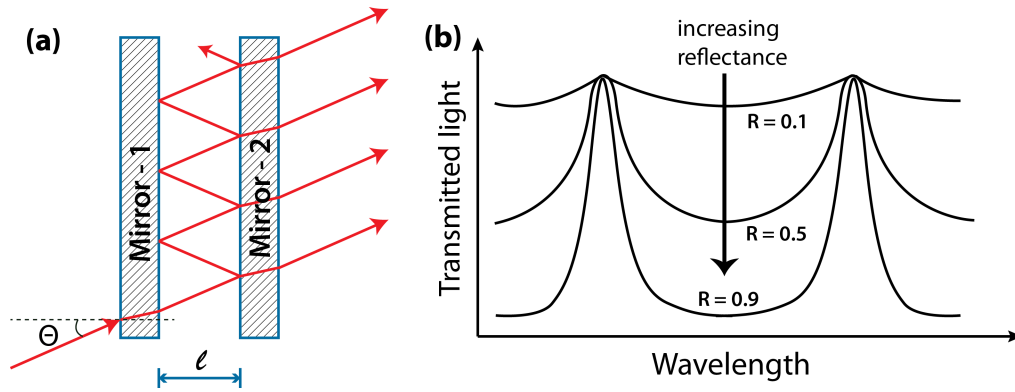


Figure 2.2: (a) Transmission from multiple reflections through a Fabry-Perot etalon – schematic; (b) Intensity of transmitted light through this structure as a function of wavelength and the reflectance of the mirror.

The periodicity in the dielectric function for such structures gives rise to a PBG, the size of which depends on the dielectric contrast (Figure 2.3(a) and (b)). Of particular

2. Background

interest to this proposal are the band edge regions where a set of degenerate standing wave solutions to Maxwell's equations is obtained such that, in the lower band edge, localization of the electric field intensity (of the incident electromagnetic wave) is maximized in the layer with higher dielectric constant (i.e. a higher refractive index) and vice versa for the higher band edge, as shown in the lower and upper diagrams, respectively, in Figure 2.3(c).

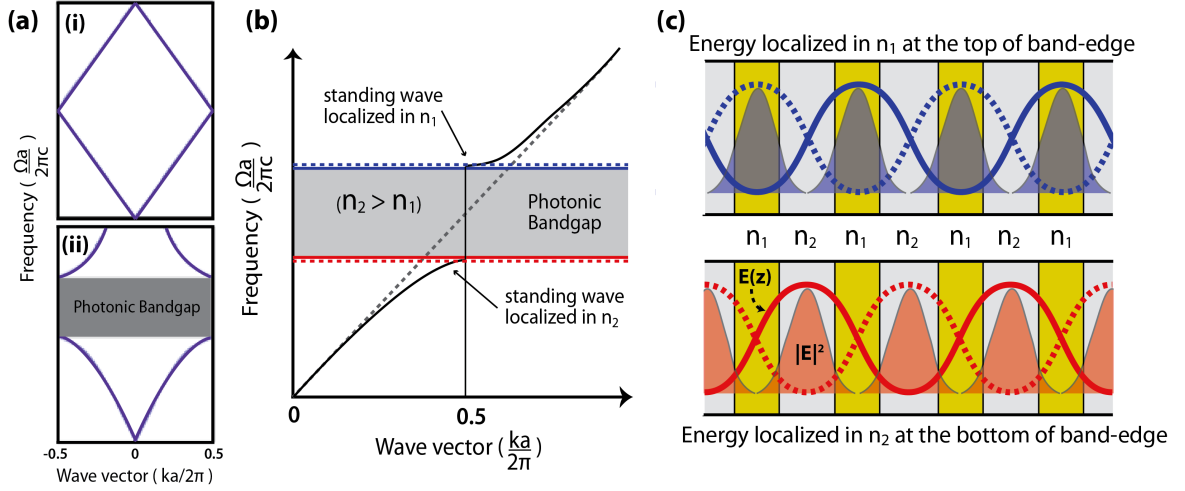


Figure 2.3: (a) Photonic band structure in a **reduced zone plot**, for multilayer films with (i) the same dielectric constant and (ii) different dielectric constants; (b) Optical dispersion curve depicting photonic bandgap and effects at the band edges in an **extended zone plot**; (c) Electric field distribution and energy localization in the 2 dielectric layers above and below the gap (Figures adopted from [47]).

The band structure for a generic photonic crystal, with periodic dielectric layers having no optical dispersion (wavelength dependent optical constants), can be numerically obtained using, for example, the plane-wave expansion method (PEM). This method numerically solves for the Maxwell's equations and generates the eigenvalue energy solution set [48]. The simplest algorithm however assumes an infinite crystal. The reflection and transmission characteristics of the same structure can be obtained using a propagation/transfer matrix method (TMM), as described in reference [49].

2. Background

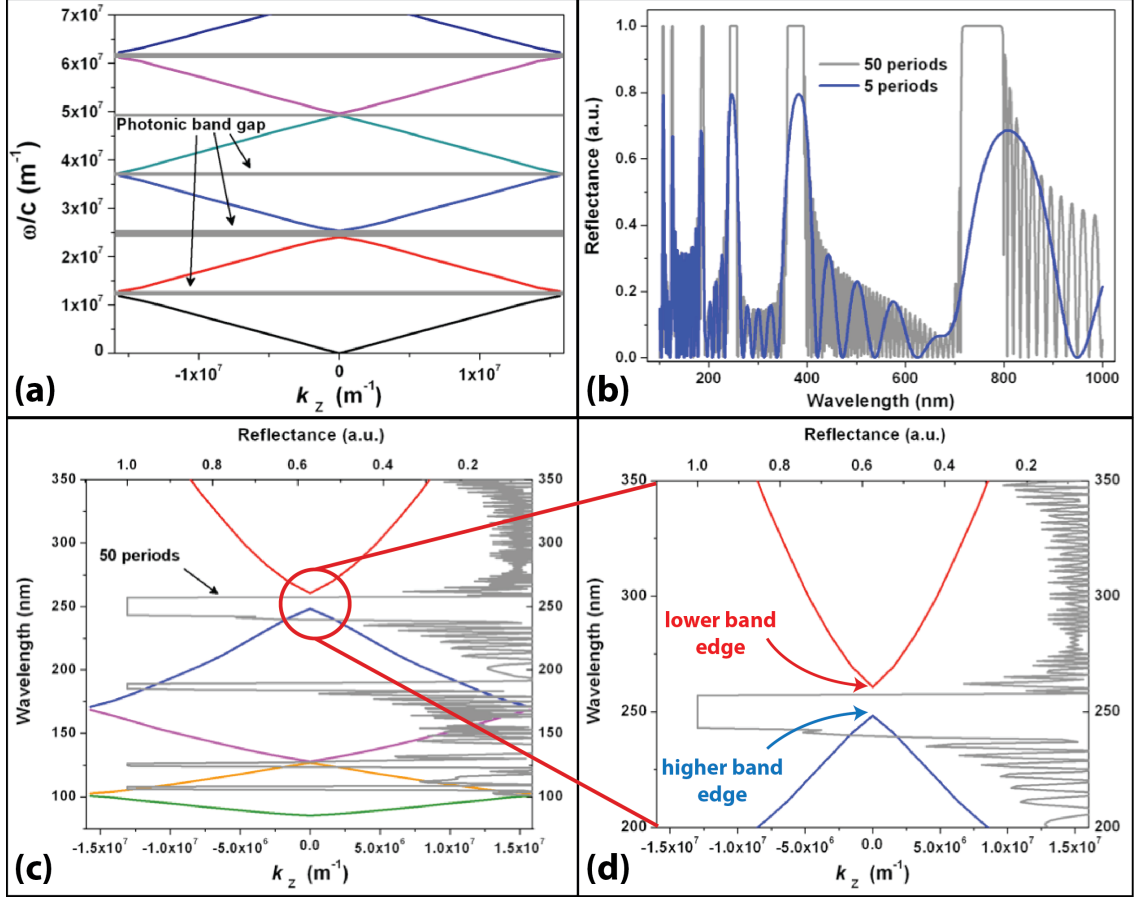


Figure 2.4: (a) Band structure for a periodic dielectric bilayered structure ($n_1 = 2$, $d_1 = 100$ nm, $n_2 = 1.5$, $d_2 = 50$ nm); (b) Reflectance spectra for the stack for 5 and 50 periods; (c) Comparison of the band structure and reflectance plotted as functions of wavelength for 50 periods and (d) a zoomed in plot showing coincidence of reflectance peak and PBG.

For example, in a periodic stack with 2 materials having refractive indices of 2 and 1.5, with thicknesses 100 and 50 nm respectively, the band structure develops as shown in Figure 2.4(a). Using TMM, the reflectance calculated is as shown in Figure 2.4(b). The number of periods in the structure determines the nature and shape of the reflectance peaks as shown in the same figure. By plotting both energy (frequency) and reflectance of the structure as a function of wavelength, as in figures 2.4(c) and 2.4(d), the photonic band gap can be directly matched with reflectance peaks, showing that the band gaps are regions of minimum transmission. Thus, the trailing edge (high wavelength edge) of the reflectance peaks corresponds to the lower photonic band-edge and the leading edge (low wavelength edge) to the higher band-edge. As the

thicknesses and optical constants of the layers are varied, so do the band structures and consequently the reflection spectra. This direct correlation between reflectance and the photonic band gap gains prominence in structures where optical dispersion is present and is complex, like for metals, because of the difficulty in obtaining the band structure.

2.4.2 Metallodielectric structures as PBGs

Metals, being conductive materials, with their free carrier plasma resonance/absorption frequencies usually inside the visible spectrum, are typically highly reflective and absorptive in all wavelength ranges of interest. The strong absorption of metals arises due to fully occupied d-states in conjunction with the high free electron density close to the metals' Fermi levels, thus giving rise to interband and plasma absorption of incident electromagnetic waves [50]. The pronounced optical absorption of metals limits the distance that light (or other electromagnetic waves) of practical wavelengths can travel through a metal without incurring significant loss. The latter is often described in terms of the '*skin depth*', δ , which corresponds to the distance along which the intensity of the wave $|E|^2$ decreases to $1/e$ of its value at the surface (where e denotes the Euler number). The small skin depth ($\delta \cong 10$ nm) of noble metals such as gold or silver in the visible wavelength range thus limits the application of metallic elements to ultra-thin films if optical transparency is to be retained. An elegant approach to reduce optical losses in metal film structures was presented by Scalora and coworkers who demonstrated that the transmittance of laminated metallodielectric structures can be increased by several orders of magnitude as compared to monolithic metal film structures by taking advantage of a phenomenon called 'optical resonant tunneling' [11, 51]. The latter refers to the effect of a suitably engineered periodic grating structure to redistribute the electric field of an incident electromagnetic wave such

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that at absorbing frequencies the field is concentrated within the non-absorbing dielectric component while being depleted from the absorbing metal regions. As a consequence light traversing the optically resonant structure experiences reduced absorption.

Scalora *et al.* originally demonstrated this concept with a system of alternating layers of Ag and MgF_2 showing enhanced transmittance even with the metal having a total thickness of several skin depths (see Figure 2.5). While the transmittance of a pure 40 nm Ag film was improved from 45% to almost 75%, by slicing into 4 equal 10 nm films sandwiched with intervening 110 nm MgF_2 layers, 20 such layers of 10 nm Ag sandwiched with intervening 140 nm MgF_2 layers effected a dramatic increase of 7 orders of magnitude in the transmittance in comparison to the original 200 nm Ag film.

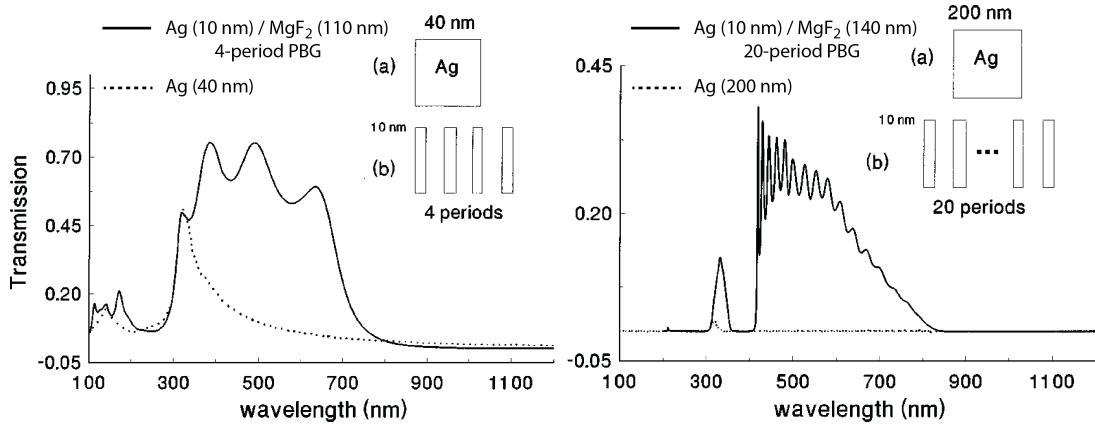


Figure 2.5: Enhancement of transmittance in Ag|MgF₂ MD-PBGs. Reprinted with permission from [11].

To date, the application of resonant tunneling to enhance the transmittance of metal-hybrid structures has focused on ceramic/metal ($\text{MgF}_2|\text{Ag}$) structures that allow for particularly efficient tunneling due to the favorable mismatch of the dielectric constants of the respective constituents (see discussion below). However, the brittle mechanical characteristics of ceramics in conjunction with the (often)

weak interfacial bonding render the ceramic/metal composite materials sensitive to mechanical damage or thermal-induced delamination that limit the application of ceramic/metal laminate structures [52].

2.4.3 Multi-functional metal-polymer composites

As described in the previous subsection, metallodielectric structures find enormous potential in several applications owing to the tunability in their optical properties. Meanwhile, metallodielectric polymer-matrix composite materials too have received attention as a material platform for applications ranging from broadband power limiters for electromagnetic shielding to antistatic coatings and optical materials [53–55]. A general drawback associated with the addition of metals to polymer matrices is the increase of absorption (as explained earlier) that – in most circumstances – prevents the application of metal-polymer composite materials in areas where optical transparency is required. An approach to circumvent this conundrum is by fabricating optically resonant polymer-metal laminate structures based on an established ‘design criteria’, such that the metal-polymer composite material can demonstrate enhanced increase of optical transparency (as compared to the respective monolithic structures) that retain the mechanical flexibility and robustness that is characteristic of polymer materials. The excellent electron conductivity of laminated polymer/metal hybrid structures that is imparted by the continuous metal component could render the resulting *transparent metallodielectric nanocomposites* a platform for innovative material technologies in areas such as plastic electronics, power limiting, or thermophotovoltaics for energy-recycling [37, 56–59].

Additionally, the use of “functional soft materials” adds a whole new dimension to the modulation of properties in these composites. For instance, large optical tunability has been reported for block-copolymer photonics gels having polyelectrolyte polymers

that are known to respond sensitively to a range of stimuli, lending themselves to chemical sensing applications [60]. The possibility of controllably localizing incident light in the dielectric layer also opens the door to optical light-limiting applications, where use of organic chromophore materials ([61, 62]) as the dielectric layer can lead to more efficient light-limiters. Another area where these structures are potentially applicable, is in the context of their thermal properties. Layered metal-polymer composites can in principle be used as tunable thermal resistors; Brillouin light-scattering spectroscopy studies, combined with theoretical calculations, for alternating porous silica (SiO_2) and poly(methyl methacrylate) (PMMA) stacks have shown the presence of large phononic band gaps [63].

2.5 Metal-NW networks and composites with polymers

2.5.1 Theory of electron transport in metal nanowires

In the context of solid-state and condensed matter physics, according to postulates of quantum mechanics, electrons are assumed to move freely within a bulk solid in all 3 dimensions. Based on this, the number of states per interval of energy that can be occupied by these electrons is what is known as the bulk ***electronic density of states (DOS)***. Owing to there being no spatial restriction on the free motion of these carriers, the density distribution so described happens to be continuous.

$$\mathfrak{D}(E)_{3D} = \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{E} \quad (2.1)$$

where,

- m_e = mass of electron
- $\hbar$ = Planck's constant
- E = Energy of electron state

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However, when the motion of the charge carrier (an electron typically) is spatially restricted in one, two or all three dimensions, the solid is no longer in the bulk state and its dimensionality reduces accordingly into either a quantum well (2D solid), a quantum wire (1D solid) or a quantum dot (0D solid) respectively. By spatial confinement, it is implied that the corresponding spatial dimension is $< \lambda_F$, which is known as the *Fermi wavelength* of the material under consideration. The *Fermi wavelength* is the wavelength corresponding to the Fermi energy level E_F of the solid as per the relation $\lambda_F = 2\pi/k_F$. For metals, λ_F is of the order of $\sim 0.5nm$, approximately the lattice spacing between atoms. Such confinement of electrons in these solids leads to a change in the electronic *DOS* as well. Additionally, depending on the dimensionality of the solid the *DOS* may or may not be a continuous function of the electron energy as shown in Figure 2.6 [64].

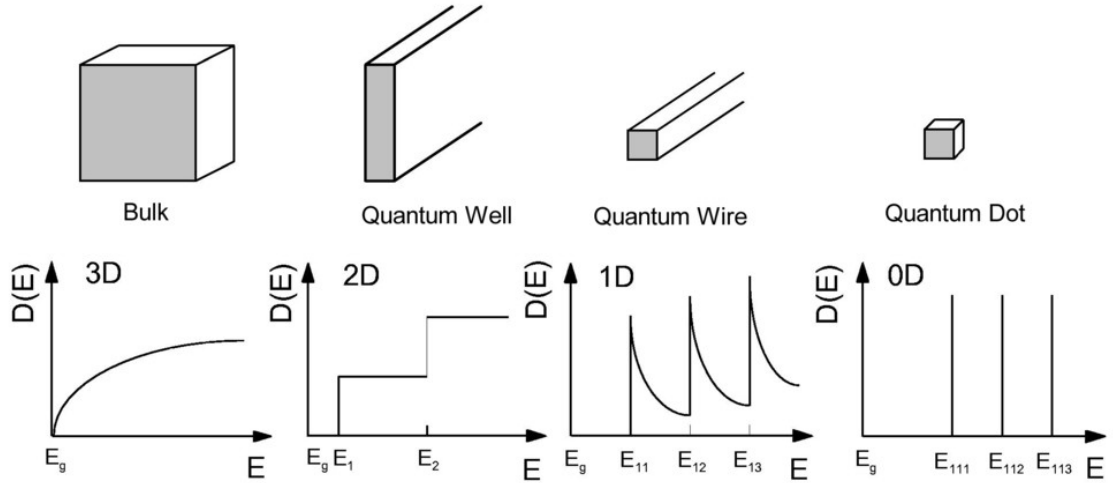


Figure 2.6: Density of states as a function of dimensionality of the solid. Figure from <http://www-opto.e-technik.uni-ulm.de/lehre/cs/> and [64]

Considering the specific case of one-dimensional quantum wires, the electronic density of states is given by the expression

$$\mathfrak{D}(E)_{1D} = \frac{1}{\pi} \left(\frac{2m_e}{\hbar^2} \right)^{\frac{1}{2}} \sum_n \frac{1}{\sqrt{E - E_n}} \tau(E - E_n) \quad (2.2)$$

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where,

E_n = Energy of the n^{th} quantized electronic state

τ = unit step function

It is evident from the above expression that energy is quantized for such systems where the electron is confined to move only in one direction.

The *electronic DOS* treatment for low-dimensional systems can be extended to understand their electronic transport phenomena as well. Based on the dimensions of the material, electron transport stands to be governed roughly by two regimes (also see Figure 2.7) –

1. **Ballistic regime** : In this regime, electrons can travel across the unconfined dimension (L) without scattering, provided $L < \lambda_{mfp}$, where λ_{mfp} is the electron mean free path for that material and $W < \lambda_F$, its Fermi wavelength. In this case, the conductance through the wire is quantized. The formalism for this was first proposed by Rolf Landauer in 1957 [65] and the quantized unit of conductance is found to be an integral multiple of universal conductance unit $G_o = 2e^2/h$ [66].
2. **Diffusive regime** : Here, carrier transport is predominantly mediated by scattering due to not only collisions between electrons, but also with phonons, scattering at the boundaries, lattice sites and other structural defects and also at impurity atoms. This is observed for nanowires that are longer than the λ_{mfp} of the carriers, i.e. $L \gg \lambda_{mfp}$ and $W \gg \lambda_F$.

The width of metal nanowires could be anywhere between a single atom to a couple of hundred nm, while the lengths could vary from a few tens of nm to even hundreds of microns. The mechanism of conduction would thus depend on the aspect ratio (length-to-diameter ratio) of the wires in consideration. Though these one-dimensional wires with diameters in the nanometer scale are loosely classified as

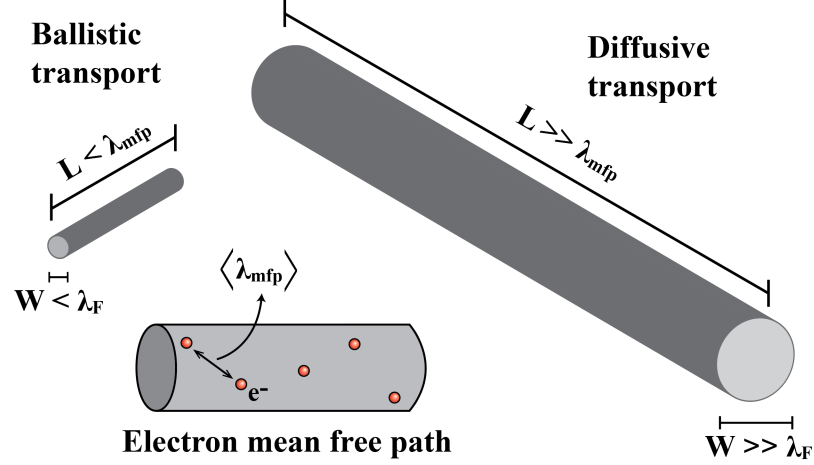


Figure 2.7: Cartoon showing criteria for charge transport in the ballistic and diffusive regimes

nanowires, accepted nomenclature in the literature suggest that wires with small aspect ratios ($\lesssim 20$) are typically referred to as nanotubes/nanorods while those with higher aspect ratios ($\gtrsim 20$) being considered as nanowires [67]. Thus, most metal nanowires in consideration have high aspect ratios, i.e. not only are they much longer than the mean free path distance of electrons, but also wider than their Fermi wavelength as a result of which electronic transport is predominantly as described for classical wires, obeying the relation –

$$G = \sigma \frac{A}{L} \quad (2.3)$$

where,

G = Wire conductance

L = Length of the wire

A = Cross-sectional area of the wire

σ = Conductivity of the wire, a material property

2.5.2 Synthesis of nanowires

Several physical and chemical techniques have been developed to synthesize metal nanowires and adoption of any of these methods is usually based on the target

application, required properties, aspect ratios, morphology and even orientation. Some of the most commonly used growth/fabrication approaches ([68]) are briefly discussed below –

Template-assisted synthesis

Templates have been used extensively to synthesize nanowires of all kinds, metallic and semiconducting, owing to the simplicity and intuitiveness of the fabrication procedure. This approach would typically involve the use of a host material with very small cylindrical pores or voids, inside which the chosen material is filled, thus adopting the structure of the pore itself. The host material thus acts as a "template" for the filler material to adopt the structure of a nanowire when inside the pores. The template can then be removed by etching or other chemical methods leaving just the nanowires behind. Despite the apparent simplicity of the process, before choosing a template, some important characteristics to consider are the chemical stability and mechanical properties, uniformity of pore size, density of pores and also chemical conformability to the material that would be used to grow the nanowires. In this regard, anodic alumina (AAO - Anodic Al_2O_3), nano-channel glass, ion track-etched polymers and even mica films are some of the most frequently used templates for nanowire synthesis.

Porous AAO templates are obtained from pure Al films that were anodized in different acids. During the anodization process the Al film, acting as the anode, gets oxidized due to migration of oxide ions through the electrolyte to the anode. Following the formation of the aluminum oxide barrier layer, an electric field focused locally on fluctuations on the surface leads to field-enhanced dissolution in turn promoting the growth of pores. Beyond this, the pores grow in a much more stable and uniform manner making it a two-step process [69]. Pore ordering occurs as a result of mechanical stresses from expansion at the aluminum-alumina interface during

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anodization. Based on the anodization conditions, pore sizes can be varied from $\sim 10 \text{ nm} - 200 \text{ nm}$ with pore densities ranging from $10^9 - 10^{11} \text{ pores/cm}^2$. The figure below (Figure 2.8) shows a schematic of the process involved in fabricating an AAO template. Another way of obtaining such templates is by bombarding non-porous sheets of Al or even polycarbonate material by ions. The damage tracks thus produced by ion-bombardment have been found to be chemically reactive and can thus be further etched to convert these tracks into pores [70]. The pore size can be controlled by the size of the ion used for bombarding the template sheet which gives greater flexibility in obtaining pores of different sizes.

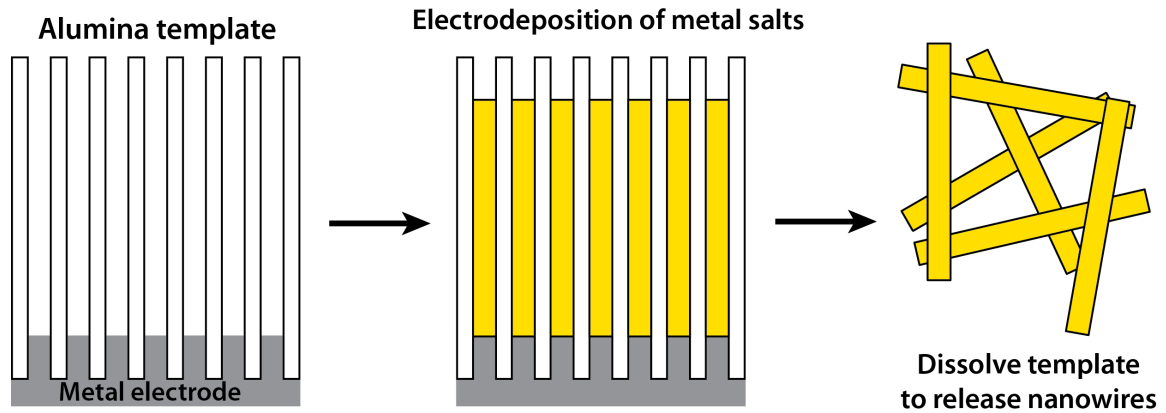


Figure 2.8: Schematic of electrodeposition of metal nanowires by a template-assisted method. Adopted from [71]

With the synthesized template, the nanowires can then be grown by various methods, the most common being an electrochemical deposition process, since growth by this method is known to be controllable in a direction normal to the substrate surface. In this process, a film of the metal to be fabricated into nanowires is deposited on the freestanding side of the membrane that would act as the electrode on which electrodeposition would eventually take place. The other side of the template with the oxide layer is etched to open the pores into which the electrodeposition solution is filled in. For AAO templates, where an Al sheet already exists as the anode metal, a thin layer of the metal, to be synthesized into nanowires, can be deposited within

the pores. By varying the current and duration of deposition, the aspect ratio can be easily controlled. Chemical etching of the template leaves behind an array of nanowires, while using a sacrificial metal layer that can be etched post deposition gives freely standing nanowires [67].

Vapor-phase synthesis

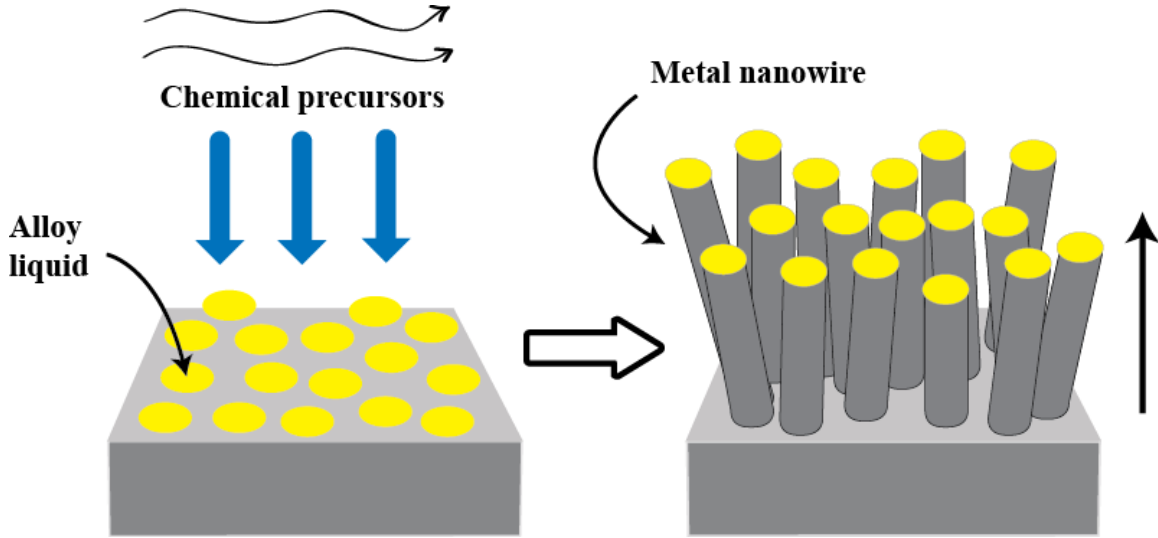


Figure 2.9: Schematic of Vapor-Liquid-Solid (VLS) method for vapor-phase synthesis of metal nanowires

Direct vapor-phase techniques like thermal evaporation and laser ablation have been known to produce nanowires, whiskers and similar 1D nanostructures of metals, metal oxides, semiconductors, etc. But among all vapor-phase synthesis techniques, the vapor-liquid-solid or VLS method has been shown to be the most successful in the growth of crystalline and metallic nanowires in large quantities. This is a technique that has been successfully used to grow different types of nanostructures including nanowires of metals and semiconductors and also carbon nanotubes. Essentially a CVD (chemical vapor deposition) process, the mechanism of growth is by the absorption of the target material introduced in the gas phase over a liquid droplet of catalyst. The absorbed metal forms a liquid alloy at high temperature which upon supersaturation precipitates the target material by way of a nucleation process. This

nucleated precipitate then acts as a seed for further deposition of material. Growth then continues over this seed in a preferential manner thereby promoting anisotropic growth in only one direction (See Figure 2.9). The nanowires so obtained are generally of high purity and the diameter of these nanowires depend on the size of the alloy particle [72].

Lithography techniques

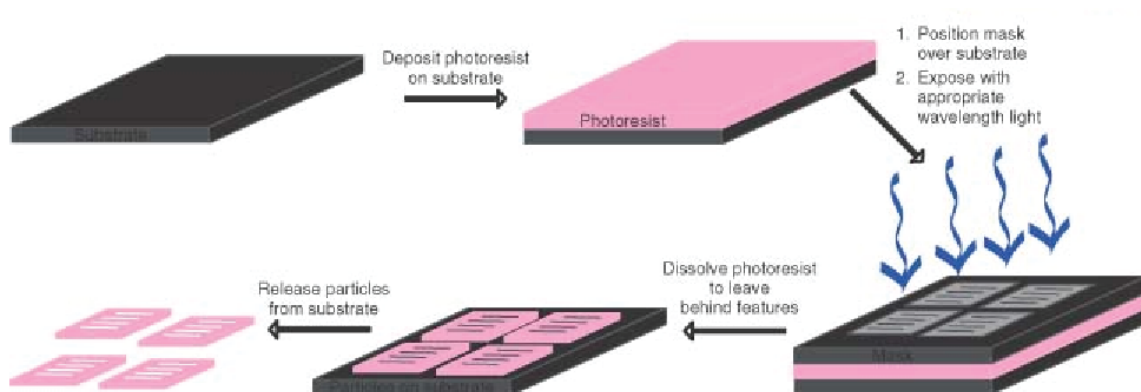


Figure 2.10: Schematic of lithography technique for fabricating metal nanowire patterns. Reproduced with permission from [71] © 2010 John Wiley & Sons, Inc.

Nanowires can be synthesized from patterns defined and created by lithographic processes also. This is especially useful when a specific pattern of nanowire(s) or even an ordered mesh of wires is required for a certain application. The fabrication steps here are fairly simple – a photoresist is applied to the substrate over which the nanowires are to be synthesized, and based on the diameter of the wires in question, the resist can then be developed either by photolithography or by electron-beam lithography. Nanowires with widths of the order of the wavelength of light can be obtained by photolithography and with improved pattern transfer techniques and higher resolution, the limit for the width can be pushed down to ~ 100 nm. For shorter widths though, an electron-beam would have to be used that can achieve widths as low as $\sim 1 - 10$ nm. The required metal can then be vapor-deposited within the patterns. An ordered array/mesh of nanowires or even strategically placed nanowires

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can be obtained post development of the photoresist (Figure 2.10). While very precise control of lengths, widths and density of nanowires is possible, this approach is not only time-consuming but expensive as well [73].

Solution-phase synthesis

Since vapor-phase methods typically require large infrastructure and expensive processing, they may not be ideal for obtaining a large quantity of nanowires at relatively low costs using simpler laboratory setups. Most electrochemical methods also use template-assisted synthesis approaches to grow nanowires. With chemical stability of the templates being an issue in addition to the problem of formation of aggregated bundles of nanowires instead of individual ones, these too are not considered ideal for large scale processing. In this regard, over the last decade or so, solution-based approaches have gained importance and wider acceptance as the predominant processing method for obtaining nanowires industrially and on a large scale, while maintaining uniformity in properties.

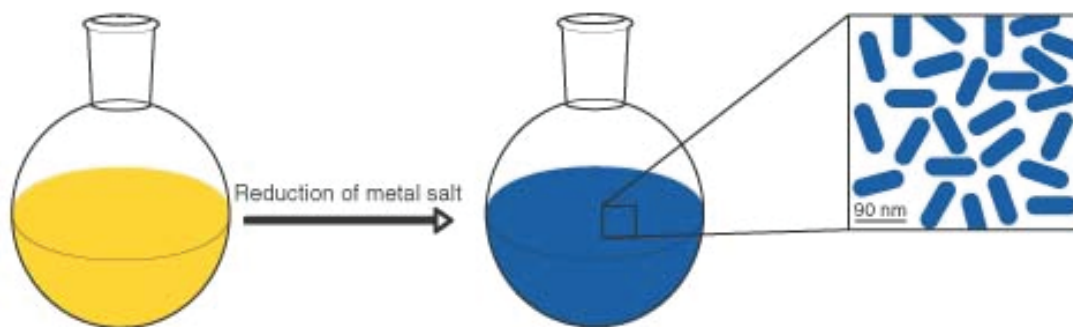


Figure 2.11: Schematic of solution-phase synthesis technique for metal nanowires as per the polyol method. Reproduced with permission from [71] © 2010 John Wiley & Sons, Inc.

Solution processing of nanowires essentially involves the formation of a seed crystal of the material in consideration (or even a similar lattice-matched material) in solution by reducing it from an ionic state, as in the case of Pt from PtCl_2 or Ag from AgNO_3 , using a reducing agent which is typically a poly-alcohol, or simply, polyol (like ethylene glycol), heated to a temperature of $< 200^\circ\text{C}$. Since a polyol is used to

reduce many metals from their ionic states in solution, this approach is also referred to as a “*polyol process*”. In the next step, solutions of the metal-ion along with a surface capping polymer (like PVP, in the case of Ag) are together added dropwise to the metal seed solution. This step leads to the nucleation and eventually, growth of metal nanowires on these preformed seeds. The temperature at which the solution is maintained determines the size of the seed crystals and hence the width of the nanowires, while the number and length of the nanowires is governed by the duration of this process. The surface capping polymer is understood to adsorb on to the seed surface and subsequently kinetically control the growth rates along its different crystalline faces. Varying growth rates along the different faces leads to highly anisotropic growth leading eventually to preferential growth along just one direction. The synthesized nanowires are usually highly uniform in their widths and have a fairly wide range of lengths. The capping polymer also makes it easier to disperse the nanowires in different solvents and hence enables the processing of these wires for a host of applications [74, 75].

2.5.3 Nanowires as transparent conductors

As has been discussed in earlier sections, in an effort to identify alternative materials/strategies to fabricate transparent conductors that not only have desirable electrical and optical properties but also favorable mechanical properties, the use of carbon nanotubes, graphene, conducting polymers and metal nanowires (particularly that of Ag and Cu) have been investigated in the recent past. Key benefits of metal-NW networks, such as those of Ag, encompass the economic viability, the ease of processing as well as favorable combination of optical transparency and electrical conductivity. In this regard, it has been reported that TCs based on Ag-NW networks show great promise and potential for most scenarios, be it the touch-screen and flexible display market or the thin film PV market. [27].

With sheet resistances of $\sim 10 \text{ } \Omega/\square$ for $> 85\%$ transmittances, silver-nanowire networks (Ag-NWs) have demonstrated properties that are comparable to those of ITO films [28, 76] and are hence considered as promising candidate materials for applications ranging from touchscreens to flexible displays and polymer photovoltaics.[16, 27] As would be intuitive, an increase in the areal density (or coverage) of nanowires in the film stands to increase the conductivity even further, however, only at the expense of a loss in transparency owing to a reduction in the porosity [77–79]. There are also reports of fabrication of Cu nanowires for use as transparent conductors as a cheaper alternative to Ag, with $R_{\text{Sheet}} \sim 30 \text{ } \Omega/\square$ and 85% transmittance [80]. However, aggregation effects prevent formation of uniform films and hence lead to lower optical transmittances and higher resistivities. In other words, they are yet to demonstrate properties comparable to that of Ag nanowires. Common synthesis methods for Ag-NWs include template-assisted and vapor-phase based synthesis approaches, lithographic patterning of Ag nanostructures and the polyol-mediated solution-phase synthesis process developed by Sun *et al.*,[74] the latter being the most widely used. Ag-NWs synthesized in solution can be cast into randomly networked porous films by different techniques such as spin-coating, drop-casting, spray pyrolysis, electrospinning, etc.[68] Despite metals, including Ag, being highly absorptive optically, the highly porous nature of these networks ensures that these films remain more or less transparent. With their widths being a few tens to hundreds of nm and lengths of a few tens of microns, the nanowires form a percolative conducting path where the carrier transport is governed by the diffusive regime. Leem *et al.*[81] and others[82, 83] have demonstrated the use of spin-coated Ag-NWs as TCs in photovoltaic (PV) devices. However, power conversion efficiencies (PCEs) in these devices have been reported to be low ($< 0.5\%$) owing to low shunt resistances and possible short-circuiting arising from high surface roughness. Whereas Lu *et al.*,[84] Madaria *et al.*[85], Lee *et al.*[76] and other groups[45, 86, 87] have

investigated the applicability of spray coating and drop-casting techniques to deposit large area films on glass and PET substrates, having 85% transparency and sheet resistances of $35 \Omega/\square$, there have also been efforts to apply other coating methods such as rod-coating[88] and vacuum filtration.[89]

2.5.4 Performance metrics for networked conductors

The performance of TC materials is described in terms of a figure of merit' (FoM), which is traditionally defined as the ratio of $\sigma_{\text{DC,B}}/\sigma_{\text{Op}}$, where $\sigma_{\text{DC,B}}$ is the bulk electrical conductivity of the film and σ_{Op} its optical absorption coefficient. Alternatively, for TCs from nanostructured materials, an analogous metric is often used where the FoM is a dimensionless quantity, defined as the ratio $\sigma_{\text{DC,B}}/\sigma_{\text{Op}}$, where σ_{Op} is optical conductivity, related to optical absorption by $\sigma_{\text{Op}} \sim \sigma_{\text{Op}}/Z_0$ (Z_0 is impedance of free space, $\sim 377 \Omega$). The FoM for nanostructured materials is then obtained by relating the transmittance of the film to its sheet resistance:

$$T_{\text{bulk}} = \left(1 + \frac{Z_0}{2R_{\text{Sheet}}} \frac{\sigma_{\text{Op}}}{\sigma_{\text{DC,B}}}\right)^{-2} \quad (2.4)$$

Thus, for a TC with $R_{\text{Sheet}} < 100 \Omega/\square$ and $T > 90\%$ (i.e. with typical values for viable TC materials), the FoM is 35.

In the case of Ag-NW network structures, optical transmittance and electrical conductivity sensitively depend on the connectivity and areal density of the network. For such structurally disordered systems, the electrical transport properties can be most ideally represented by percolation models that describe the behavior of the connected clusters within the network. Such a treatment is necessary owing to large observed deviations from bulk behavior (i.e. behavior similar to that of thick nonporous films of Ag) as described by De *et al.*[34, 43] For networks of metal nanowires and carbon nanotubes (CNTs), electrical conductivity scales with

the network coverage and can be described using percolation theory as $\sigma_{\text{DC}} \propto [(\zeta - \zeta_{\text{C}})/\zeta_{\text{C}}]^n$, where σ_{DC} is the DC conductivity of the network, ζ is the areal NW network density, ζ_{C} is the critical areal NW network density and n is the empirically-determined percolation exponent. Thus, for a network of nanowire conductors, percolation limits conductivity resulting in a steep increase of R_{Sheet} in comparison to T , indicating a transition from a bulk-like conduction regime to a percolation-like one, with electrical conductivity being limited by the percolation threshold. Equation 2.5 describes the resulting relation between T and R_{Sheet} accounting for changes in the network structure.[89]

$$T_{\text{percolation}} = \left[1 + \frac{1}{\Pi} \left(\frac{Z_0}{R_{\text{Sheet}}} \right)^{\frac{1}{n+1}} \right]^{-2} \quad (2.5)$$

where Π is the percolative FoM for these TCs, defined as:

$$\Pi = 2 \left[\frac{\sigma_{\text{DC,B}}/\sigma_{\text{Op}}}{(Z_0 t_{\text{min}} \sigma_{\text{Op}})^n} \right]^{\frac{1}{n+1}} \quad (2.6)$$

Here, the parameter Π represents the percolative FoM while t_{min} is the thickness below which the conductivity switches from being bulk-like to percolation-like. The factor n relates to the percolation exponent and depends on the dimensionality of the system ($n_{2\text{D}} = 1.3$ and $n_{3\text{D}} = 2$); n has been known to vary widely between 0.36 and 6.5 for networked structures in the literature.[43]

2.5.5 Challenges with Ag-NW TCs

Despite having favorable optical and electrical properties and the ease of processing large-area thin films of these Ag-NW based TCs, aggregation effects in solution-processed NWs prevent formation of uniform films and hence directly hamper optical transmittances and electrical conductivities. Additionally, process-related effects can cause non-uniformity in these networked structures. For example, drop-cast films

show “coffee ring” patterns that lead to discontinuous films, spray-coating techniques result in sparse and non-uniform networks and vacuum filtration methods too suffer from irregular morphologies and high film roughness.[88–90] The inherent mechanical fragility of Ag-NW network structures presents a limitation in applications requiring mechanical robustness (such as flexible electronic devices).[91] In conclusion, the inhomogeneity of the network structures along with the mechanical fragility of Ag-NW films, pose major challenges to the technological impact of Ag-NW based TCs and have motivated research in using polymer-based Ag-NW composite materials as alternatives to pristine Ag-NW TCs. Recent research has focused on the fabrication of composites of Ag-NWs in PEDOT:PSS[45, 76, 79], a conducting polymer that is widely being used as a hole-transport layer in current polymer PV designs. However, while the use of PEDOT:PSS is appealing due to its inherent electronic conductivity, its application as TCs is limited due to the strong optical absorption. Additionally, corrosion of Ag-NW and ITO electrodes as a consequence of the highly acidic and hygroscopic nature of PEDOT:PSS is a growing cause for concern especially in the context of performance-stability in organic photovoltaic devices.[92]

2.5.6 Dispersion stability of nanowires

As mentioned in the previous section, aggregation effects are known to be detrimental to uniformity and reproducibility in solution-processed nanowire films. In this regard, the stability of nanowire-dispersions remains to be studied more closely with an intention of not only understanding the causes for aggregation but also ways to mitigate it. The simplest way of doing this is by assuming the nanowires to form a colloidal system although technically, for reasons that will be described in the following subsections, nanowires with high aspect ratios cannot be classified as colloids. However, since the science of colloids and colloidal stability has been fairly well understood and documented it is only reasonable to assume a generalization in

the properties of colloids to nanowires.

Colloids and colloidal stability

A colloidal system consists of dispersed microscopic substances called the ‘*dispersed phase*’, in a medium called the ‘*dispersion medium*’ (also referred to as the ‘*continuous phase*’). While in most cases the dispersion medium is a liquid, the dispersed phase which is typically a solid, could be a liquid or even a gas. By definition the size of the dispersed phase particles is approximately between 1 and 1000 nm. The high surface area of the dispersed phase determines the physical properties of the colloidal system. It also determines the motion of particles which essentially consists of rotational and translational Brownian motion. This random motion of particles leads to frequent collisions between them, and such interactions in turn determine the stability of the colloidal system. These interactions can basically be classified into two kinds – attractive and repulsive. An attractive force between the dispersed particles will lead to aggregation and in some cases even coalescence, while repulsive forces between the particles, if dominant, will keep them apart and in a well-dispersed state thereby maintaining a stable system [93].

Interaction forces between disperse particles

The primary forces of interaction between particles dispersed in a fluid are –

- **Electrostatic interaction:** Colloidal particles carrying electrical charge can attract or repel each other based on the charge of the dispersed phase as well as the mobility of the two phases under consideration. While the charge on the surface of the particle surface is immobilized, ions in the adjacent solution, i.e. the dispersion medium (if ionizable), can move freely influenced by electrical forces and Brownian dynamics. The interfacial charges can arise due to differences between the electron affinities of the two phases, ionization of surface moieties and entrapment of ions [94]. The interaction between colloidal

particles arising out of this is usually repulsive and only under certain geometric constraints assumes an attractive nature [95]. The repulsive free energy per unit area between two spheres of radius a , as described by the well-established DLVO (Derjaguin-Landau and Verwey-Overbeek) theory, is given as [96, 97]

$$U(r)_R \propto \frac{Z^2}{\epsilon} \left(\frac{e^{\kappa a}}{1 + \kappa a} \right)^2 \frac{e^{-\kappa r}}{r} \quad (2.7)$$

where,

Z = charge number of the spheres

ϵ = dielectric constant of the medium

$1/\kappa$ = Debye screening length

r = distance between the two particles

- **Van der Waals-London forces:** These are the primary source of attraction between colloidal particles and exist between identical/similar particles. These are typically short range forces that decay rapidly away from the surface. The origin of van der Waals (VDW) forces is in the generation of an instantaneous dipole due to fluctuation of electron clouds around charge-neutral atoms. The interaction energy between two spherical particles (in the limit $a \gg r$) is given as -

$$U(r)_A \approx -\frac{Aa}{12r} \quad (2.8)$$

where, A is the Hamaker constant [98]

The total interaction energy between the particles is given by adding the contributions from both the repulsive electrostatic forces and the attractive VDW forces. The balanced interaction energy is approximated as (depicted in Figure 2.12)–

$$U(r) = U(r)_R + U(r)_A \sim -\frac{A}{6} \left(\frac{2a^2}{r^2 - 4a^2} + \frac{2a^2}{r^2} + \ln \frac{r^2 - 4a^2}{r^2} \right) \quad (2.9)$$

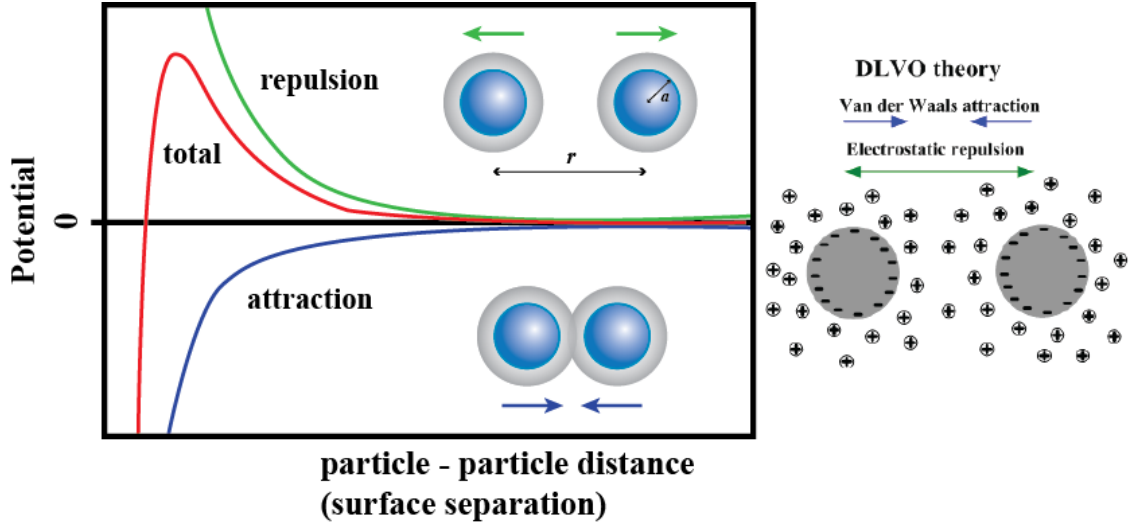


Figure 2.12: Schematic depiction of variation of colloidal interaction energy vs. distance between the colloid particles as described by the DLVO theory

- Entropic, steric and hydrodynamic effects:** As in the case of any physical system, a colloidal one also tends towards a state of maximum entropy and is closely related to size and shape-isotropy of the particles in consideration. Steric effects exist in colloidal systems where the surfaces of colloids are covered with polymers, counterions or surfactants adsorbed onto them or even in dispersions containing non-adsorbing polymers that present steric forces between the particles, thus modulating interparticle forces. The nature of these steric forces could be either repulsive (of entropic origin) or attractive (due to creation of a local depletion layer of the dispersion medium).

The adsorption of polymers or surfactants onto the colloid surface presents a steric hindrance to other colloidal particles during collision arising out of interaction between the adsorbed polymers on both particles. With long-chain polymers, compression and penetration of the chains leads to a reduction in conformational entropy and hence by an elastic effect, the system tends to revert back to a more stable conformation with lower free energy by separating the particles. For short polymer chains however, interpenetration of the

segments causes a local increase in the polymer concentration and depending on the balance between the polymer-polymer and polymer-medium interactions, osmotic forces may lead to either repulsion or attraction between the colloids. On the other hand, addition of non-adsorbing polymers leads to aggregation (or flocculation) by a *depletion mechanism*, wherein an imbalance between the structural entropy of colloidal particles and free-volume entropy of the polymer chains occurring as a result of overlap of the *excluded volume zones* of the particles in proximity, makes aggregation more energetically favorable.

Additionally, the nature of the dispersion medium can also modulate hydrophilic (by solvation) or hydrophobic interactions between particles and in turn affect the stability of the colloidal system.

Role of interaction forces in stability of the colloidal system

The interplay of the attractive and repulsive forces as described above (arising out of relative motion between particles and the continuous phase) with the random Brownian forces eventually determines the overall stability and phase behavior of the dispersed colloid particles in the system [99]. In addition to the forces mentioned above that describe interaction between particles, some other forces that directly affect Brownian dynamics of the particles are viscous forces (that can be estimated by Stokes' law, as a function of the viscosity of the medium), inertial forces (that depend on size and mass density of particles) and also effective gravitational forces (taking into account buoyancy as well).

While the above has been studied in great detail experimentally and theoretically for spherical particles, the same cannot be said for particles with shape-anisotropy, like cubes, nanorods, nanowires, etc. It was Onsager in 1949 [100] who laid out a theory to describe phase behavior of rod-like particles with high aspect ratios. One

important criterion in maintaining stability of the dispersed phase in colloidal systems is its size or dimension. Sharma *et al.* [99] describe how it is necessary for the size of the particle to be $< 5 \mu\text{m}$ in order for it to be dispersed as a Brownian particle in a solvent with density comparable to that of water. Further increase in size would lead to gravitational forces dominating over all other forces, eventually leading to collapse of the colloidal system from the loss of its Brownian character. The same would apply to systems with shape-anisotropic particles, like nanorods and nanowires; continuous increase in the aspect ratio may lead to easy aggregation or sedimentation of the dispersed entities, thereby destabilizing the entire system.

Methods for stabilizing colloids

A colloid can be stabilized by providing long-range repulsion between particles so as to compensate for the strong, long-range attractive forces that exist between them. This can essentially be achieved by surrounding the colloidal particles with an environment that would negate or suppress these attractive forces [93, 94, 98] (Figure 2.13). The environment could be –

1. An electrical double layer - that can provide electrostatic or charge stabilization.
2. An adsorbed or chemically attached polymeric/surfactant molecule - that can provide steric stabilization.
3. Free polymer in the dispersion medium - that can account for either steric or depletion stabilization

Characterizing dispersion stability

To investigate and understand the stability of such suspended media, two common experimental methods include electrophoresis and dynamic light scattering.

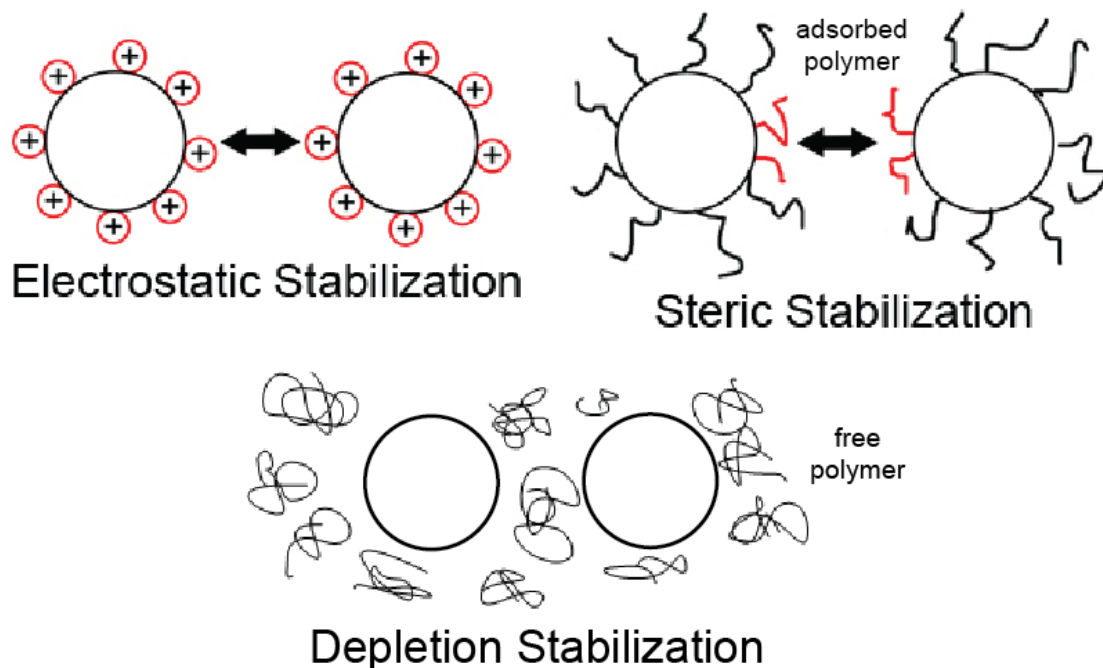


Figure 2.13: Schematic depiction of methods of stabilizing a colloid (adopted from http://en.wikipedia.org/wiki/Polyelectrolyte_adsorption and <http://www.substech.com>).

Electrophoresis: This refers to the motion of colloidal particles under the influence of an applied electric field and knowledge of this particle-field interaction provides vital information on the stability of these colloids, since it is the magnitude of surface charge and potential near the colloid surface that dictate inter-particle electrostatic attraction/repulsion. On the application of an electric field, the colloid migrates at a certain velocity from which its mobility can be determined. From the mobility data is calculated a quantity known as the *zeta potential* (ZP, ζ), which qualitatively is a measure of the electrical state of the moving entity.

The stability of such colloidal system depends on the balance between attractive Van der Waals type forces and repulsive forces arising from overlap of inter-particle electrical double layers (EDLs) as discussed in the previous section. Since the ZP corresponds to the extent of repulsive forces in the system, it is often considered as an indicator of colloidal stability. At the so-called *isoelectric point* where $\zeta =$

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0, electrostatic repulsive forces are no longer able to counteract the Van der Waals attractive forces, thus leading to instability and aggregation. Generally, colloids are electronegative when suspended in distilled or tap water and larger the electronegative ζ , greater the stability. Quantitatively speaking, the following ranges for ζ indicate the nature of dispersion stability –

$\zeta > -14$ mV :- onset of aggregation;

-14 mV $> \zeta > -30$ mV :- moderately stable, common range for ζ ;

-30 mV $> \zeta > -45$ mV :- stable; and

-45 mV $> \zeta > -70$ mV :- highly stable

By considering the motion of liquid surrounding a flat, charged surface von Smoluchowski derived the mobility (u_E) of the particle, defined as the ratio of the velocity of the liquid parallel to the plane of motion (v) to the applied electric field (E_z), using Poisson's equation as –

$$u_E = -4\pi\epsilon_o \frac{D\zeta}{4\pi\eta} = -\frac{\epsilon\zeta}{\eta} \quad (2.10)$$

where ζ refers to the zeta potential of the colloid, D , its diffusion coefficient and η , the viscosity of the system. This analysis was however limited to the electrophoretic motion of a large particle, with a thin double layer, in a fixed volume of fluid, without taking into consideration potential distributions within the electrostatic double layer. Debye and Hückel later presented a modified theory taking into account the behavior of strong electrolytes and their interactions with the double layer, assuming however the particles to be small, and obtained the electrophoretic mobility to be –

$$u_E = -4\pi\epsilon_o \frac{D\zeta}{4\pi\eta} = -\frac{2\epsilon\zeta}{3\eta} \quad (2.11)$$

In 1931, Henry integrated the above two treatments by superimposing the external field on the local field around the particle, obtaining an effective electrophoretic mobility with the form –

$$u_E = -(4\pi\epsilon_o) \frac{D\zeta}{6\pi\eta} f_1(\kappa a) = -\frac{2\epsilon\zeta}{3\eta} f_1(\kappa a) \quad (2.12)$$

where the function $f_1(\kappa a)$ depends on the shape of the particle, varying from 1 for small κa to $\frac{3}{2}$ for large κa . [101, 102]

Dynamic light scattering: This is a technique used to determine the size distribution of particles in a suspension or of polymers in solution based on the scattering of light upon incidence on the particle or polymer under investigation.

Here, the scattered light and its fluctuations as a function of time are measured following which an autocorrelation function for the signals is determined that is a measure of the degree of similarity, or correlation, of a signal at a fixed time t_0 , with itself at various times $t_0 + \delta t$. This autocorrelation of scattered-light intensities can be mathematically represented as -

$$g_2(t) = \frac{\langle i(t)i(0) \rangle}{\langle i(0) \rangle^2} \quad (2.13)$$

where $g_2(t)$ is the normalized autocorrelation function of scattered light having intensities $i(0)$ at time t_0 and $i(t)$ at some arbitrary time t .

However, since light detectors measure only light intensities and not electric fields directly, a normalized autocorrelation function of the scattered electric fields, $g_1(t)$, can be defined as -

$$g_1(t) = \frac{\langle E(t)E(0) \rangle}{\langle E(0) \rangle^2} \quad (2.14)$$

where $E(t)$ and $E(0)$ are corresponding electric fields of the scattered light at times

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t and t_0 respectively. The phase information of the signals is also maintained while converting between the autocorrelation functions g_1 and g_2 by Siegert's relation[103]

$$g_2(t) = (\langle i(t) \rangle^2 + C \langle i^2(t) \rangle g_1^2(t)) \quad (2.15)$$

where C is an instrument constant.

These relations are based on the assumption that the scattering particles are undergoing simple Brownian motion, i.e. the motion is completely random and is dictated solely by self-diffusion and by no external stimuli. Since large particles move slowly, the scattering intensities fluctuate gradually, while for smaller particles, this fluctuation is comparatively quicker. Consequently, the extent of correlation decays more rapidly over time for smaller particles than for larger ones. This difference in correlation of signals as a function of time is depicted in Figure 2.14.

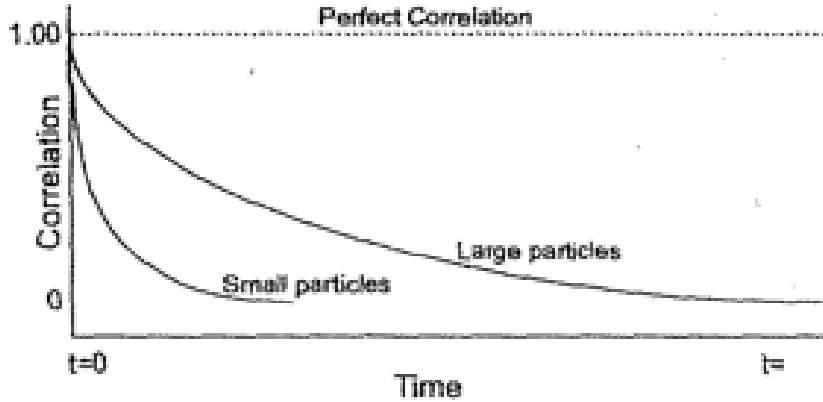


Figure 2.14: Idealized correlation functions for large and small particle colloidal systems. The decay in correlation is faster for small particles than it is for the large ones.

For mono dispersed systems, the autocorrelation function can be mathematically represented by a single exponential decay, which is of the form -

$$g_1(t) = e^{-\Gamma t} \quad (2.16)$$

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where $\Gamma = 1/\tau$, the decay rate (in units of t^{-1}) with τ being the relaxation time (the time it takes for the particle to diffuse a distance sufficiently large such that its position relative to that at t_0 can no longer be correlated). The term Γ is also related to the diffusion coefficient D_T for the particle (at a given temperature T) by the relation -

$$\Gamma = \frac{1}{\tau} = D_T q^2 \quad (2.17)$$

with q being the modulus of the scattering vector that is directly related to the wavelength of light, λ , refractive index of the medium n and the scattering angle θ by the relation -

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (2.18)$$

Knowledge of the relaxation time τ measured by DLS can thus help determining the diffusion coefficient of the particle, which in turn can be used to calculate the hydrodynamic radius, r_h (the effective size of a sphere diffusing at the same speed as the particle), of the particles (provided the system is dilute such that self-diffusion is the only aspect governing motion and also assuming that particles are spherical), using the Stokes-Einstein equation as follows -

$$r_h = \frac{k_B T}{6\pi\eta D_T} \quad (2.19)$$

where k_B is the Boltzmann constant and T , the absolute temperature.[102, 104]

However, for polydisperse or size-disperse systems, the autocorrelation function is influenced by multiple decay/relaxation processes that occur simultaneously and can be represented mathematically by a sum of the autocorrelation functions of each particle in the system (which in the case of a continuum in size dispersion becomes

an integral sum) -

$$g_1(\tau) = \sum_i a_i e^{-\frac{\tau}{\tau_i}} \cong \int P(\tau) e^{-\frac{\tau}{\tau}} d\tau \quad (2.20)$$

where $P(\tau)$ represents the distribution describing the occurrence of relaxation modes τ . In particular, for systems with limited size dispersity, the autocorrelation function obtained experimentally for typical size-disperse particle systems has been shown to mimic the behavior of a stretched exponential decay function[105, 106] -

$$g_1(\tau) = \int P(\tau) e^{-\frac{\tau}{\tau}} d\tau \approx C e^{[-(\frac{\tau}{\tau})^\beta]} \quad (2.21)$$

with the stretched exponential decay parameter, β , describing the distribution in particle sizes. The smaller the value for β for a system, the wider its particle size distribution.

2.5.7 Percolation in nanostructures

For structurally disordered systems like that of a metal nanowire network, the properties can be represented by a percolation model that describes the behaviour of the connected clusters within the network. Such a theory essentially predicts how a certain property of the said disordered system would evolve as a function of the connectivity of the individual clusters under the influence of a certain stimulus. Some of the applications of percolation theory include diffusion, flow and transport of fluids through porous media, prediction of earthquakes and fault patterns in rocks, kinetics of chemical reactions, polymerization reactions, vibrations and density of states of disordered materials, electrical transport properties of composite materials and semiconductors and even in biological systems as in the case of antigen-antibody reactions, to name a few [107]. In this regard, it is only appropriate that a metal nanowire network also be treated in terms of a percolating system in order that one can accurately predict its properties.

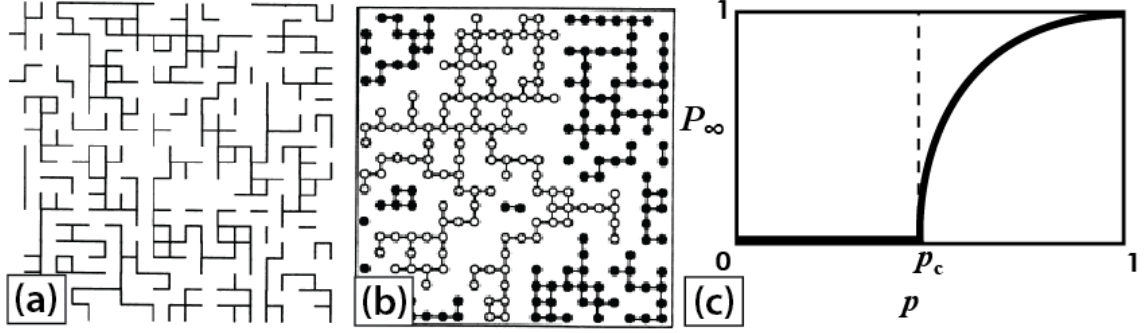


Figure 2.15: Schematic representation of (a) bond percolation, (b) site percolation and (c) the probability P_∞ as a function of the occupancy, p of the network. Reproduced with permission from [108] © 2005 Springer-Verlag Berlin Heidelberg

Based on the nature of the disordered system, percolation through it can be modeled using either the (a) bond percolation model or (b) site percolation model, where the “*connectedness*” of the system is described by the probability of occupancy of either the bonds in the percolating network or the sites, respectively. A ‘bond’ is essentially the edge between two neighbouring components of the network, while a ‘site’ is the intersection of two ‘bonds’ or edges. In a typical percolation problem, the *openness* or *occupancy* of any random bond or site is denoted by a probability p while the *closedness* or *vacancy* of the same (independent of the other sites and bonds) is $1 - p$. Two sites are said to be *connected* if at least one path exists between them that consists of *occupied* bonds alone. A *cluster* is thus a set of connected sites surrounded by closed bonds. When the value of p is small and close to 0, the size of any connected cluster is small and when p is large and close to 1, the network would be expected to be completely *connected*. A transition in the topology of network structure from a macroscopically *disconnected* one to a *connected* one occurs as the value of p gradually increases from 0, i.e. at this point, there is at least one path connecting two sites located at two extreme ends of the macroscopic network. This value is referred to as the *percolation threshold*, p_c . In the context of electrical conductivity, this can be understood as the minimum concentration of conductors within the network that would ensure that electrical current can *percolate* from one edge of the macroscopic

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network to the other, inducing a insulator $\rightarrow$ conductor transition [108]. In other words, for $p < p_c$ the network is insulating, whereas for $p > p_c$ it is electrically conducting.

As would be expected, the average size of the cluster also increases with the value of p and at p_c it becomes large enough to connect opposite edges of the lattice. This cluster is called an *infinite* cluster whose density increases with p as more sites get added to it (See figure 2.15(c)). The probability P_∞ of a site belonging to this *infinite* cluster is said to be 0 below the percolation threshold and increases exponentially above it according to

$$P_\infty \sim (p - p_c)^\beta \quad (2.22)$$

where, β is known as the critical exponent.

This probability-based model can be extended to describe the conductivity of a network of conductors. Such a network, as in the case of a random network of nanowires, represents an open or infinite cluster as the case may be, depending on the density of the nanowires, such that

$$\sigma_{DC} \sim (p - p_c)^\mu \quad (2.23)$$

$$\sim (\xi - \xi_c)^\mu \quad (2.24)$$

where, σ_{DC} is the DC conductivity of the network and ξ the areal density of the network conductors, eg. nanowires or nanotubes.

For networks of metal nanowires and carbon nanotubes (CNTs), such percolative conduction is possible and has been extensively reported in literature [6, 43]. This means that a film made out of a dense network of nanowires or nanotubes would

be highly conducting as expected for an *infinite* cluster. As the density of the wires or tubes decreases, i.e. the size of the cluster is reduced, the conductivity also decreases as per the relation described by Equation 2.24. Once the size of the cluster reaches a critical density (ξ_c), the conductivity decreases exponentially, eventually to 0. This has been experimentally demonstrated for Ag nanowire and carbon nanotube networks [6, 43]. It was observed that a dense network of CNTs have low sheet resistances with low transmittances (because of higher optical absorption) characteristic of an ohmic conductor. With reducing density however, the transmittance increased (due to lowering of optical absorption), simultaneously with sheet resistance until a point after which while the transmittance remained steady, the sheet resistance of all the networks increased exponentially (see Figure 2.16). This is indicative of a percolation transition between non-conducting and conducting phases of the network. The problem of percolation thus tends to limit the electrical properties of networked conductors that in turn stands to affect the performance and energy-conversion efficiencies of any device that make use of these.

While percolation is a problem concerning performance of networked conductors, there is evidence in literature that suggests that percolation and the threshold can be controlled. Bergin *et al.* [44] have shown that controlling the length and diameter of the nanowires have a direct effect on the percolation threshold, while Kyrylyuk *et al.* [109] have demonstrated lowering of the percolation threshold in CNTs by introducing them into a matrix of a conducting polymer like PEDOT:PSS.

2.5.8 Conducting polymers revisited – a closer look at PEDOT:PSS

Within the past decade or so, considerable energy and effort has been put into research and development of devices based on organic materials like carbon-based materials (CNTs, graphene, etc), (semi)conducting π -conjugated polymers and even

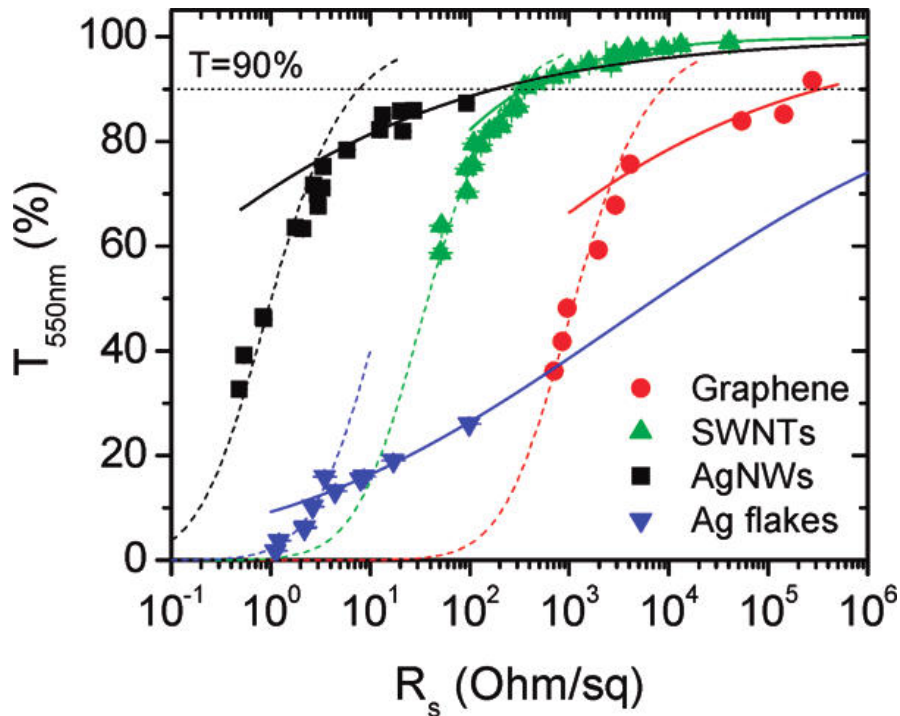


Figure 2.16: Transmittance -vs- sheet resistance curves for different nanostructured films - Ag-NWs, Ag flakes, carbon nanotubes and graphene. Reproduced with permission from [43]. © 2010 American Chemical Society

small organic molecules, for use in applications ranging from LEDs to flat panel displays and solar cells that are currently growing thinner and more flexible by the day. In particular, conjugated polymeric systems are essential materials that are already being used in organic electronic devices because of the ease with which they can be synthesized, their mechanical flexibility, low cost and simplicity of film processing as well as the freedom they allow in tuning of properties during synthesis. Some of the common conjugated (semi)conducting polymers include polythiophene (PT), poly(3-alkyl thiophene) (P3AT), poly(2,3-ethylene dioxythiophene) (PEDOT), polypyrrole (PPy), poly-(p-phenylene vinylene) (PPV), polyaniline (PANi), etc., among which the polythiophenes are the most commonly used in both semiconducting and conducting applications.

PEDOT is one such conducting polymer from the polythiophene family that is known

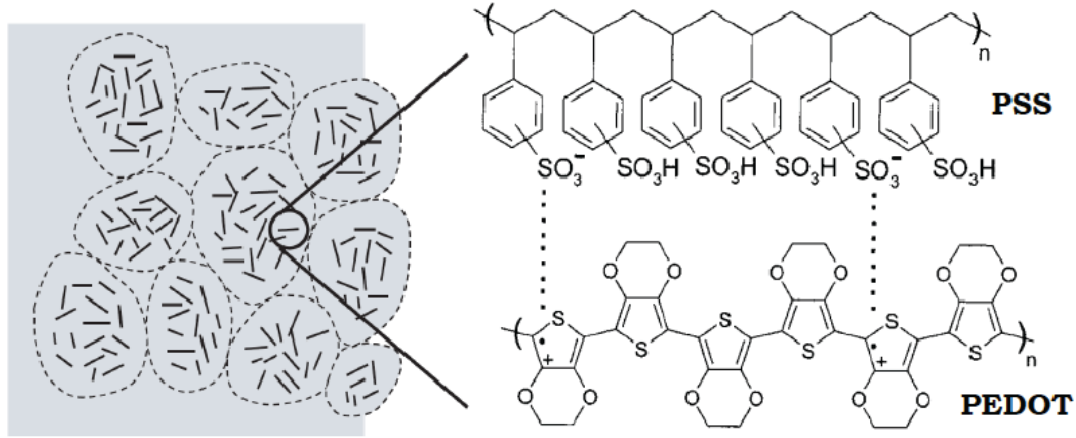


Figure 2.17: Cartoon of film morphology of PEDOT:PSS with grains of PEDOT-rich grains surrounded by a shell of PSS. Reproduced with permission from [29].

for its relatively high conductivity and high optical transmittance in the visible region as well, in addition to good chemical, mechanical and thermal stability. The typical degree of polymerization of PEDOT is low and it is known to be a collection of oligomers of ethylene dioxythiophene (EDOT), each having about ~ 20 repeating units. Being insoluble in common organic solvents and unstable in its neutral state, a polyelectrolyte, namely poly(styrene sulfonate) (PSS), is added resulting in an aqueous dispersion of PEDOT:PSS. The PSS, with its sulfonate counter-ion is known to stabilize the oxidized PEDOT chain segments and keep them dispersed in the aqueous medium (Figure 2.17) [29].

Because of the high disorder in the assembly of the polymer chains in PEDOT:PSS, charge transport is anisotropic and dominated by “*hopping*” of carriers from one chain to another even at practical temperatures. Films of PEDOT:PSS are understood to have a phase-segregated morphology where grains of PEDOT:PSS are surrounded by a shell of excess PSS. While conductivity within and in the plane of the PEDOT-rich grains is known to be isotropic, the conductivity between these grains and out of plane of the lamellar layer is much lower and anisotropic, in comparison. As a result of this, PEDOT:PSS films have lower effective conductivities. This can marginally be

improved by the use of chemical additives (polar solvents) that can bring about orders of magnitude change in the conductivity of untreated PEDOT:PSS. It has been shown that these additives effect changes in the morphology of PEDOT:PSS, such as larger PEDOT-rich grains with thinner insulating PSS shells, a more uniform distribution of PEDOT-rich regions throughout the film, screening effects of polar solvents, etc [29, 110–112]. Different solvents have been used to achieve this, that include dimethyl sulfoxide (DMSO) [110], ethylene glycol (EG), *N*, *N*-dimethyl formamide (DMF), tetrahydrofuran (THF) [111], sorbitol [112], hexafluoroacetone (HFA) [113] and even inorganic acids [114, 115], to name a few.

2.6 Photovoltaics, organic solar cells and flexible TCs

2.6.1 Photovoltaic energy conversion

Solar energy is widely considered one of the most promising alternatives to fossil fuels owing to its large-scale availability and sustainability, provided the energy from the sun is harnessed and distributed efficiently and economically. This is typically done by converting the incoming solar radiation into electrical energy, a directly usable form of energy, through devices known as solar cells. Such a photovoltaic energy conversion consists primarily of two steps - absorption of solar radiation and the subsequent production of electrical energy.

The solar energy current density per photon energy interval $dj_E/d\hbar\omega$, also known as spectral irradiance, as a function of the energy of photons incident on the earth just outside the earth's atmosphere is illustrated in Figure 2.18(a). This so-called solar spectrum can be compared to a black body at a temperature of $T_S = 5800$ K. Based on this plot, the maximum of the incident spectrum is located at $\hbar\omega_{\max} = 1.41$ eV, i.e. within the infrared region. Conventionally, however, the incident spectrum is

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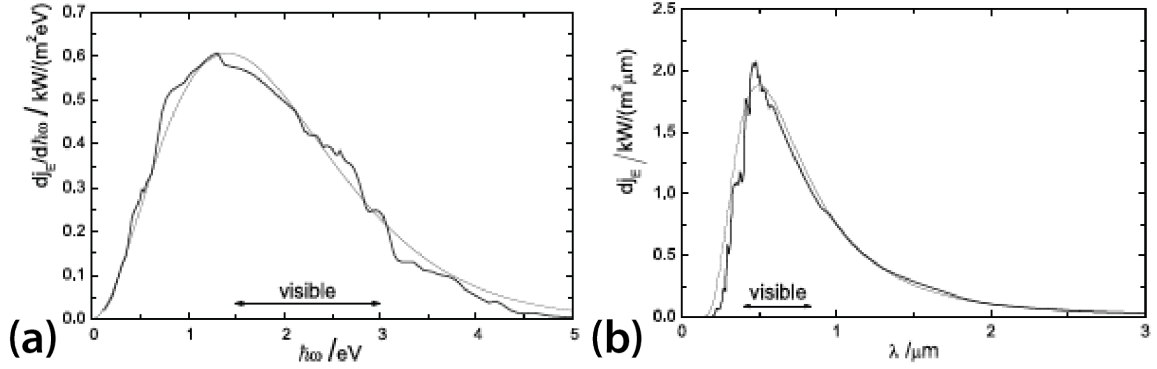


Figure 2.18: Solar energy current density (a) per photon energy as a function of the incident photon energy and (b) per wavelength of incident light as a function of wavelength, just outside the earth's atmosphere. Reproduced with permission from [116] © 2005 John Wiley & Sons, Inc.

plotted as the energy current density per wavelength interval $dj_E/d\lambda$ as a function of the wavelength of light, as in Figure 2.18(b), for which the maximum lies at $\lambda_{\max} \sim 500 \text{ nm}$ ($\hbar\omega \sim 2.48 \text{ eV}$). The reason for differences in the respective spectrum maxima arises from the latter not corresponding to a constant energy interval, $d\hbar\omega$. The net integral radiant flux on the earth just outside the earth's atmosphere is calculated to be $j_E = 1353 \text{ W/m}^2$. [117]

However, all of this radiation from the sun incident on the earth does not make it to the surface as some of it gets partially absorbed within the earth's atmosphere. Moreover, the absorption increases with the length of the path of passage through the atmosphere. For radiation from the sun incident at an angle α relative to the normal to the earth's surface, the ratio of the path length l of incident radiation through the earth's atmosphere to the thickness of the atmosphere l_0 is defined as the "air-mass coefficient" (AM), and is given by $l/l_0 = 1/\cos\alpha$. The spectrum measured just outside the earth's atmosphere is considered $AM0$ while that on the surface of the earth at normal incidence is $AM1$. Under moderate climatic conditions, the incoming solar radiation is considered to be incident on the earth at an angle of 48° to the surface normal, which gives an air-mass coefficient of 1.5. The $AM1.5$ spectrum (Figure 2.19)

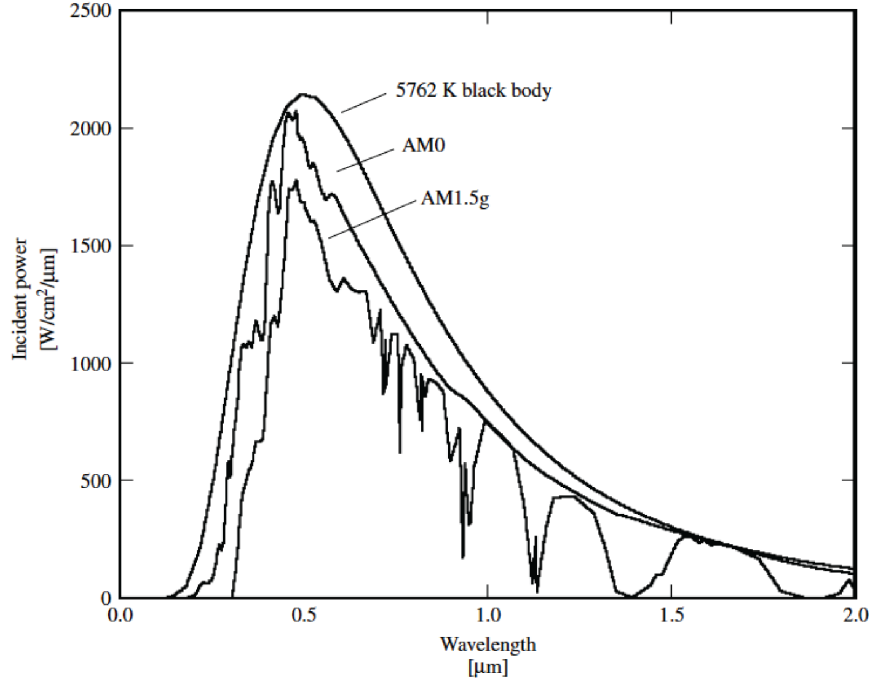


Figure 2.19: The *AM1.5* Global spectrum (*AM1.5G*) of solar radiation compared with that of the *AM0* spectrum as well as that of a black body at $T = 5762$ K. Reproduced with permission from [118] © 2010 John Wiley & Sons, Inc.

has a total energy flux of $1 \text{ kW/m}^2 = 100 \text{ mW/cm}^2$, and is thus considered the standard spectrum for measuring terrestrial solar cell efficiencies. Solar simulators most commonly use xenon arc lamps since they provide for high intensities and a spectrum that matches well with that of the *AM1.5G* solar spectrum.

2.6.2 Working principles of solar cells and materials used

Traditionally, solar cells have been realized using semiconductor *p-n* junctions having front ohmic contact stripe with fingers, a back ohmic contact covering the back surface and optionally an antireflection coating on the front surface to reduce losses in light available for absorption from reflection off the top surface. Such a device is schematically represented in Figure 2.20(a).[64] Upon incidence of monochromatic light of energy $h\nu > E_g$, the band gap of the semiconductor used, charge carriers in the form of excitons (electron-hole pairs) are generated at the junction. Under equilibrium or under the influence of a forward bias, these excitons diffuse across

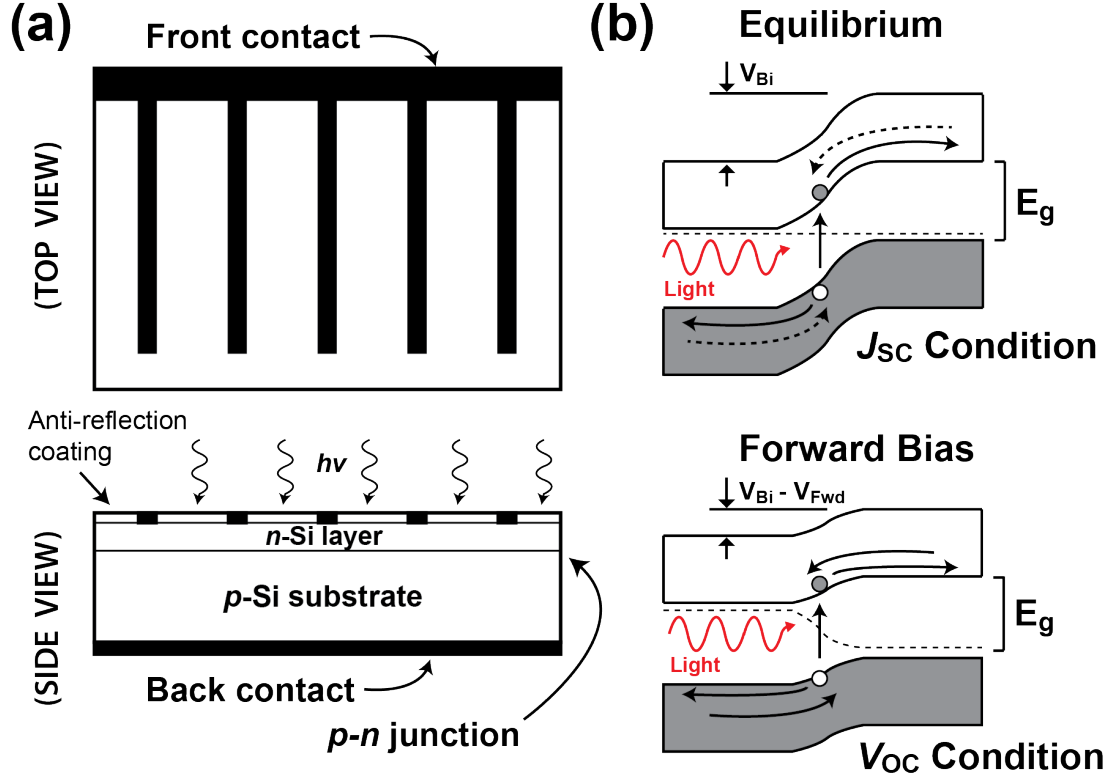


Figure 2.20: (a) Generic structure of a Si p - n junction solar cell (adopted from [119]); (b) schematic of the photocurrent generation process and energy band structure at equilibrium and under forward bias conditions.

to opposite electrodes where the charge carriers are collected, thus contributing to the flow of current through the resulting circuit. The photocurrent thus obtained directly depends on various material parameters such as doping level, mobility, carrier diffusion lengths and carrier lifetimes, to name a few. A schematic for the photocurrent generation process is illustrated in Figure 2.20(b).

Solar cell output characteristics

Under “zero-illumination” or “dark” conditions, the p - n junction behaves as a standard diode for which the total current, which is the sum of electron and hole currents, is given by:

$$J_{\text{total}} = J_p + J_n = \left(\frac{qD_p p_{no}}{L_p} + \frac{qD_n n_{po}}{L_n} \right) (e^{qV/k_B T} - 1) \quad (2.25)$$

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where,

- q = charge of electron
- D_p, D_n = hole and electron diffusion coefficients
- L_p, L_n = hole and electron diffusion lengths
- p_{no}, n_{po} = minority carrier concentrations in n and p regions
- V = applied bias
- k_B = Boltzmann constant
- T = temperature

From this equation, the ideal diode dark current can thus be written as -

$$J = J_S(e^{qV/k_B T} - 1) \quad (2.26)$$

Under illumination, the effective change in current density across the junction is directly proportional to the rate of generation of electrons and holes, G . Neglecting the effect of recombination in the p - n junction depletion region, the net current is obtained as -

$$J = J_S(e^{qV/k_B T} - 1) - J_L \quad (2.27)$$

where, J_L is the ideal light-generated current, assuming collection of all carriers generated by illumination, within the depletion region. The J - V characteristics for a solar cell in the dark and under illumination are schematically illustrated in Figure 2.21.

The performance of a solar cell is characterized primarily using three parameters -

1. Open-circuit voltage, V_{OC} – This is the maximum voltage available from a solar cell and is obtained by setting the total current $I = 0$. The ideal value for V_{OC}

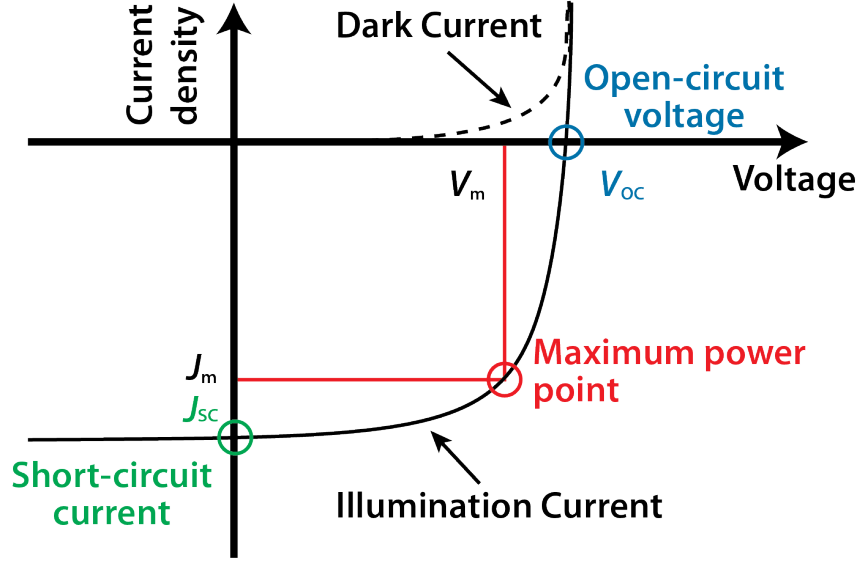


Figure 2.21: Illustration of the J - V characteristics of a typical solar cell in the dark and under illumination along with parameters that influence performance and efficiency of the cell

can then be derived as -

$$V_{OC} = \frac{k_B T}{q} \ln \left(\frac{J_L}{J_S} + 1 \right) \quad (2.28)$$

V_{OC} is thus determined by the properties of the semiconductor owing to its dependence on J_S .

2. Short-circuit current, J_{SC} – This is the maximum photocurrent derivable from the solar cell. For an ideal device, it is equivalent to J_L
3. Fill factor, FF – This parameter is qualitatively a measure of the squareness of the output characteristics and helps in quantifying the maximum power derivable from the device. Since the power derived at any point on the $I - V$ curve is given by $P = IV$, the maximum power density achievable is when $dP/dV = 0$ is satisfied. The corresponding current and voltage points, J_m and V_m respectively, can be derived for, and the product of these two quantities specifies the maximum power output P_m . The fill factor is then defined as -

$$FF = \frac{V_m J_m}{V_{OC} J_{SC}} \quad (2.29)$$

Having extracted the above parameters, the ideal power conversion efficiency η , is then defined as the ration of the maximum power output to the incident power, i.e.

$$\eta = \frac{P_m}{P_{in}} = \frac{V_m J_m}{P_{in}} = \frac{V_{OC} J_{SC} FF}{P_{in}} \quad (2.30)$$

Factors affecting solar cell efficiency

Even under ideal conditions there are theoretical limits to the efficiency of a solar cell. Moreover, while the photocurrent J_{SC} increases with decrease in E_g of the material, the open circuit voltage, V_{OC} has an opposite trend, i.e. an increase with increasing E_g . Thus, there exist optimum values for E_g so as to maximize the efficiency and extractable power for the device (Figure 2.22). Temperature also affects device parameters such as minority-carrier diffusion lengths, lifetimes and also V_{OC} and J_{SC} ; overall, an increase in temperature effects a reduction in efficiency of the cells.

In addition to these external limitations, several factors contribute to the non-ideality in material and testing conditions as well, that directly affect the aforementioned device parameters, V_{OC} , J_{SC} and the FF .

- Short-circuit current (J_{SC}) losses stem from reflection of light or inefficient light capture, owing to light-blocking metal contacts. Furthermore, material defects either at the surface or in the bulk of the semiconductor lead to higher probability of electron-hole recombinations thereby reducing the current.
- Open-circuit voltage (V_{OC}) losses primarily arise from increased recombination in the depletion region of the p - n junction through trap states. The non-ideality lent to the I - V characteristics can be represented by modifying the

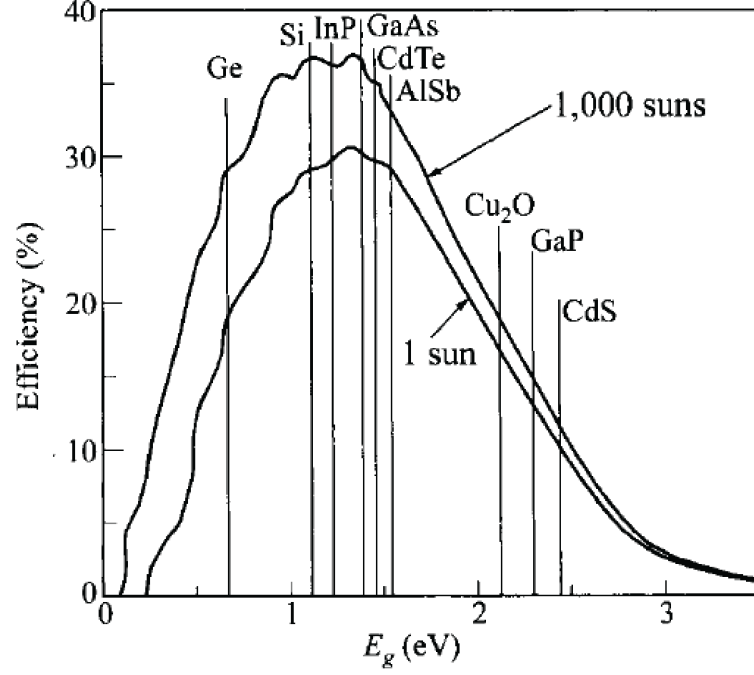


Figure 2.22: Variation of ideal efficiencies of solar cells as a function of the energy bandgap E_g , at 300 K under 1-sun and 1000-suns solar illumination. Reproduced with permission from [119] © 1981 John Wiley & Sons, Inc.

diode equation as -

$$J_{\text{total}} = J_S(e^{qV/nk_B T} - 1) \quad (2.31)$$

where n is known as the *ideality factor*. The value of n typically decreases from 2 at low currents to 1 at higher currents. The fill factor FF , being directly related to V_{OC} is subsequently affected by this non-ideality in diode behavior.

- Series resistance (R_{series}) - Contact resistances at the electrode-semiconductor junctions, low conductivity in the semiconductor and resistivity of the circuit-wiring contribute to ohmic losses in the device, that get added to the resistance of the load connected to it. The series resistance thus drops some of the voltage and hence reduces the voltage output from the device to be made available to the connected load.
- Shunt resistance (R_{shunt}) - Material-level defects within the semiconductor lead

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to current leakage that in turn reduce the current output from the device that would ideally be available for use by a connected load.

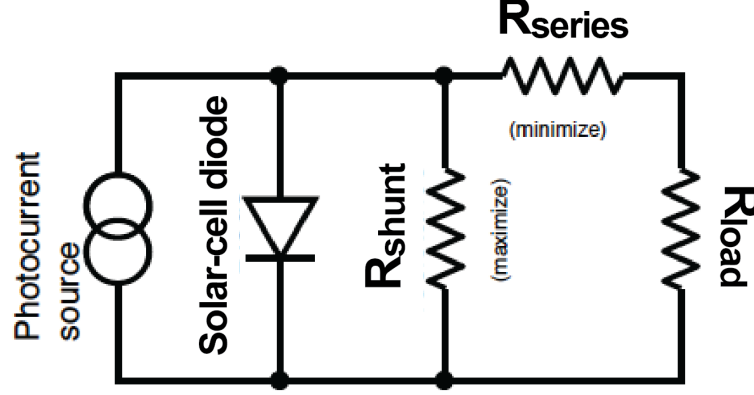


Figure 2.23: Effective equivalent circuit for a solar cell taking into account series and shunt resistances.

An equivalent circuit that accounts for these resistances and also the ideality factor n is illustrated in Figure 2.23, where R_{series} is added in series with the load R_{load} , while R_{shunt} is connected parallel with the diode. Based on such a configuration, the corresponding I - V characteristics (for a cell of area A) are modified from Equation 2.27 to –

$$J_{\text{total}} = J_{\text{S}}(e^{(qV + JAR_{\text{series}})/nk_{\text{B}}T} - 1) + \frac{V}{R_{\text{shunt}}} - J_{\text{L}} \quad (2.32)$$

Device configurations and materials

Many different solar-cell configurations have been devised over the past few decades wherein the primary aim has been to realize and improve upon devices that consistently have high efficiencies, are cheap to manufacture and are robust and reliable. Some of the most prominent device configurations and the corresponding materials used that have been extensively researched are briefly described below –

Crystalline-Si solar cell: Crystalline-Si was among the first materials to be used for realizing commercial solar cells and still continue to be the material

of choice for high-quality and high-efficiency ($\eta > 22\%$) solar cells. Since the main cost lies in growth of the crystal, several advances have been made in reducing cost in crystal growth, cutting of wafers and in minimizing material waste. Furthermore, rapid improvements in cell architecture - high aspect ratio metallization to maximize light-capture and minimize contact resistances, well-passivated surfaces to minimize carrier recombination, textured surfaces and advanced optical design to minimize light reflection and increase light-trapping - have given rise to solar cells with $V_{OC} \sim 0.7$ V, $J_{SC} \sim 41$ mA cm⁻², $FF \sim 81\%$ and efficiencies around 23%. [120]

Thin-film solar cells: Such cells comprise active semiconductor layers that are polycrystalline or even amorphous thin films deposited by various methods such as PVD, plasma-assisted evaporation and electroplating. The substrates on which the films are deposited are also very diverse in that they could be electrically active or passive, such as silicon, glass, ceramic, metal, plastic and the likes. Polycrystalline/amorphous-Si, CdTe (cadmium telluride), CdS (cadmium selenide), CIS (copper indium diselenide), CIGS (copper indium-gallium diselenide), etc. are some of the most common material systems that fall under this category.

While a-Si ($\eta \sim 9\text{-}10\%$) and multicrystalline-Si solar cells ($\eta \sim 16\text{-}18\%$) have lower efficiencies than their crystalline counterpart, they are easier and cheaper to process and are also amenable to large-area deposition. CdTe:CdS, CIS, CIGS, etc. fall under the category of what is known as heterojunction solar cells, wherein the junctions formed are between two semiconductors with differing energy bandgaps. Typically, these are fabricated in a superstrate configuration, i.e. the materials are deposited bottom-up on glass substrates coated with a transparent conducting (TC) layer, which is generally an oxide

of In, Sn or Zn (TCOs) as discussed in Section 2.1. The CdS layer acts as a resistive window layer and helps in improving shunt resistances. Efficiencies of up to 20% in these cells have been reported. Despite their advantages, grain-boundary effects, reduced quality of films grown on different substrates, chemical instability on long-term exposure to ambient O₂ and water vapor, high processing temperatures, etc. pose limitations on these material systems. The use of TCOs also is a limitation in realizing flexible devices.[121, 122]

Multi-junction solar cells: Also known as “tandem cells”, these have enabled the solar-cell industry to breach the 30% efficiency limit mark and even push the envelope of efficiencies > 40%. By stacking multiple junctions of different bandgaps on top of each other a much larger portion of the incident solar spectrum is made available for carrier-generation. Two- and three-junction solar cells based on compound semiconductors such as GaAs, GaInAs, InP, InGaP (for example, combinations GaInP/GaAs/GaInNAs and GaInP/GaInAs/Ge [123]) have been reported to have efficiencies $\sim$ 42-43%.

Organic solar cells: These constitute what are known as the third generation of solar cells and have the potential to be cheaper to manufacture. Although efficiencies are not as high as compared to their inorganic counterparts, rapid strides in this field over the last decade have lifted cell efficiencies from a meagre 1% up to $\sim$ 10% based on recent reports (See following Section 2.6.3 on organic photovoltaics for details). Concerted efforts in advancing synthesis of newer and more complex derivatives of thiophene and fullerene compounds, that act as electron donors and acceptors respectively, have helped tune and optimize efficiencies in organic solar cells.[124] These will be discussed in greater detail in the following section.

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Figure 2.24 provides an illustration of sample structures of some of the solar cell material configurations discussed above, while Figure 2.25 represents a chart of record solar cell efficiencies for the various solar cell configurations providing a historical account of the progress made in this field.[125]

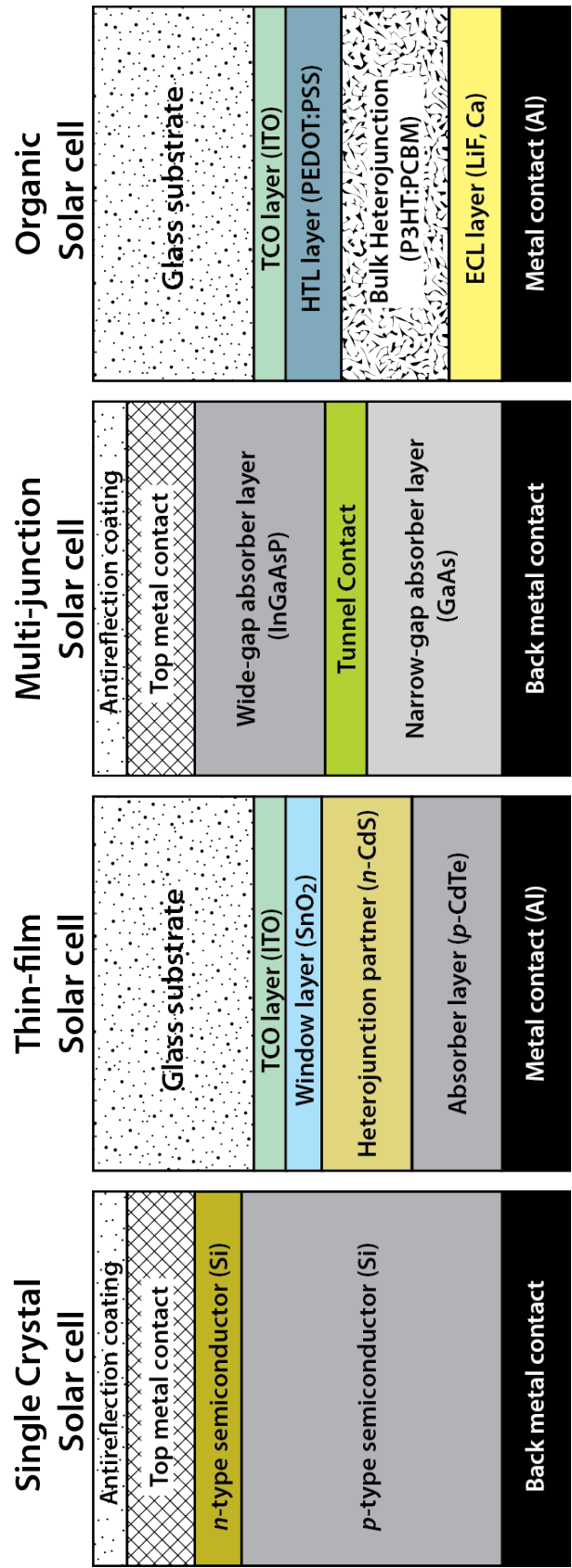


Figure 2.24: Schematic illustration of typical solar cell structures. Some standard materials used in these have been included in parentheses

2. Background

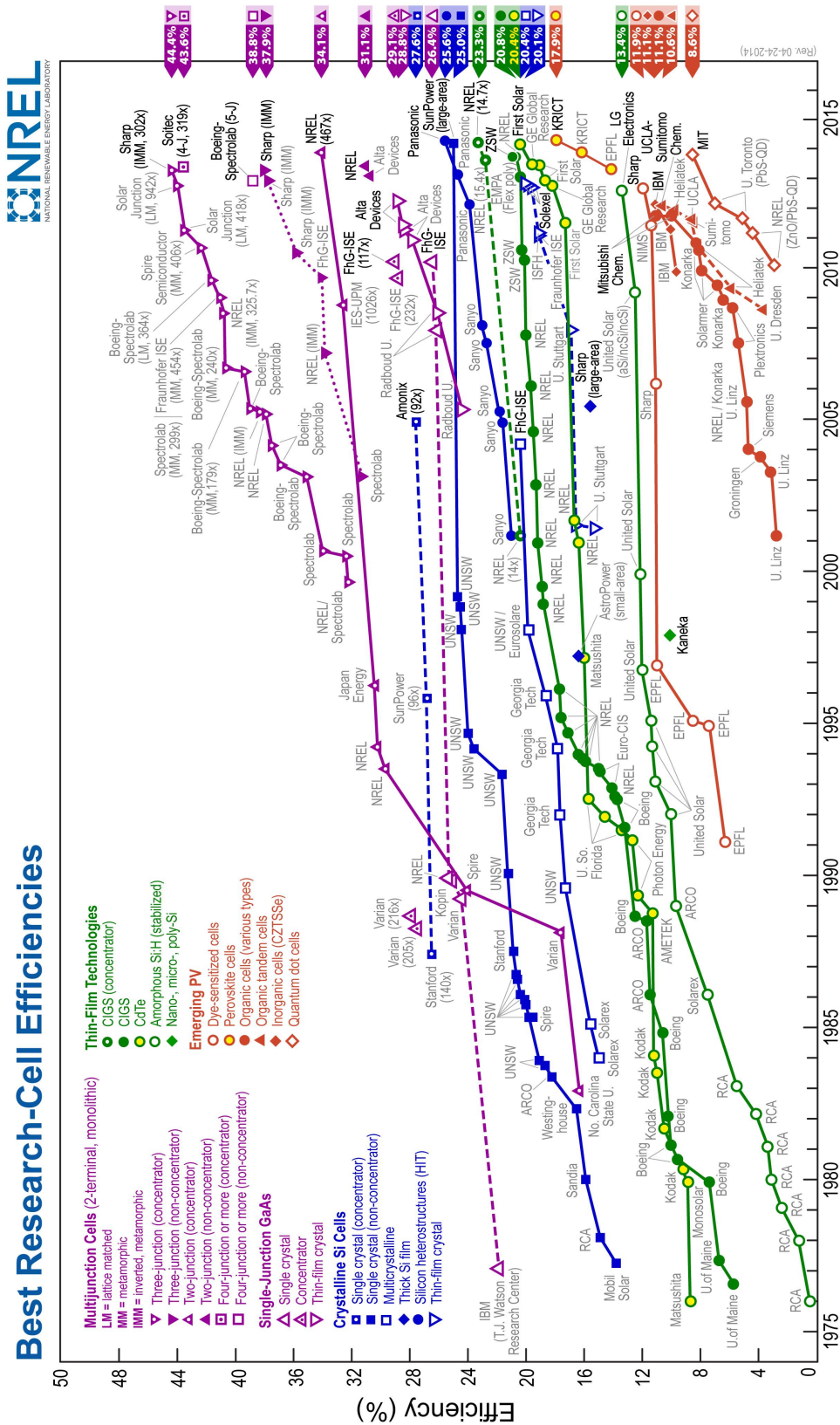


Figure 2.25: Chart of the latest record efficiencies for research-solar cells compiled by the National Renewable Energy Laboratory (NREL), Golden CO - 2014.[125]

2.6.3 Organic photovoltaics

The synthesis of a class of semiconducting organic compounds based on conjugated polymers has paved way for the manufacture and commercialization of “plastic” electronic devices that are flexible, cheap and easy to process.[32, 126]

Energetics of organic semiconductors

The electronic energy structure for these organic semiconductors are analogous to those of inorganic semiconductors; the organic equivalents of the valence band and the conduction band in inorganic semiconductors are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The delocalized electron cloud from the sp^2 hybrid conjugated π -system lends electronic conductivity to these materials; analogous to the valence band being filled with electrons with the conduction band being empty in inorganic semiconductors, the HOMO levels correspond to the electron-filled bonding states of the sp^2 hybridized system and the LUMO levels to the anti bonding states. This idea is schematically illustrated in Figure 2.26.

There are however some major differences between organic and inorganic semiconductors –

1. In inorganic semiconductors, an electron when provided with sufficient energy gets excited from the valence band to the conduction band while in organic semiconductors, an electron excited from the HOMO to the LUMO level reflects a change of state for the entire molecule.
2. Carrier transport in organic semiconductors is via thermally activated ‘hopping’ of the charge carriers. This mechanism is much less efficient than the free carrier transport observed in inorganic materials and hence leads to low mobilities; Hole mobilities $\mu_{\text{organic}}^p \sim 10^{-2}\text{--}10^{-3} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ in comparison to $\mu_{\text{Si}}^p \sim 4.5 \times 10^{-2}$

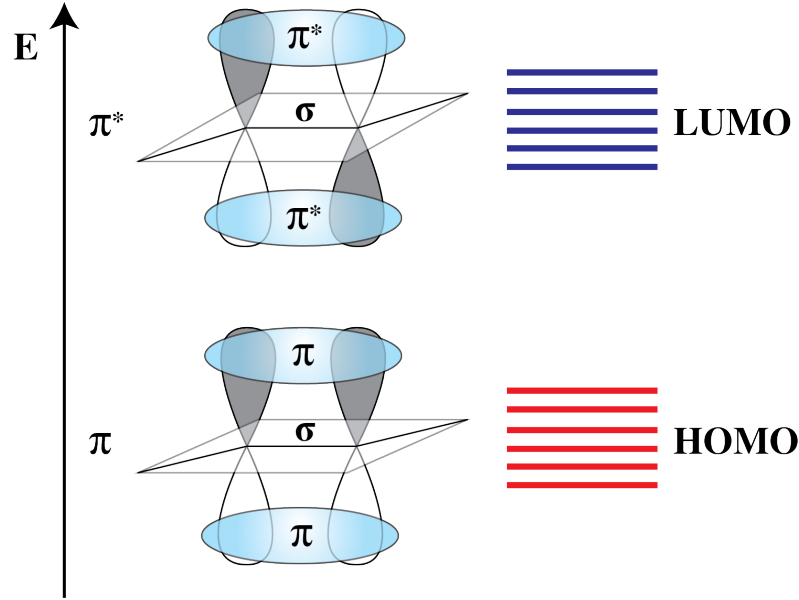


Figure 2.26: Illustrated depiction of energetics in organic semiconductors having sp^2 hybridized conjugated π -systems that lead towards electron-filled HOMO levels and electron-empty LUMO levels analogous to valence and conduction bands, respectively, in inorganic semiconductors.

$\text{m}^2 \text{V}^{-1} \text{s}^{-1}$ and electron mobilities $\mu_{\text{organic}}^n \sim 10^{-5} \text{m}^2 \text{V}^{-1} \text{s}^{-1}$ in comparison to $\mu_{\text{Si}}^n \sim 0.1 \text{m}^2 \text{V}^{-1} \text{s}^{-1}$. Consequently efficiencies of photovoltaic devices using organic materials are much lower as well.

3. The absorption of a photon leads to the formation of a bound exciton where the binding energy between the electron-hole pair is of the order of 0.1–1.4 eV, due to strong Coulombic attraction. In the analogous case of excitons in inorganic semiconductors, the binding energy is only a few meV making dissociation of the charges much easier in the latter case.

Working principles of organic solar cells

As in inorganic p - n junction solar cells, conventional organic solar cells (OSCs) comprise donor-acceptor heterojunctions that constitute the “active layer” of the structure. The working of such an organic solar cell can be divided into four stages - (1) light absorption/exciton generation, (2) exciton diffusion and dissociation, (3) charge transport, and (4) charge collection at electrodes. These are briefly discussed

below:

- (1) **Light absorption/exciton generation:** As mentioned earlier, the absorption of a photon of energy $h\nu > E_g$, which is essentially the energy difference between the top of the HOMO and the bottom of the LUMO levels, the organic molecule is excited to the LUMO, resulting in the formation of an exciton. The tightly bound excitons (with binding energies of 0.1–1.4 eV) or polarons as they are also called, are more difficult to dissociate. Since many organic semiconductors such as P3HT, poly(3-hexylthiophene), have bandgaps ~ 2 eV, they are unable to harness a larger portion of the incident solar spectrum.
- (2) **Exciton diffusion and dissociation:** The large binding energies of the excitons generated poses a major challenge in separating the electrons and the holes for effective functioning of the device. This problem was addressed by Tang *et al.* [127], by the introduction of a two-layer (electron donor-acceptor) heterojunction with aligned energy band levels that would not only allow for exciton diffusion and dissociation at the junction but also reduce the probability of recombination. The difference in energies of the HOMO of the donor material and the LUMO of the acceptor material should be lower than the bandgap of either material minus the exciton binding energy. This would ensure that the process of exciton migration to the heterojunction and subsequent dissociation and transfer of the electron (excited to the LUMO of the donor) to the LUMO of the acceptor material, is energetically favorable. However, exciton diffusion lengths (the distance excitons can travel without recombining) in organic semiconductors are very small, of the order of few tens of nanometers. As a result, active layers cannot be very thick, that in turn also affects the amount of light that is absorbed by the material. Novel materials and device structures have been envisaged to circumvent such issues.

(3) **Charge transport:** Following exciton dissociation at the heterojunction, the charges are transported towards the respective electrodes (electrons to the cathode and holes to the anode) primarily driven by drift and diffusion currents. The drift current is maintained by maintaining a potential gradient within the solar cell, either by means of the built-in electric field that is related to the open-circuit voltage, V_{OC} , or by the application of an external bias. The built-in electric field is brought about by the difference in work functions, ϕ , of the two electrodes (high work function at the anode and low work function at the cathode). The diffusion current arises from the carrier concentration gradient that exists between the heterojunction and the electrodes as a result of excess light-generated carriers at the junction. Under low bias conditions, charge transport is primarily by diffusion while at large biases, drift currents dominate.

(4) **Charge collection at electrodes:** The charges thus transported are then extracted out of the active layer at the respective electrodes. For efficient charge collection, the work functions of the electrodes should be aligned with the corresponding MO energy level of the charge carriers, so as to minimize the potential barrier for extraction. In other words, the anode should have a work function that matches the HOMO level of the donor and the cathode should have one that matches the LUMO level of the acceptor, such that the active layer/electrode interfaces have ohmic contacts.

To achieve work function matching at the anode side, traditionally TCOs such as ITO with $\phi \sim 4.8$ eV have been used that match well with the HOMO of thiophene-derivative donor materials such as P3HT ($E_{HOMO} \sim 5.1$ eV). Alternatively, high work function metals such as Au ($\phi_m = 5.1$ eV) can also be used as an anode but owing to poor transmission the resulting efficiencies

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are low. On the cathode side, low work function metals such as Al ($\phi_m = 4.3$ eV) have been typically used to match the LUMO level of acceptor materials such as PCBM, a fullerene derivative.

The process described above is pictorially depicted in Figure 2.27.

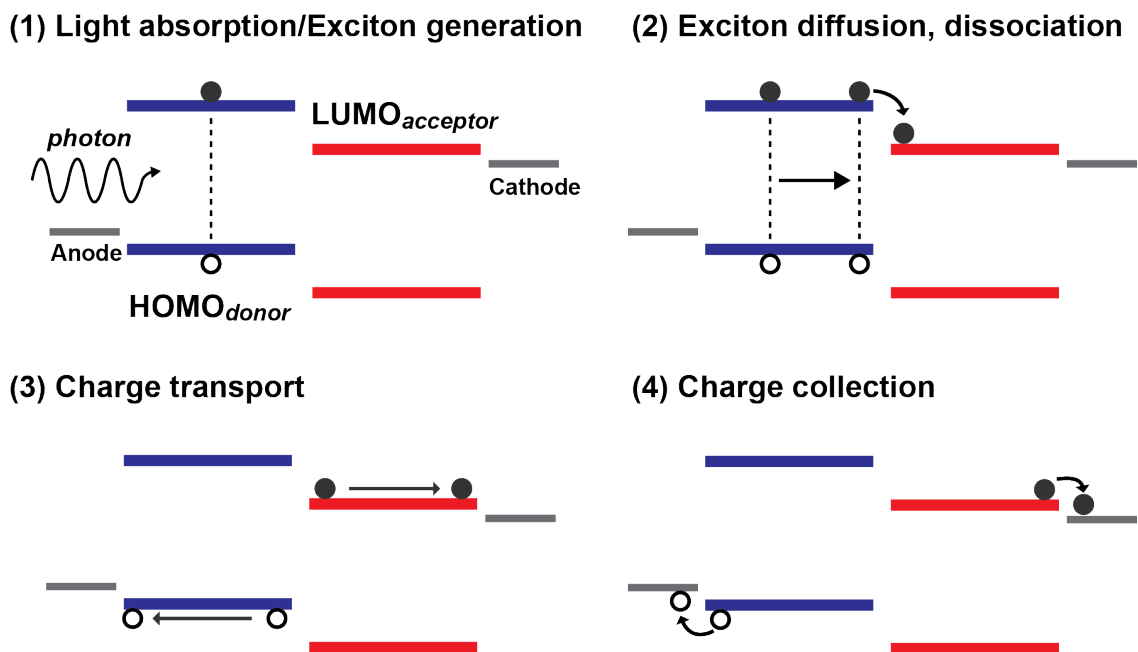


Figure 2.27: Schematic of the working principles of an organic solar cell illustrating the processes of (1) light absorption/exciton generation, (2) exciton diffusion/dissociation, (3) transport of dissociated charge and lastly, (4) collection of charges at the electrodes

Device architectures and materials

Bilayer solar cells

As mentioned earlier, bilayer solar cells have an active layer where the donor and acceptor materials are separate layers, forming a heterojunction. A typical cell would be in a superstrate configuration comprising a glass substrate with an anode coating followed by the active layer and finally the cathode layer. Additionally an intermediate hole transport layer (HTL) is also commonly used between the anode and the donor and a similar electron collection/channel layer (ECL) between the cathode and the acceptor layers (Figure 2.28). By improving the work function matching

between the anode and the HOMO of the donor, and the cathode and the LUMO of the donor, the HTL and ECL respectively improve hole and electron collection at the electrodes.

The short exciton diffusion lengths necessitate the use of thin donor and acceptor layers in order to minimize carrier recombination. However, thin layers also limit the extent to which incident light can be absorbed, in turn reducing the carriers generated. The tradeoff in the choice of thickness of the donor and acceptor layers in bilayer solar cells presents a major challenge in achieving high efficiencies with such a structure.

Bulk heterojunction solar cells

To address the issue of having to deposit thin layers of donor-acceptor layers as in the case of bilayer cells, bulk heterojunctions (BHJs) were discovered in the mid 1990s that have enabled the blending of the two materials within a single interpenetrating nano structured network (Figure 2.28). The resulting blends contain both donor and acceptor phase separated from each other within a length scale of 10–20 nm, which is sufficiently lower than exciton diffusion lengths in many such organic semiconductors. Thicker active layers can be deposited in such structures where generated carriers are transported through percolated pathways toward the active layer/electrode interface before being extracted.

The performance of BHJ solar cells depends strongly on the morphology and composition of the BHJ. Various post-deposition processing steps such as thermal and solvent annealing, modification of polymer functional groups as well as incorporation of metal nanoparticles[128] have been studied to optimize the performance and improve efficiencies.

Tandem/multi-junction solar cells

Analogous to the multi-junction solar cells with inorganic materials (Subsection 2.6.2), to maximize the range of wavelengths of the incident solar spectrum absorbed by the active layers, OSCs have been fabricated with multi-heterojunctions (Figure 2.28). In these cells, each junction generates carriers by absorbing light from different wavelength ranges; the stacked or tandem cells in series contribute towards higher V_{OC} 's while cells connected in parallel bring about larger J_{SC} 's.[129]

The difficulty in matching energy levels of each subcell so as to maximize carrier generation is a particular challenge in such cells. A good interlayer between the subcells is typically necessary to address this concern and also improve charge transport across the electrodes. The fabrication of multiple layers, one on top of the other, also increases chances of damage to underlying layers either from solvent conditions or by thermal/mechanical stresses.

The structures of the aforementioned organic solar cells are schematically represented in Figure 2.28.

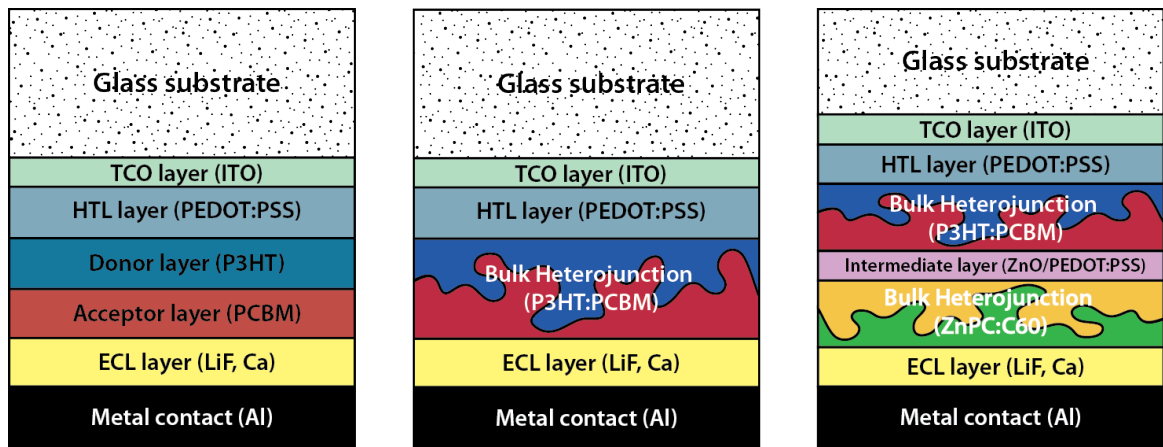


Figure 2.28: Schematic illustration of typical organic solar cell structures. Some standard materials used in these have been included in parentheses

Materials

As a consequence of advances in organic and polymer synthesis and processing techniques, various polymer or small-molecule based active layer materials have been developed in the recent past. Historically, for OSCs, polymer derivatives of polythiophenes such as P3HT (poly (3-hexylthiophene)), have been the donor material of choice while fullerene C_{60} derivatives such as PCBM ([6,6]-phenyl- C_{61} -butyric acid methyl ester) are the most commonly used acceptor materials. Moreover, in present-day OSCs, BHJ active layers are most widely used wherein the donor and acceptor are mixed to form a homogeneous phase-segregated active blend layer. The choice of materials used as donor and acceptor would depend on the electronic energy levels of the two, such that the excitons generated at the heterojunction are effectively dissociated, following which the carriers can be transported to the respective electrodes. As mentioned earlier, the V_{OC} of the device is directly related to the energy gap between HOMO of the donor and LUMO of the acceptor.

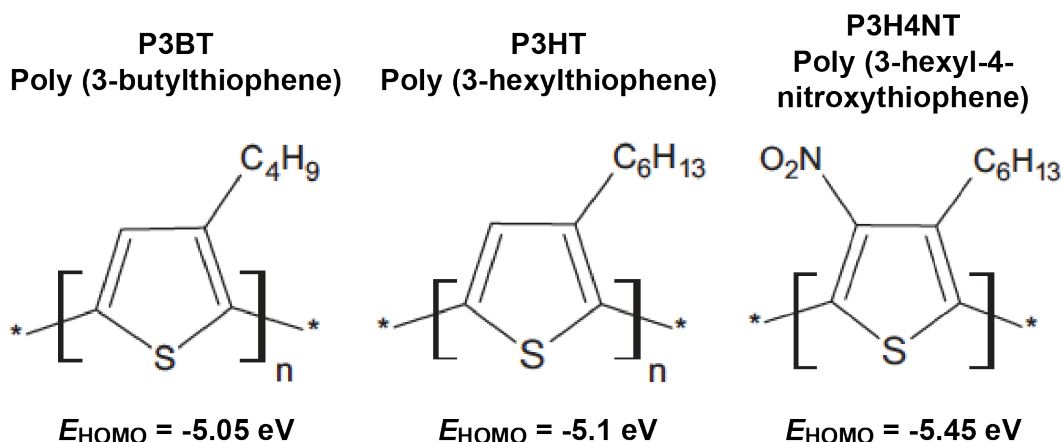


Figure 2.29: Effect of sidegroups in tuning HOMO levels of organic semiconductors. As an example, side groups (electron donating/withdrawing) on polythiophenes have been shown to considerably alter the HOMO level.[124]

The performance of the OSC depends to a great extent on the molecular energy levels, i.e. the HOMO and LUMO of the semiconductors. A major advantage of organic materials as in the case of these semiconducting polymers is that their properties

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can be very easily tuned by modifying their functional groups. Likewise, the HOMO and the LUMO, and hence the bandgap can be suitably modified by varying the molecular backbone or side groups through chemical/synthetic means. Figure 2.29 shows an example of how the HOMO level can be tuned by adjusting the sidegroup in polythiophenes.[124]

Donor materials: The materials used as electron donors in OSCs most commonly fall under the following class of polymers – polythiophenes (PTs), poly(phenylene vinylene)s (PPVs), polymers with 2,1,3-Benzothiadiazole (BT), pyrrolo[3,4-c]pyrrole-1,4-diones (DPPs), benzo[1,2-b;4,5-b']dithiophenes (BDTs) and thieno[3,4-b]pyrazines (TPZs). The chemical structures of some of these polymers are shown in Figure 2.30. Table 2.3 summarizes some of the properties of several of these polymers along with their HOMO energy levels and reported device efficiencies.[130]

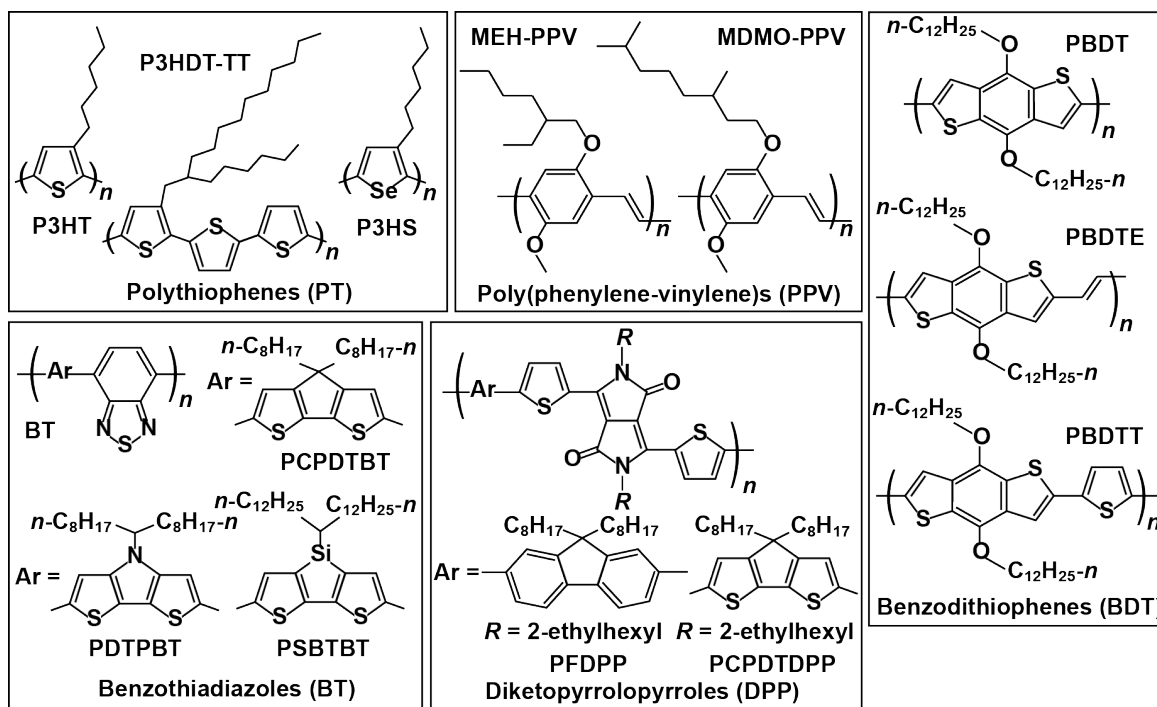


Figure 2.30: Chemical structures of various donor materials, namely, polythiophenes (PT), poly(phenylene vinylene)s (PPV), benzodithiathiazoles (BT), diketopyrrolopyrroles (DPP) and benzodithiophenes (BDT). Adopted from [130].

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Table 2.3: OPV device characteristics for various donor materials with PC₆₀BM as the common acceptor material

Polymer	E_g (eV)	HOMO/ LUMO (eV/eV)	$J_{sc}^\dagger$ (mA/cm ²)	$V_{oc}^\dagger$ (V)	$FF^\dagger$	PCE [†] (%)	Ref.
Polythiophenes (PT)							
P3HT	1.9	-4.8/-2.9	10.6	0.61	0.67	4.37	[131]
P3HDTT	1.9	-5.3/-2.7	6.33	0.82	0.66	3.4	[132]
P3HS	1.6	-4.5/-2.9	6.5	0.5	0.5	2.7	[133]
Poly(phenylene vinylene)s (PPV)							
MEH-PPV	2.2	-5.4/-3.2	3.2	0.86	0.45	1.3	[134, 135]
MDMO-PPV	2.2	-5.0/-2.8	5.25	0.82	0.61	2.5	[136]
Benzodithiazoles (BT)							
PCPDTBT	1.40	-5.30/-3.57	16.2	0.62	0.55	5.5	[137]
PDTPBT	1.43	-4.81/-3.08	11.9	0.54	0.44	2.8	[138]
PSBTBT	1.45	-5.05/-3.27	17.3	0.57	0.61	5.9	[139, 140]
Diketopyrrolopyrroles (DPP)							
PTDPP	1.30	-5.17/-3.16	11.8	0.65	0.60	4.7	[141]
PCPDTPDPP	1.39	-5.25/-3.74	5.73	0.61	0.49	1.7	[142]
Benzodithiophenes (BDT)							
PBDTE	2.03	-5.07/-2.86	1.16	0.56	0.38	0.25	[143]
PBDTT	2.06	-5.05/-2.69	3.78	0.75	0.56	1.60	[143]
PBDTTTPD	1.73	-5.49/-3.47	11.5	0.85	0.70	6.8	[144, 145]
[†] - Values typically from devices with the configuration Glass/ITO/PEDOT:PSS/(Donor-PC ₆₀ BM blend)/LiF/Al							

Acceptor materials: The acceptor material used in a significant majority of OSCs currently are fullerene molecules and their derivatives, in particular, the compound [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₀BM) and its corresponding C₇₀ derivative, PC₇₀BM. Fullerene derivatives are ideal acceptor materials based on their ability to receive four electrons per each C₆₀ molecule. In contrast to donor materials

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where the HOMO level is carefully tuned to maximize efficient charge collection and high V_{OC} 's, the LUMO level for acceptor materials plays an important role in determining V_{OC} ; higher the LUMO level, larger the $HOMO_{donor}-LUMO_{acceptor}$ energy difference and thus, greater V_{OC} 's. While unsubstituted C_{60} has its LUMO level as ~ -4.2 eV, the addition of substituents (such as bis- or multi adducts) can further elevate the LUMO level to energies > -4.0 eV. Figure 2.31 shows some of the aforementioned acceptor materials while Table 2.4 lists corresponding device performance parameters reported in literature.

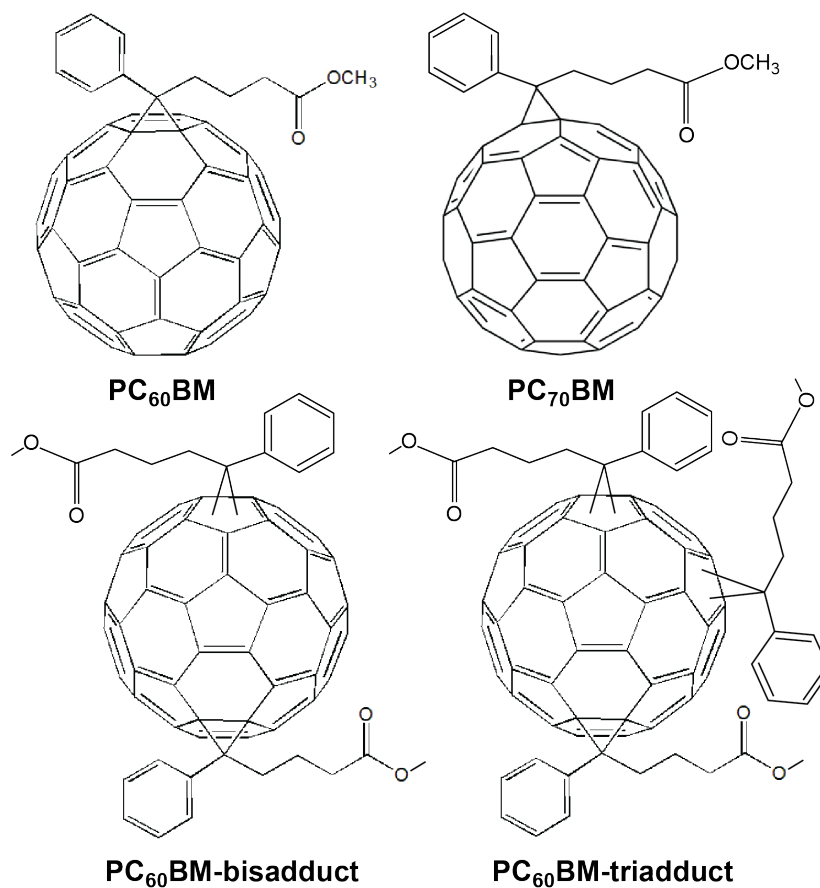


Figure 2.31: Chemical structures of various fullerene-derived acceptor materials, namely, phenyl- C_{61} -butyric acid methyl ester (PC₆₀BM), phenyl- C_{71} -butyric acid methyl ester (PC₇₀BM) and related compounds - PC₆₀BM-bisadduct and PC₆₀BM-triadduct. Adopted from [130].

Electrode materials: At the anode side, which is typically the direction in which light enters the solar cell, transparent conducting materials having high work

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Table 2.4: OPV device characteristics for fullerene-derived acceptor materials with P3HT as the common donor material

Donor/Acceptor (weight ratio)	$J_{SC}^{\ddagger}$ (mA/cm ²)	$V_{OC}^{\ddagger}$ (V)	$FF^{\ddagger}$	PCE [‡] (%)	Ref.
P3HT/PC ₆₀ BM (1:1)	10.8	0.58	0.62	3.88	[146]
P3HT/bisPC ₆₀ BM (1:1.2)	7.3	0.73	0.63	2.4	[147]
P3HT/PC ₇₀ BM (1:0.6)	9.6	0.6	0.61	3.54	[148]
P3HT/IC ₆₀ BA (1:1)	9.67	0.84	0.67	5.44	[146]
P3HT/IC ₇₀ BA (1:1)	9.73	0.84	0.69	5.64	[149]
[‡] - Values typically from devices with the configuration: Glass/ITO/PEDOT:PSS/(P3HT-Acceptor blend)/LiF/Al					

functions are used as the electrode, in particular, degenerately doped wide bandgap semiconducting oxides of In, Sn and Zn, the properties of which have been discussed in greater detail in Section 2.1. A major advantage in using TCOs is the ease with which the Fermi level of these can be matched with the HOMO levels of typical donor materials in OSCs (Figure 2.32). Among these, ITO is most often the anode of choice, with a work function of $\sim 4.6\text{--}4.8$ eV. The high conductivity ($\sim 2 \times 10^4$ S cm⁻¹) combined with high transmittance ($> 85\%$) makes ITO most suitable for such applications. Other oxides include FTO, AZO, IZO, and the likes. Alternatively, conducting polymer electrodes, such as derivatives of polythiophenes (PT), polyanilines (PA), polypyrroles (PP) and polyacetylenes (PAC) to name a few, have also been incorporated in similar device applications.[31, 150] Among these, poly(ethylene dioxythiophene) or PEDOT is by far the most commonly used conducting polymer and is discussed in greater detail in Section 2.5.8.

For the cathode, where the electrode contacts the acceptor material (in conventional OSC structures), a low work function metal, such as Al ($\phi_m \sim 4.3$ eV), is typically used that can be aligned energetically with the LUMO of the acceptor (Figure 2.33).

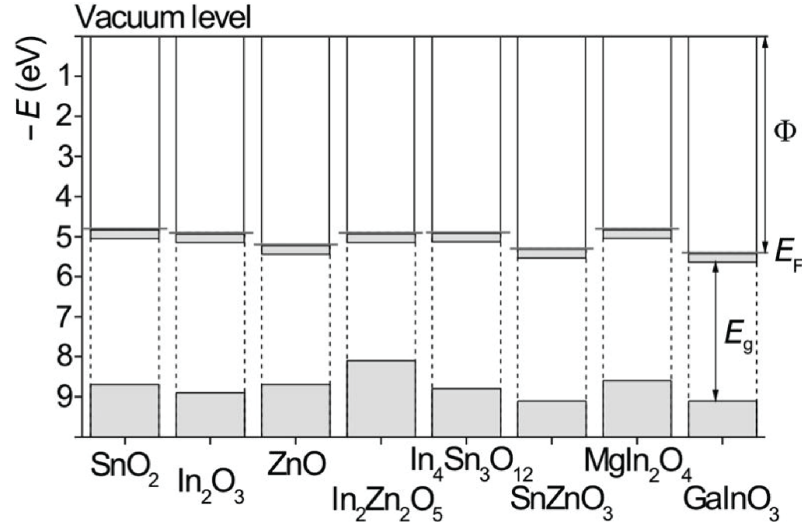


Figure 2.32: Energy band diagram depicting energy gap (E_g) and work functions of various commonly used TCO materials as the transparent anode in OPV devices. The TCO anode is chosen so as to match the HOMO level of the donor material. Reproduced with permission from [150] © 2008 John Wiley & Sons, Inc.

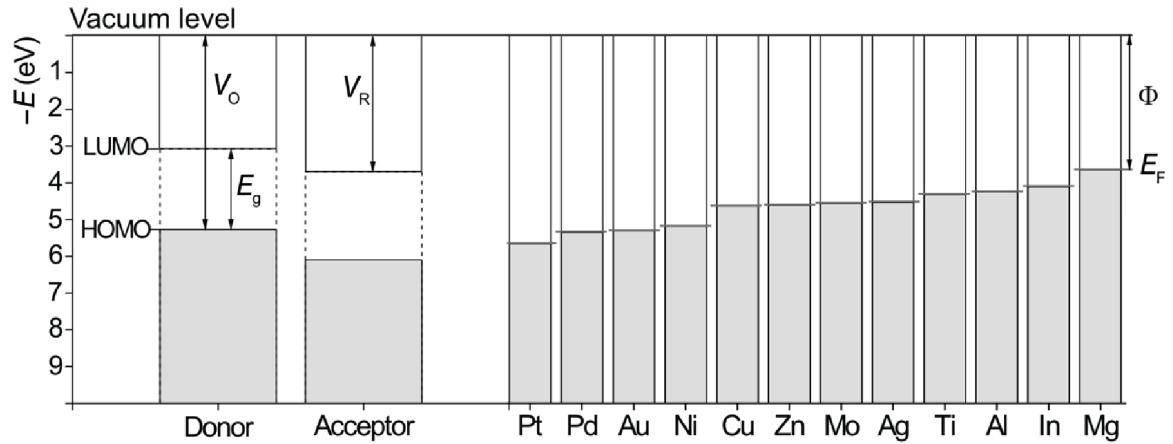


Figure 2.33: Energy band diagram depicting Fermi levels (E_f) and work functions (ϕ) of various commonly used metals as the cathode material in OPV devices. The metal is chosen so as to match the LUMO level of the acceptor material. Reproduced with permission from [150] © 2008 John Wiley & Sons, Inc.

Transport layers: The relatively higher energy of the conduction band edge of commonly used TCOs relative to the HOMO levels of most donors, on the anode side, presents a barrier for holes that impede charge injection into the TCO. To improve collection of charges at the anode, buffer layers also known as hole transport layers (HTL) are used between the TCO and the active layer material. PEDOT:PSS is the most widely used HTL that not only reduces roughness on the TCO surface but

also increases collected photocurrent owing the good alignment in the HOMO levels of PEDOT:PSS (~ 5.0 – 5.2 eV) and the adjacent active layer. The TCO/PEDOT:PSS electrode combination thus provides an ohmic contact to the organic semiconductor, thereby improving device performances. On the cathode side too a similar approach is used to match the LUMO of the acceptor to the work function of the metal used as cathode. To effect collection of more electrons at the cathode, buffer layers such as LiF, Ca, Ba, or MoO₃ are used.[150, 151]

2.6.4 Challenges for electrode materials

The growing interest in organic photovoltaics (OPVs) stems primarily from the ability to use these organic materials in fabricating flexible, robust devices and modules that can be processed easily and on a large scale. Specific to the fabrication of OPVs, the most commonly adopted superstrate configuration involves deposition of a TC anode on the substrate followed by the active layers and hence particular emphasis is laid on the choice of TC electrode material. Among other requirements, the TC electrode is expected to be mechanically flexible and robust, easily processable on plastic substrates, have good adhesion, be chemically and thermally stable, while at the same time being chemically and electronically compatible with the adjacent active layer materials.

A major disadvantage with ITO, the anode of choice for OSCs, is its brittleness. Being a ceramic, it loses its structural integrity upon bending/flexing and hence becomes inappropriate in device applications where flexibility is required. The band structure of ITO has also been reported to prevent effective photo-injection of charge carriers at the active layer/ITO interface. While the problem of photo-injection can be partially addressed by the use of a HTL, the diffusion of indium into PEDOT:PSS, which is a widely used HTL, degrades the device performance over time. In addition to the

above, some other limitations with similar TCOs have been discussed in Section 2.2. Other TC anode materials such as graphene, carbon nanotubes, silver nanowires, conducting polymers, metallic grids, etc. have been suggested that are much more resilient to mechanical deformation and can maintain their electrical conductivities over multiple bending/flexing cycles. In particular, solution-processed silver nanowires have shown great promise and potential as TC anodes that are highly conductive, transparent as well as flexible.[28, 87, 89] Moreover, there is tremendous scope in the use of polymer matrices to embed these silver nanowire networks not only as a means to stabilize dispersions and improve processability but achieve superior mechanical properties as well.[152]

2.7 References

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Chapter 3

Experimental – Materials and methods

3.1 Thin film deposition

3.1.1 Metal evaporation

Thin films can be fabricated by various vapor deposition techniques, the most popular being DC/RF sputtering and thermal or electron-beam assisted evaporation. Among these, electron-beam deposition is a very common method employed for fabricating thin metal films with good precision; in our case ultra high vacuum (UHV) conditions enabled by the use of a cryogenic pump allow for enhanced control of the background ambient during deposition. In this process, an electron-beam heats the metal source, which is contained in a water-cooled crucible, such that the metal either evaporates or sublimates (See Figure 3.1a). The UHV conditions within the deposition chamber allow for the evaporated/sublimed materials to deposit via direct line-of-sight onto the sample placed vertically above. The rate of deposition can be easily controlled by adjusting the electron beam current. In this work, metals such as Au, Ti and Ag, were deposited using this technique.

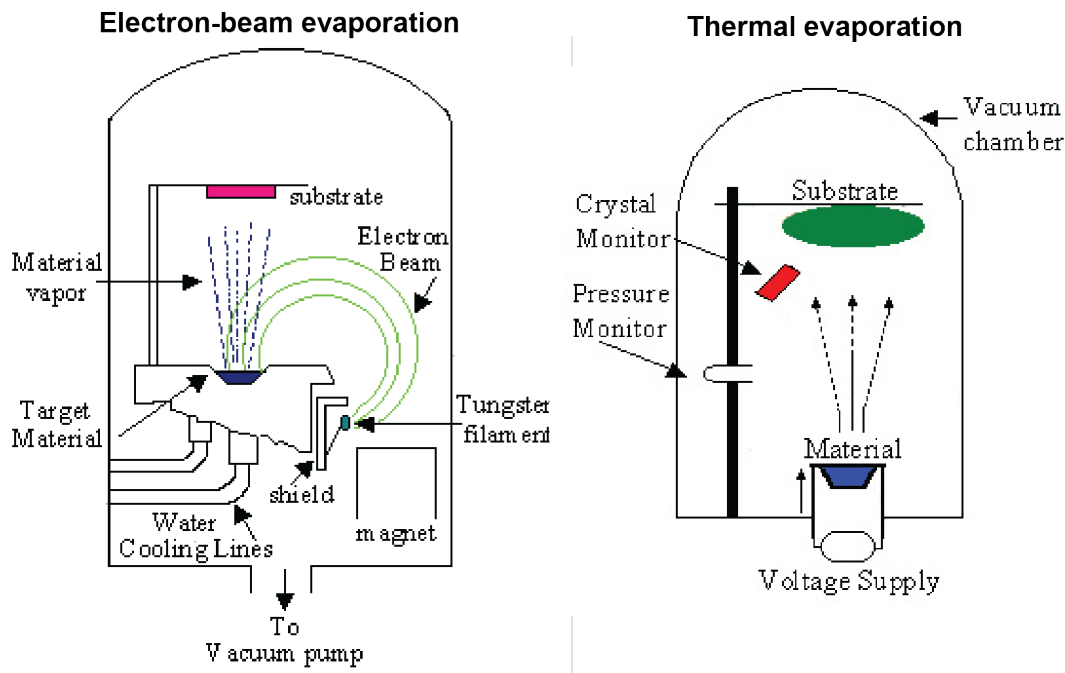


Figure 3.1: Schematic of the process for deposition of thin metal films by two physical vapor deposition methods, namely (a) thermal evaporation and (b) electron-beam evaporation. Image source: <http://www.ece.utep.edu/research/cdte/Fabrication/>

The other oft-employed method to deposit thin metal films is by thermal evaporation of the metal source. In contrast to the electron-beam evaporation technique, the metal source contained in an electrically conducting boat/crucible is resistively heated to the point of evaporation or sublimation by passing a large amount of current through the crucible. The entire setup is enclosed within a glass bell-jar that is evacuated using a mechanical pump/diffusion pump combination (Figure 3.1b). In this work, the metal Al was deposited by thermal evaporation, for use as the low work-function cathode in organic solar cells.

3.1.2 Polymer thin film deposition

Thin polymer films can be fabricated using various techniques, namely, spin-coating, drop-casting and spray-coating. Among these, spin-coating is by far the most commonly employed process to fabricate sub-100 nm polymer films that have large-area uniformity and minimal defects. In a typical spin-coater, the substrate on which

a polymer film is to be deposited (glass, Si, poly(ethylene terephthalate) or PET, etc.) is held onto a chuck by vacuum and then spun at high speeds by a motor connected to the chuck, once a small amount of the polymer solution is dropped onto the substrate surface. The thickness of the polymer film can be varied by adjusting the spin-speed. As the substrate spins, the solvent in which the polymer is dissolved, evaporates slowly leaving behind a thin film containing only the polymer uniformly coated over the substrate. Generally, this process is followed up with a thermal annealing step that would completely remove any remnant solvent from the film. A simple schematic of this process is provided in Figure 3.2.

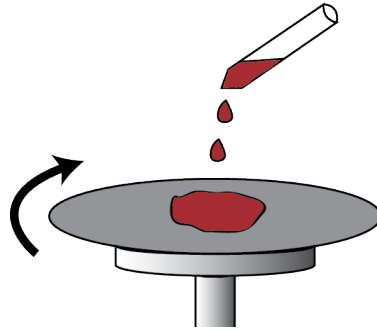


Figure 3.2: Schematic of the process for deposition of thin polymer films by spin coating.

This process is very sensitive to the viscosity of the polymer being spun and since this parameter is different for various polymers, based on their molecular weights, their concentration and the nature of the solvent, the thickness of the films needs to be calibrated in order to fabricate films of a particular thickness. Calibration can be done by spin-casting films on a substrate like Si at various spin speeds and subsequently measuring their thicknesses using ellipsometry or a spectral reflectometer.

In this work, thin films of the polymers polystyrene (PS), poly(vinyl alcohol) (PVA), sodium salt of poly(styrene sulfonate) (NaPSS) and poly(ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) were fabricated by spin-coating and their thicknesses calibrated by using a spectral reflectometer (Filmetrics F50-200). Networked films of Ag-NWs (Ag-NWs purchased from Blue

Nano, Inc., having a diameter of ~ 100 nm and lengths ranging from $10\ \mu\text{m}$ - $30\ \mu\text{m}$) were also obtained by spin-casting dispersions of the same in isopropyl alcohol (IPA). Since this study involves characterization of polymer-embedded Ag-NW films, dispersions of these Ag-NWs in various polymers were first obtained by centrifuging out the original IPA solvent using a VWR-Clinical 200 centrifuge before redispersing them in a polymer of choice. Thereafter, the Ag-NW/polymer composite solutions were spun cast on glass, PET and Si substrates for further characterization.

3.2 Electron microscopy for imaging

The size and scale of materials and structures in this work are predominantly in the nanometer range, which cannot be seen either with the naked eye or even with a powerful optical microscope. Electron microscopes, however, are capable of resolving at the nanometer scale. The use of electrons for imaging extremely small objects stems from the fact that electrons have wavelengths that are $\sim 100,000$ times smaller than those of visible light, thereby enabling them to resolve objects of much smaller dimensions. Based on the nature of characterization, viz. study of a surface, imaging the cross-section of a film, or even electron diffraction, electron microscopes can broadly be classified into two categories - scanning electron microscope (SEM) and transmission electron microscope (TEM).

Scanning electron microscope (SEM)

For this work, SEM images were taken using a Philips XL-30 instrument with a tungsten (W) filament, with the samples mounted on a sample holder using conductive carbon tapes. Cross-sectional images were obtained by using a slanted sample holder and tilting the sample stage in-situ. Some of the images for determining Ag nanowire densities on conductivity were obtained using a PHENOM-Pro desktop SEM.

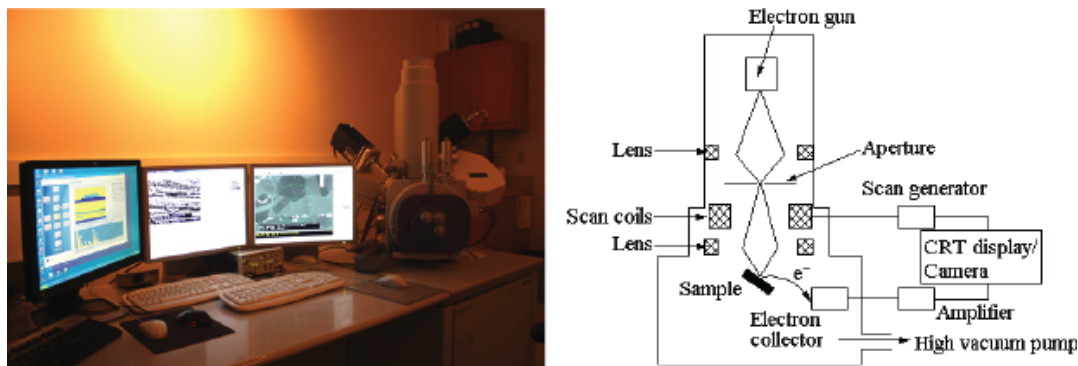


Figure 3.3: A photo of the SEM used in this work (Philips XL-30) and a schematic illustration of the instrument (schematic obtained from http://www.chm.bris.ac.uk/pt/diamond/stuthesis/Chapter2_files/image007.gif).

Figure 3.3 shows a photo of the SEM used in this work (left) and a simple schematic of the internal components of an SEM (right).

Transmission electron microscope (TEM)

A TEM works on a similar principle as that of the SEM. A beam of electrons is generated as in the case of an SEM, by the use of a filament or a field emission gun; the electron beam interacts with an ultra-thin specimen (that is typically placed on a *Cu*-grid). Unlike in an SEM, the electron beam in a TEM is accelerated to much higher voltages ($\sim 100\text{--}300$ kV) enabling it to pass through the sample. In order that the electrons pass through the specimen, they must have thicknesses of the order of ~ 100 nm or lower. Thus, sample preparation for TEM imaging is in itself a complex process that requires special techniques to extract thin sections from the “bulk” sample specimen.

In this work, a TEM was used for imaging nanoparticles as well as cross-sections of thin films. For the former, the sample-preparation is rather simple, wherein a solution of nanoparticles is drop cast on carbon-coated *Cu*-grids. The solvent is subsequently allowed to evaporate, leaving behind a thin film containing only the nanoparticles. Preparing TEM samples for cross-sections of thin films is more involved. Small



Figure 3.4: A photo of the TEM used in this work (left-JEOL JEM 2000EX) and a schematic illustration of its primary working components (schematic obtained from http://www.gitam.edu/eresource/nano/nanotechnology/tem_files/image002.jpg).

portions of the film to be sectioned were mounted vertically onto a holder and placed inside a Reichert Ultracut ultra-cryomicrotome that was maintained at a temperature of $T = -120\text{ }^{\circ}\text{C}$, from which thin cross-sections were cut away using a diamond knife. TEM imaging of the sectioned film microstructures and of nanoparticles were performed using a JEOL JEM 2000EX electron microscope operating at 200 kV. Imaging was based on the amplitude and phase contrast, and images were recorded by a Gatan Orius SC600 high resolution camera. Figure 3.4 shows a picture of the TEM used in this work as well as a simple schematic that illustrates the functioning of the microscope.

3.3 Atomic force microscopy

AFM is a technique for scanning the surface of a specimen at a very high resolution wherein a cantilever with a sharp tip (also called a probe) at the end is made to traverse the sample surface, with its motion being controlled by a piezoelectric feedback system.

In this work, to study the surface profile and also obtain a conductivity map for Ag-

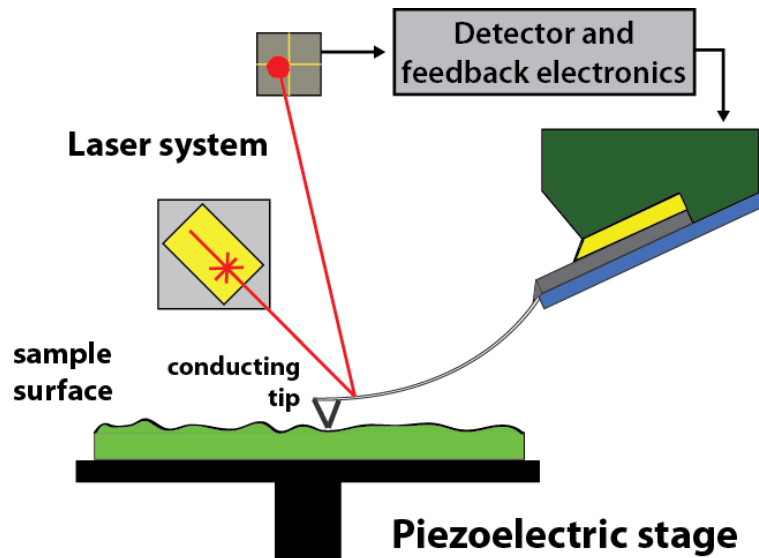


Figure 3.5: Schematic of the working of an atomic force microscope (AFM).

NW film surfaces, an AFM with a conductive probe tip in contact mode was used. The instrument used was an NT-MDT Solver AFM with conductive probe tips (Si tips coated with Cr and Pt) from Budget Sensors (Tap-190-EG). Figure 3.5 shows a schematic of the functioning of an AFM.

3.4 Dispersion characterization



Figure 3.6: Instrument used for measuring zeta potential and particle size using electrophoresis and dynamic light scattering. The solution being tested is filled into the capillary cell.

In this study, the dispersion stability of Ag-NWs in various media was indirectly determined by measuring the zeta potential (ζ) by electrophoresis and particle size

by dynamic light scattering (DLS). Both parameters were measured using a Malvern Zetasizer Nano ZS instrument in the CPS laboratory within the department of Chemical Engineering at Carnegie Mellon University. Dilute Ag-NW dispersions were filled into a disposable capillary cell before placing the same inside the instrument (Figure 3.6). Sample parameters such as material type, dispersant type, their dielectric constants, etc. were input to the software controlling the instrument.

3.5 Electrical conductivity measurement

Sheet resistances for the fabricated films were measured by the four-point probe Van der Pauw method using a Signatone probe station connected to an Agilent HP 4155C semiconductor parameter analyzer. To ensure effective contact between the probe-tips and the film, small quantities of Ag paste were applied to the film surface in a square pattern and the films then placed on a hot plate for an hour, at 100 °C to evaporate out solvent from the paste. The porosity of these nanostructured films obviates the need for such a step.

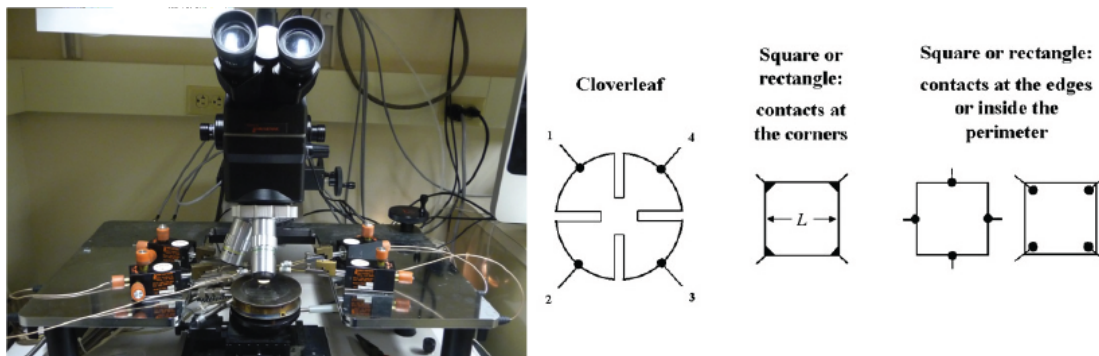


Figure 3.7: The Signatone probe station used for measuring current-voltage relationships and four-point probe sheet resistivities using van der Pauw method [1]. A schematic of different possible sample geometries for measurement is also shown; van der Pauw sheet resistances in this study were measured using a square geometry with contacts at the corners. (http://www.nist.gov/pml/div683/hall_resistivity.cfm)

3.6 Optical transmittance

Transmittances of these films were measured using an Optronics OL770 spectroradiometer with an integrating sphere attachment and also using a Cary-5000 UV-Vis spectrometer.



Figure 3.8: An image of the Optronics OL 770 integrating sphere reflectance attachment used for measuring transmittances of the fabricated thin films

3.7 Image analysis for percolation characteristics

To study electrical percolation in networks of Ag-NWs and of Ag-NW/polymer composites, i.e. identify the critical threshold areal density at which electrical conduction begins, SEM images of films with varying areal coverages were taken. The images were processed using ImageJ and a Python script to obtain spatial characteristics of the films. Here, the processing of images involved thresholding, binarization, morphological dilation and calculation of area based on pixel counts. These analyses allowed us to not only determine the variation of sheet resistance (and film conductance) as a function of the NW areal coverage but also quantify uniformity in film morphologies of various NW networks.

Ag-NW network simulation:

Simulated 2-D networks of Ag-NWs were generated using MATLAB, by considering randomly oriented, filled rectangles with a constant width of 90 nm and a statistical distribution of lengths (Gaussian) with an average length of 20 μm , confined to a box 100 μm x 100 μm in dimensions (See Appendix A for details). The graphs thus generated were saved as images and analyzed for dilation characteristics.

3.8 Solar cell device characterization

3.8.1 Materials

Electron donor

The donor material used in this work was regioregular poly(3-hexyl thiophene) (*rr*-P3HT) from Plextronics, Inc. (OS-2100), a polymer commonly used in the OPV community. These *p*-type conjugated polymeric systems are considered to be among the most versatile and extensively studied polymers for use in electronic devices owing to the ease with which they can be synthesized and chemically modified. The structure of a *rr*-P3HT polymer chain is depicted in Figure 3.9.[2] Typical synthesis methods for *rr*-P3HT are described in references [3–5]. The HOMO for P3HT is at ~ -5.0 eV while the LUMO level is at ~ -3.1 eV - these make P3HT a material highly favorable for photovoltaic devices because of an energy gap ~ 1.9 – 2.0 eV corresponding to an optical wavelength of ~ 620 nm, that essentially covers a good portion of the visible solar spectrum available for carrier generation (Section 2.6).

Electron acceptor

The acceptor material used in this work was phenyl- C_{61} -butyric acid methyl ester (PC₆₀BM) procured from Nano-C, Inc., a fullerene derivative which is also a widely used *n*-type semiconductor used as an acceptor in solution-processed OPV devices both in the blend form as well a separate layer. While several chemical modifications

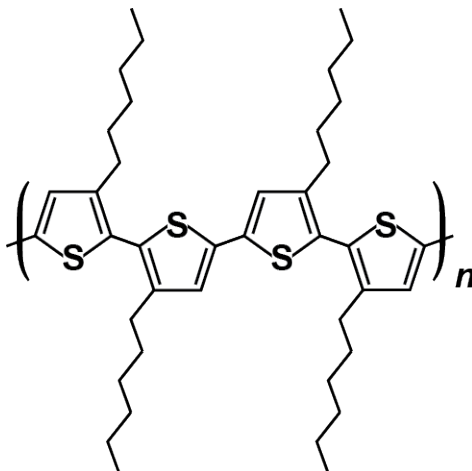


Figure 3.9: Chemical structure of *rr*-P3HT chain.

to donor materials are suggested to improve solar cell device efficiencies, in all these, no modifications for PC₆₀BM are required, reiterating its efficacy as a universal *n*-type material for OPV applications. The HOMO for PC₆₀BM is at ~ -6.0 eV while the LUMO level is at ~ -4.2 eV and its structure is shown in Figure 3.10.[6]

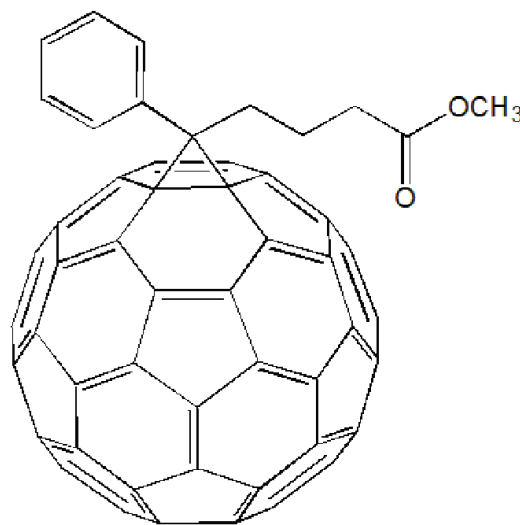


Figure 3.10: Chemical structure of a PC₆₀BM molecule.

3.8.2 OPV device fabrication

To match the pattern of electrode pins on the OPV device measurement setup (an 8-pin configuration as described in Section 3.8.4), the OPV device must be fabricated

accordingly. The device pattern scheme is schematically shown in Figure 3.11a. The device, essentially a superstrate structure, comprises of a square glass substrate ($19\text{ mm} \times 19\text{ mm}$) with a patterned TC electrode over which active and other hole-transport/electron blocking organic layers are to be deposited. Finally, the Al cathode is deposited on top of these layers using a suitable shadow mask. The device, fabricated thus, will then contain 4 different isolated cells, $3\text{ mm} \times 3\text{ mm}$, that can each be individually tested for their I - V characteristics under illumination (light enters the device from the glass side) and in the dark. To ensure good electrical contact between the OPV device electrodes and the electrode pins of the measurement apparatus, a small amount of quick-drying Ag-paste is applied on to each of the device electrodes.

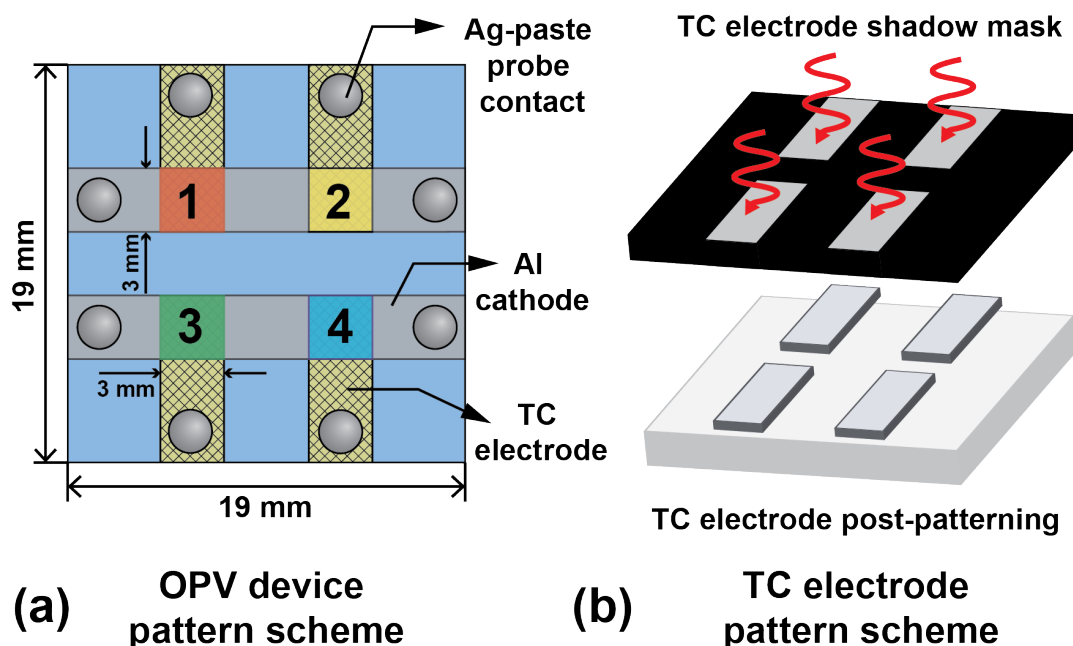


Figure 3.11: (a) Pattern scheme for the OPV device used in this study, along with major dimensions. The pattern allows for the realization of 4 different, isolated solar cells that can individually be measured for I - V characteristics; (b) depiction of process of patterning substrate for TC electrode features.

3.8.3 Substrate patterning

To obtain OPV devices as described in the previous subsection, the substrate needs to be patterned first so as to have the TC electrode specific to the pattern scheme of the device (Figure 3.11a). Standard lithography techniques are used to achieve such a pattern, wherein, glass substrates coated with a photoresist are exposed to UV light through an appropriate shadow mask (Figure 3.11b). The exposed substrates are then developed using a photoresist developer thus dissolving away the exposed regions. The TC electrode (ITO or other Ag-NW based TCs) can then be deposited on top of the patterned feature before finally removing unwanted TC material by lift-off (i.e. by dissolving of remaining unexposed photoresist in a solvent like acetone) (to overcome poor wetting characteristics of the various aqueous dispersions of Ag-NWs, as in PEDOT:PSS and PVA, over non-aqueous photoresists, another patterning procedure was developed wherein unwanted electrode material was simply scratched away using a Q-tip leaving only the material in the desired pattern). At this stage, only the patterned TC electrode remains on the glass substrate (also shown in Figure 3.11b) and can be used for subsequent processing.

In this study, the photoresist used for patterning glass substrates was AZ 4210 while the patterns were subsequently developed using an AZ 400K developer diluted in deionized water to a ratio of 1:3 (developer:water). Patterns were exposed to UV light (i-line, 365 nm) using a Karl Suss MJB3 Contact Mask aligner.

3.8.4 OPV device measurement apparatus

To measure OPV device characteristics, a customized TFI-BC test fixture from PVmeasurements, Inc. was used. The fabricated device is mounted onto the fixture in an inverted manner so as to allow for the electrode pins on the fixture to come in intimate contact with the electrodes on the OPV device. A 140W Xe bulb with

3. Experimental – Materials and methods

a Newport/Oriel 69907 research solar light source, filtered and calibrated to provide light of intensity 100 mW cm^{-2} with a spectrum similar to that of the *AM1.5G* solar spectrum was used to illuminate the cells. A GENTEC-EO UP25N-40S-H9 Laser Power Meter is used to calibrate the intensity of the solar simulator by moving closer to or farther from the light source on an optical rail. The *I-V* characteristics of the cells were measured using a Keithley 240 source-measure unit USB-switched to a computer and controlled through a custom software interface written in MATLAB by Jacob Mohin of the Kowalewski group. The instruments along with a cartoon of the described apparatus are shown in Figure 3.12.

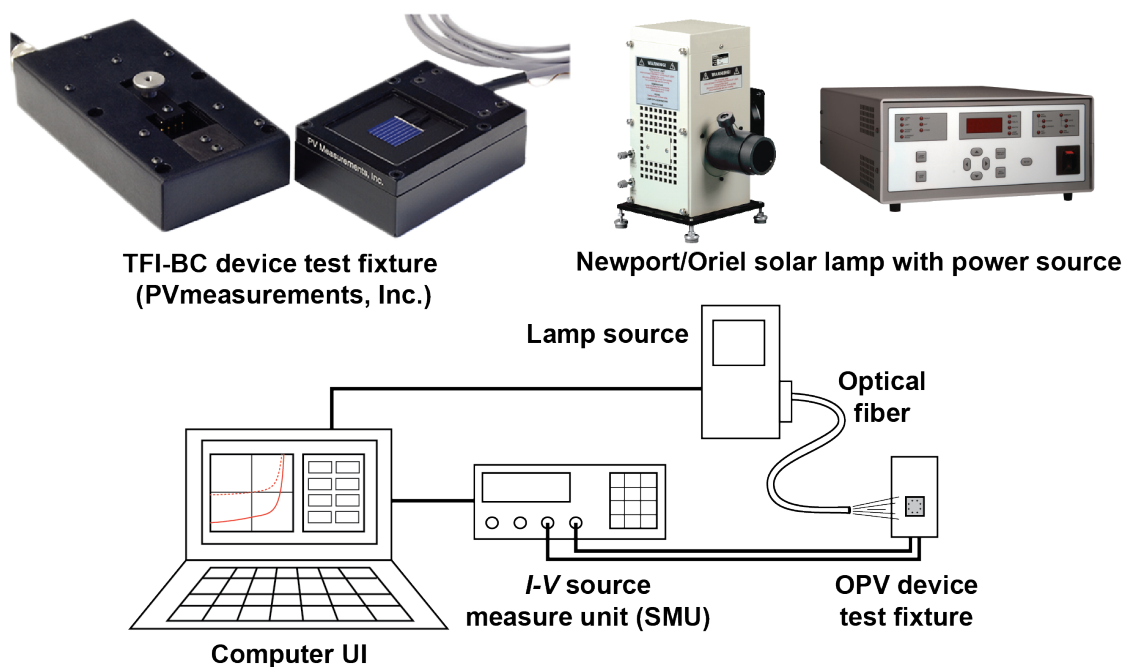


Figure 3.12: Images of (a) Test fixture used to mount the OPV device (Image source: <http://www.pvmeasurements.com>); (b) Xe lamp with power source (Image source: <http://www.newport.com>); and (c) cartoon depicting instrumentation and apparatus for OPV device testing

3.9 References

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Chapter 4

Optically Resonant Au-PS Hybrid Structures

The contents of this chapter have been published in a slightly modified form in the journal “ACS Applied Materials and Interfaces”. The particular reference is –

S. Narayanan, J. Choi, L. Porter, and M. R. Bockstaller: “Flexible Transparent Metal/Polymer Composite Materials Based on Optical Resonant Laminate Structures”, *ACS Appl. Mater. Interfaces*, **2013**, vol. 5, pp. 4093–4333.

4.1 Introduction

As mentioned in Chapter 2, and in particular, Section 2.3, a variety of material systems are being considered as alternatives to conventional oxide-based TCs (ITO, FTO, AZO, and the like) with reasonable combinations of optical transmission in the visible region and electrical conductivity, without compromising one property for the other.[1] Additionally, recently there has been increasing interest to look for quality TC materials that are not only easy and inexpensive to process, but also readily available and mechanically robust and non-brittle, as might be required, for example, in the case of flexible, printable electronics.[2]

In this part of the study, a novel approach to engineer transparent materials is introduced, based on constructing one-dimensional photonic bandgap (PBG) structures with periodic dielectric layers. In particular, suitable design of periodic metal/polymer composite materials is shown to facilitate resonant tunneling of light at absorbing wavelengths and to provide a means to significantly reduce optical absorption losses in polymer-based metallodielectric composite structures. The conditions for resonant tunneling are established based on the concept of “photonic band edge alignment” in 1D-periodic systems (Section 2.4).

4.2 Experimental methods

The material system in our study consists of a lamellar stack of gold (Au) and polystyrene (PS) that were chosen because of the following property characteristics: PS (molecular weight $M_n = 300,000$ g/mol) is a transparent amorphous polymer with high softening temperature ($T_g \simeq 110$ °C) and thus mechanically robust over a wide range of operating temperatures. PS also has been shown to exhibit good wettability by metals such as Au or Ag (a key prerequisite for the deposition of thin, uniform films); Au was chosen as a metal due to its chemical inertness and its good ductility that supports the flexural stability of polymer/metal laminate structures [3, 4].

Thin films of the polymer PS were fabricated by spin coating solutions of PS dissolved in toluene with the concentration, rotation speed and duration of rotation adjusted as per a calibration for concentration- and rotation speed-dependent thickness curve (Figure 4.1). Thin Au films were deposited from Au pellets (purchased from Kurt J. Lesker, Inc., 99.99% purity, metals basis) onto unheated substrates using electron-beam evaporation; the deposition rate was $0.5 \text{ \AA/second}$. The ultra-high vacuum (UHV) conditions within the deposition chamber allow for the evaporated/sublimed materials to deposit via direct line-of-sight onto the sample placed vertically above.

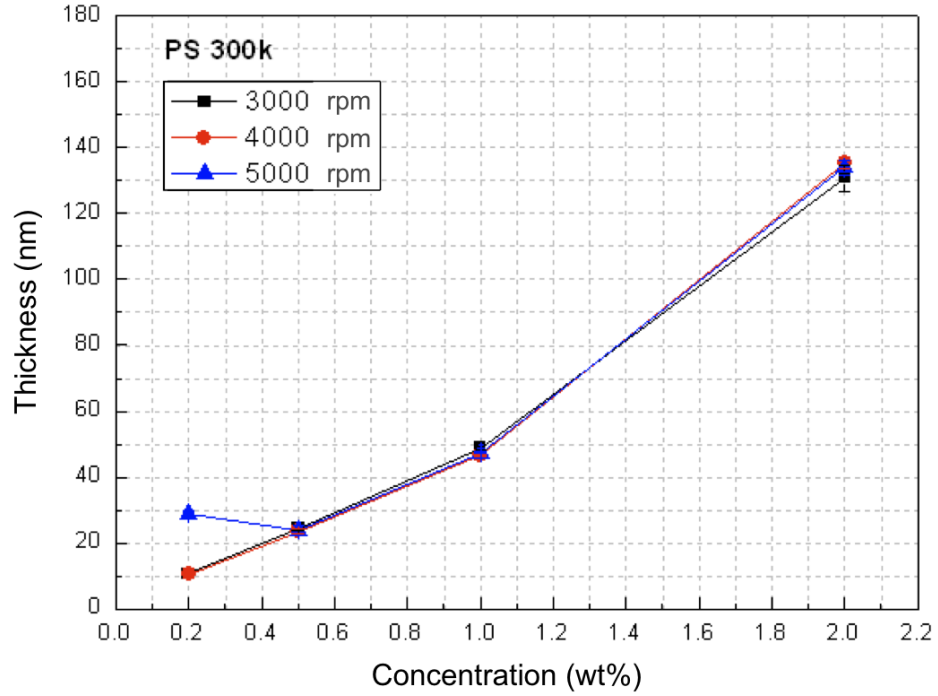


Figure 4.1: Calibration curve for PS films - thickness as a function of polymer wt% in solution and spin speed.

The base pressure and deposition pressure in the chamber were $\sim 10^{-8}$ Torr and $\sim 10^{-10}$ Torr, respectively. The thicknesses of the Au films were determined by an in-situ quartz crystal microbalance.

Metal-polymer stacks were prepared by alternating evaporation of Au and spin-coating of PS layers on glass (Corning cover glass slides) and PET substrates. While the concept of optical resonant tunneling through metal-polymer laminated structures can be demonstrated by depositing alternating metal and polymer films on transparent glass substrates, PET was chosen as another substrate because of its optical transparency in the visible range as well as mechanical flexibility and toughness. The appropriate deposition conditions were determined by spin casting films on silicon and subsequently measuring their thicknesses using ellipsometry and a spectral reflectometer (Filmetrics F50-200).

4.3 Results: Evaluation of design criteria by computer simulation

From Maxwell's theory of electromagnetism, the propagation of light through a dielectric medium can be described by a set of eigenvalue differential equations as follows -

$$\frac{1}{\epsilon(r)} \nabla \times [\nabla \times E(r)] = \frac{\omega^2}{c^2} E(r) \quad (4.1)$$

$$\nabla \times \left[\frac{1}{\epsilon(r)} \nabla \times H(r) \right] = \frac{\omega^2}{c^2} H(r) \quad (4.2)$$

where, $E(r)$ and $H(r)$ describe the electric and magnetic fields of the incident light; $\epsilon(r)$, the dielectric function, ω and c , the frequency and speed of light, respectively. As mentioned previously, multiple reflections at each interface of the photonic crystal interfere constructively or destructively to facilitate either transmittance or reflection of incident light, making it difficult to analytically solve for transmittance/reflectance. However, by applying a treatment similar to that used in quantum mechanics while considering interaction of EM radiation with periodically arranged atoms, one can set up a system of Bloch functions to characterize the eigenmodes [5] and evaluate the electric field through and across the dielectric layers accounting for some simple boundary conditions across the photonic crystal, using a system of transfer matrices. This is known as 'Transfer Matrix Method' (TMM) and is a well established method used to determine the transmittance, reflectance, absorbance and even the electric field distribution in the medium, as described by Pettersson *et al.* [6]. The Bloch functions used to characterize these eigenmodes can also be used to obtain the band structure of the stack, by the planewave expansion method (PEM) [7].

The chosen system of materials consists of Au as the metal and PS as the polymer dielectric owing to properties favorable for this study. In the following discussion,

laminate structures will be abbreviated as $(\text{Au}_x|\text{PS}_y)_N$ where x and y represent the thickness (in nm) of the Au and PS layer, respectively, and N represents the number of lamellar repeats. To identify suitable architectures for $(\text{Au}_x|\text{PS}_y)_N$ laminate structures that facilitate maximum tunneling efficiency, the transmission spectra as well as the electric field distribution of 1D-periodic metal-dielectric structures were calculated using TMM [8]. The primary prerequisite for enhanced optical transmission is that at the absorbing wavelength the electric field is concentrated within the transparent (polymer) layer. If the absorption of metals is dominated by free carrier excitation (approximately correct for noble metals) then the wavelength corresponding to the characteristic plasma absorption frequency ω_P should be chosen as a reference to minimize absorption (see discussion below). For example, Figure 4.2a depicts the electric field intensity distribution in an optimized metal-polymer stack comprised of four double layers of Au and PS $(\text{Au}_{10}|\text{PS}_{140})_4$ with layer thicknesses $d_{Au} = 10$ nm and $d_{PS} = 140$ nm, respectively. The figure reveals that at the absorption wavelength $\lambda = \lambda_P \simeq 520$ nm the field intensity is concentrated within the PS layers. For this resonant condition the energy loss is significantly reduced as compared to an off-resonant condition (shown in the figure is the field distribution for $\lambda = 350$ nm) as is confirmed by the increase of $|E|^2$ of the transmitted wave for $\lambda = \lambda_P$. The comparison with the calculated field intensity $|E|^2$ of a monolithic film structure of equal overall thickness $d_{Au} = 40$ nm (depicted in Figure 4.2b) demonstrates the significant increase of transmittance at the plasma frequency of gold as compared to the monolithic film architecture.

An alternative but useful approach to determine ‘optimum’ film geometries is based on the analysis of the photonic band structure of the corresponding periodic metal/polymer stack. Because a photonic band gap in lamellar structures can be shown to arise as a consequence of the divergence of the electric field distribution

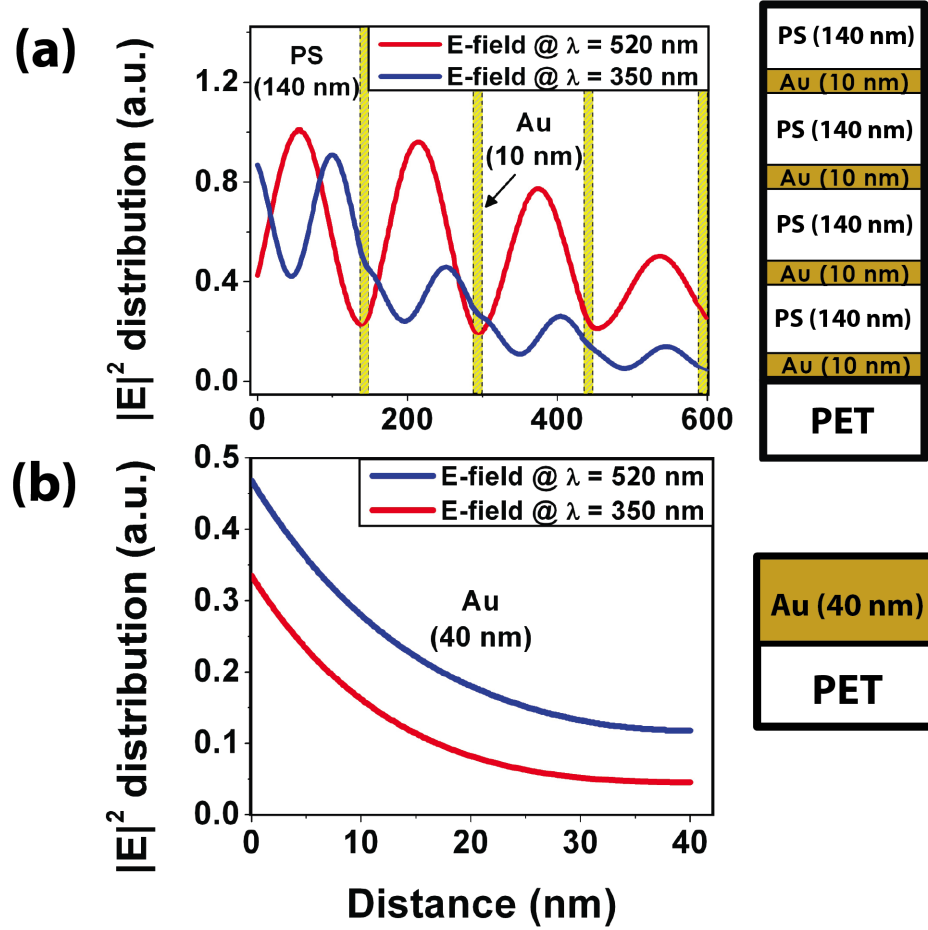


Figure 4.2: (a) Illustration of a $(Au_{10}|PS_{140})_4$ model resonant metallodielectric stack and calculated distribution of the electric field intensity $|E|^2$ determined by TMM. (b) Illustration and calculated distribution of the electric field intensity $|E|^2$ of a monolithic gold film with thickness $d_{Au} = 40$ nm demonstrating rapid decay of the electric field. Reproduced from [9] © 2013 American Chemical Society.

at the band edges (with the field being concentrated in the high (low) refractive index layer at the lower (upper) band edge, respectively), the transmission condition is equivalent to the line-up of the plasma frequency with the lower band edge of the photonic structure (this is because the refractive index of metals approximately vanishes at the plasma frequency and thus the localization of the field in the transparent polymer layer is the greatest if the lower band edge matches the plasma frequency) [10]. Figure 4.3 illustrates the reflection spectrum of the $(Au_{10}|PS_{140})_4$ structure calculated for an arbitrary angle of incidence for both TE and TM polarization along with the approximate position of the lower band edge (white dotted

line) that was calculated using TMM [8] ^a.

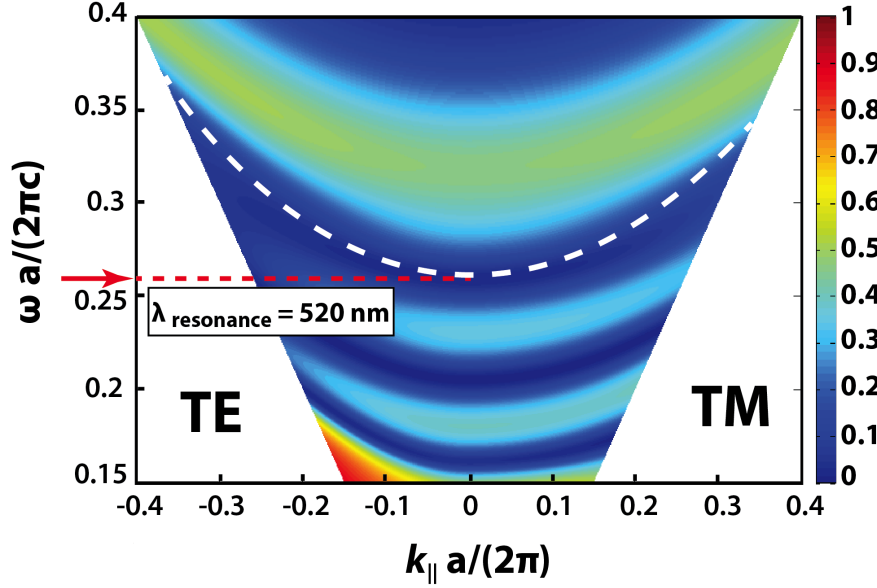


Figure 4.3: Calculated frequency dependence of reflectivity for TE and TM polarization for a $(\text{Au}_{10}|\text{PS}_{140})_4$ metallodielectric stack. Reproduced from [9] © 2013 American Chemical Society.

The simulation assumes optical constants of bulk gold. In Figure 4.3, ‘ ω ’ denotes the radial frequency, ‘ c ’ is the vacuum speed of light, ‘ a ’ denotes the lamellar repeat, and ‘ $k_{||}$ ’ is the parallel component of the wavevector with respect to the layer orientation. Reflectivity of normal incidence corresponds to $k_{||} = 0$. The dashed white curve indicates the approximate location of the band gap (estimated for an infinite stack) and the red arrow indicates the approximate frequency of the lower band edge at $k_{||} = 0$. Although the consideration of the ‘photonic crystal analogy’ does not provide explicit new insights for transparent laminate structures, it does highlight the relevance of the ‘band edge’ in photonic structures and could provide a basis for the extension of the resonant tunneling approach to 2D and 3D periodic structures as well as to other forms of wave propagation (such as phonon propagation) [11, 12]. To rationalize the particular choice of $(\text{Au}_{10}|\text{PS}_{140})_4$ in the present study, Figure 4.4

^aIn Figure 4.3, TE (TM) correspond to the magnetic (electric) field being normal to the layer orientation. Note that for normal incidence both polarizations are equivalent.

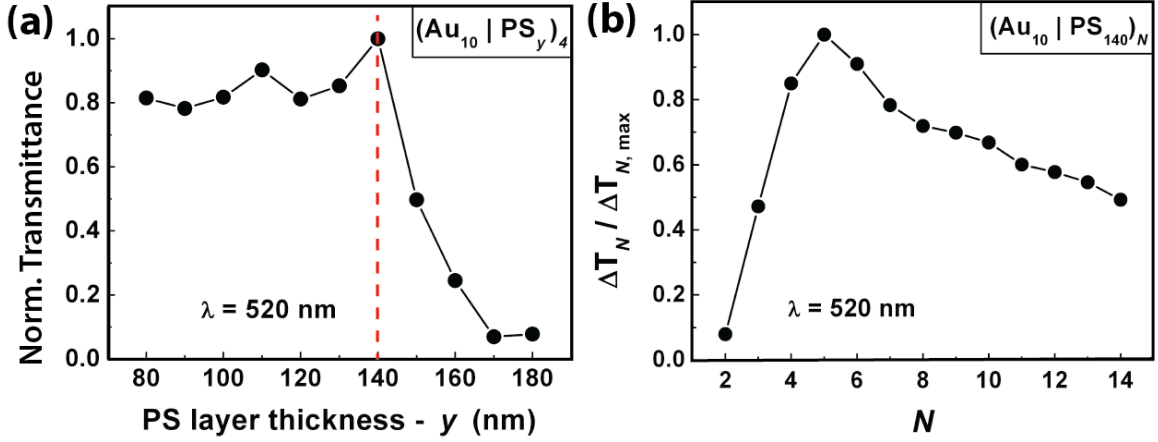


Figure 4.4: Dependence of tunneling efficiency on film architecture calculated using TMM. (a) Calculated transmission at $\lambda = 520$ nm of $(Au_{10}|PS_y)_4$ resonant structure (on glass substrate) as a function of the PS-layer thickness in the range $y = 80 - 180$ nm; (b) Dependence of quality factor for transmission enhancement $\Delta T_N = T_{stack,N} - T_{bulk,N}$ on the number of repeat units in $(Au_{10}|PS_{140})_4$ laminate structures. Reproduced from [9] © 2013 American Chemical Society.

illustrates the effects of PS thickness variation and the number of stacked lamellae on the film transmittance and tunneling efficiency of light ($\lambda = 520$ nm) in the $(Au_{10}|PS_y)_4$ system. We note that in the above discussion the layer thickness of gold is fixed at $d_{Au} = 10$ nm. Although thinner films would be expected to facilitate higher transmittance (because the electric field concentration within the metal layer decreases with film thickness), eventually a decrease in electrical conductivity (as well as mechanical ductility) would be expected due to surface scattering [13].

Thus in reality, a compromise has to be made to balance optical transmission, electric conductivity as well as mechanical ductility; $d_{Au} = 10$ nm was determined to be an appropriate choice for the present system. The effect of layer non-uniformity on film transmittance was evaluated by simulating multilayer structures with variable thickness of the PS layer. For thickness variations within 5% of the average layer thickness $\langle d_{PS} \rangle = 140$ nm, the transmittance was found to remain within 10% of its maximum value, as shown in Figure 4.4a (the effect of random thickness fluctuations will be discussed more extensively in a later section). Optical resonant

tunneling in metal/polymer structures is thus reasonably tolerant against variations and imperfections of the layering process – an important feature for the application of the approach to the fabrication of transparent metallodielectric composites.

To evaluate the number of periods corresponding to the maximum enhancement of light transmission, a quality factor was introduced as $\Delta T_N = T_{\text{stack},N} - T_{\text{bulk},N}$ where $T_{\text{stack},N}$ and $T_{\text{bulk},N}$ represent the transmittance of the $(\text{Au}_{10}|\text{PS}_y)_4$ stack and the corresponding monolithic film of equal respective total thickness. ΔT_N thus provides a measure for the increase of transmittance due to resonant tunneling. As illustrated in Figure 4.4b, ΔT_N attains a maximum value at $N \simeq 5$, however, will remain within 10% of the maximum attainable transmission within the range $N = 4 - 6$. For reasons of practicality and to obtain omaximum overall transmittance, $N = 4$ was chosen in the present study and thus the experimental demonstration of optical resonant metallodielectric structures will focus on the $(\text{Au}_{10}|\text{PS}_y)_4$ architecture.

4.4 Results: Structural characterization of Au|PS stacks

As mentioned in Section 4.2 on Experimental methods, Au and PS films were deposited alternately on glass and PET substrates by e-beam evaporation and spin coating, respectively. PS films were prepared by spin-coating the PS solution (3 wt % of the polymer dissolved in toluene) for 30 seconds. The spin rate was varied between 1500 and 4000 rpm to arrive at a thickness of 140-150 nm, consistent with the thickness required as per simulations.

Characterization of the film microstructure was performed by scanning (SEM) and transmission (TEM) electron imaging of cross-sectioned films. Figure 4.5 depicts representative SEM (Figure 4.5a) and TEM (Figure 4.5b-d) images of a typical

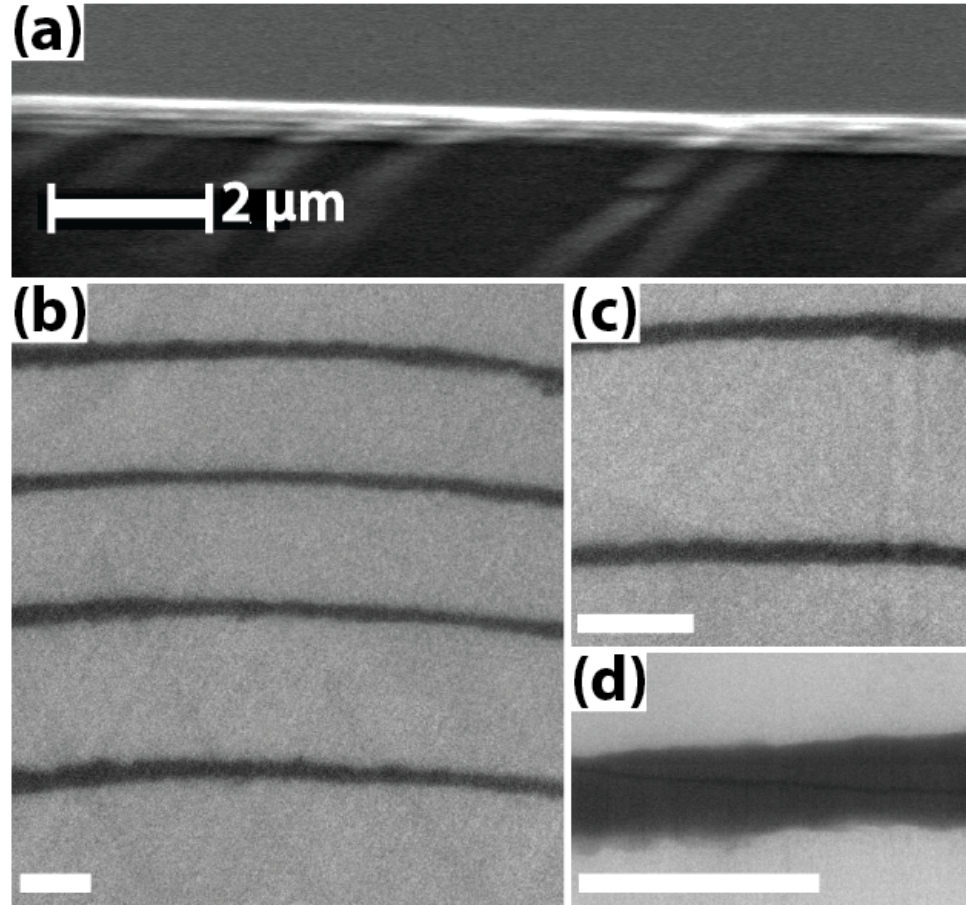


Figure 4.5: Electron micrographs of the $(\text{Au}_{10}|\text{PS}_{140})_4$ film microstructure. (a) Cross-sectional SEM image of Au-PS stack deposited on glass substrate; (b)-(d) Cross-sectional TEM images of the stack prepared on a PET sheet, at different magnifications (substrate location is along the lower edge of micrographs). Scale bar is 100 nm. Reproduced from [9] © 2013 American Chemical Society.

$(\text{Au}_{10}|\text{PS}_{140})_4$ stack demonstrating the uniform structure and layer dimensions of the PS/Au model system (the substrate is located along the lower edges of the images in Figure 4.5b-d). High magnification (Figure 4.5d) reveals partial diffusion of gold into PS-layers. Minor tilt misorientation of sectioned samples gives rise to distortions of the layer thicknesses. We note that the precise thickness of the Au layer cannot be determined from cross-sectional TEM because of the potential mechanical distortion during sectioning. Rather, the thickness of the gold layers was determined in-situ by a quartz crystal microbalance during evaporation and independently verified by ellipsometry. A small asymmetry of the evaporated Au films (with respect to the

substrate orientation) can be discerned from high magnification micrographs (see Figure 4.5d) that is attributed to the partial diffusion of Au into the surface region of the PS layers during the early stages of metal deposition [14]. While it is possible to account for the effect of metal/polymer interdiffusion on the film optical properties, we found the diffusion lengths to be less than a few nanometers (i.e. much smaller than the wavelength of light) and thus the effect of interdiffusion on optical properties is assumed to be negligible.

4.5 Results: Effect of optical dispersion in metals

A comment should be made regarding the effect of film thickness on the optical properties of the gold layer. As the thickness of the metal layer is decreased below a critical threshold value that is of the order of the electron mean free path l (for gold $l \cong 30$ nm), surface scattering is expected to alter the optical constants of the metal. The implications of spatial confinement on the optical properties of metals are well understood for the case of spherical nanocrystals for which it has been shown that, within the realm of free electron approximation, the effect of surface scattering on the dielectric constant of metals can be approximately accounted for by the introduction of additional damping terms in the Drude-Lorentz-Sommerfeld model [15].

In this case the effect of spatial confinement is primarily on the imaginary component of the dielectric constant $\epsilon_2 = 2nk$ (where n and k correspond to the real and imaginary part of the refractive index, respectively) such that $\epsilon_2 \sim R^{-1}$ (with R denoting the particle radius)[15]. In contrast to spherical systems, little information is available regarding the effect of spatial confinement in thin metal films. To the best of our knowledge the first experimental studies on the effect of film thickness on the optical constants of metals are due to Krautkrämer and coworkers as well as Malé and coworkers who systematically evaluated the effect of film thickness on the

optical constants of thin films of gold and silver [16, 17].

A compilation of studies on the optical properties of thin metal films is provided in recent reviews by Heavens [18]. The conclusion of these previous studies is that a significant reduction of the films' refractive index can be expected for film thicknesses below 20 nm in the case of Au (and similarly for other metals such as Ag, Cu, Pt, and Pd). Since for the present (Au₁₀|PS₁₄₀)₄ system the thickness of the gold layers is significantly below the electron mean free path (and since for 10 nm layer thickness no experimental data is available in the wavelength range of interest), the optical constants n and k were determined experimentally to facilitate proper modeling of the films optical response. Optical constants were measured for a series of gold films (deposited on glass) using variable-angle spectroscopic ellipsometry (VASE). Figure 4 summarizes the results for n and k for a range of tested film thicknesses $d_{Au} = 5, 10$ and 20 nm.

In agreement with previous reports, the optical constants of Au are found to sensitively depend on the film's thickness. While for thickness $d_{Au} = 20$ nm the optical constants are close to bulk values (red curve in Figure 4.6), both the real and imaginary parts of the refractive index differ markedly for smaller film thicknesses. Similar to spherical nanocrystal systems the observed trend of n and k with d_{Au} is consistent with an increase of ϵ_2 with decreasing film thickness; however, no simple proportionality relation as for spherical particle systems could be established^b. For the simulation of film transmittance, experimental values corresponding to a film thickness $d_{Au} = 10$ nm were assumed.

^bWe note that the present data set is not sufficient to allow for quantitative comparisons of the confinement effect on spherical and planar systems.

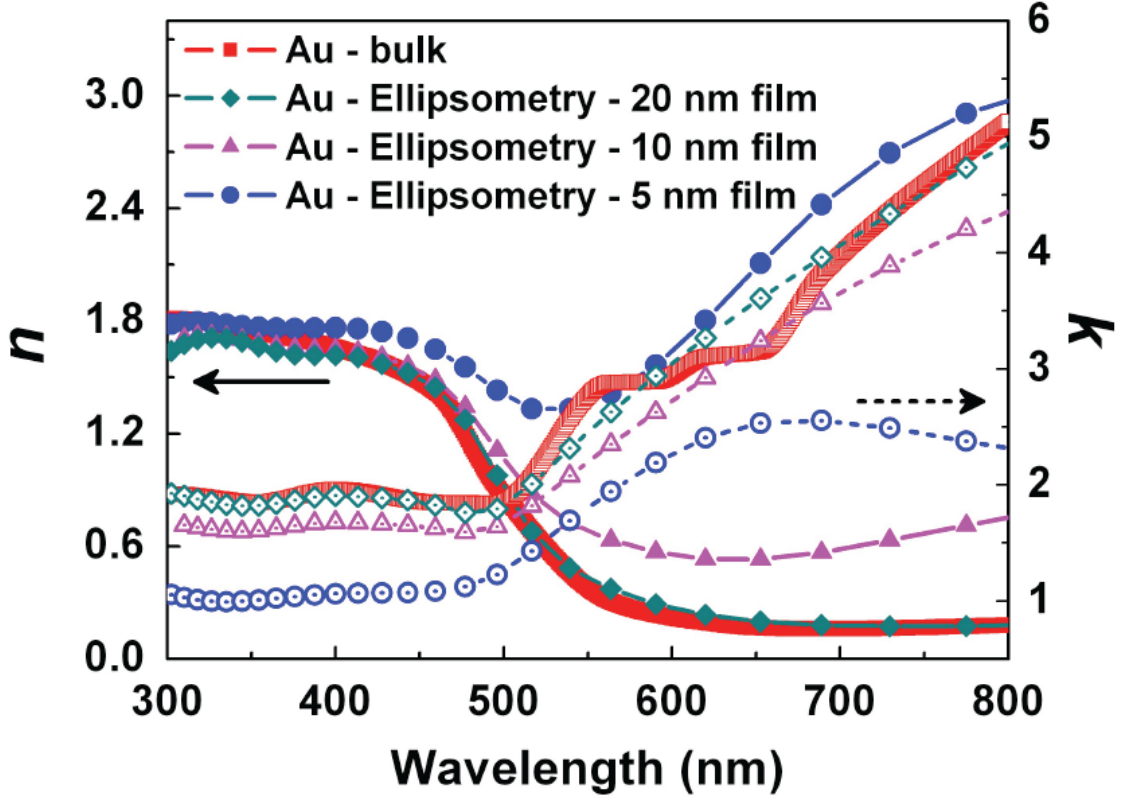


Figure 4.6: Comparison of the real part (n , solid lines), and imaginary part (k , dotted lines) of the refractive index of gold films of thickness $d_{Au} = 5, 10$ and 20 nm that were determined by VASE. (VASE data courtesy of J. A. Woollam, Inc.) Reproduced from [9] © 2013 American Chemical Society.

4.6 Results: Optical transmittance - experiment and simulation

Figures 4.7a and 4.7b show pictures of the monolithic Au-film ($d_{Au} = 40$ nm, Figure 4.7a) and the corresponding metallodielectric $(Au_{10}|PS_{140})_4$ resonant structure on a PET substrate (Figure 4.7b) demonstrating the significant increase in transparency facilitated by resonant tunneling. The optical properties as well as film structure were retained during repeated flexural deformation of the PET substrate (see Figure 4.7c) thus illustrating the potential applicability of polymer-based metallodielectric resonant structures as, for example, transparent, flexible conductive substrates or electrodes in polymer electronics.

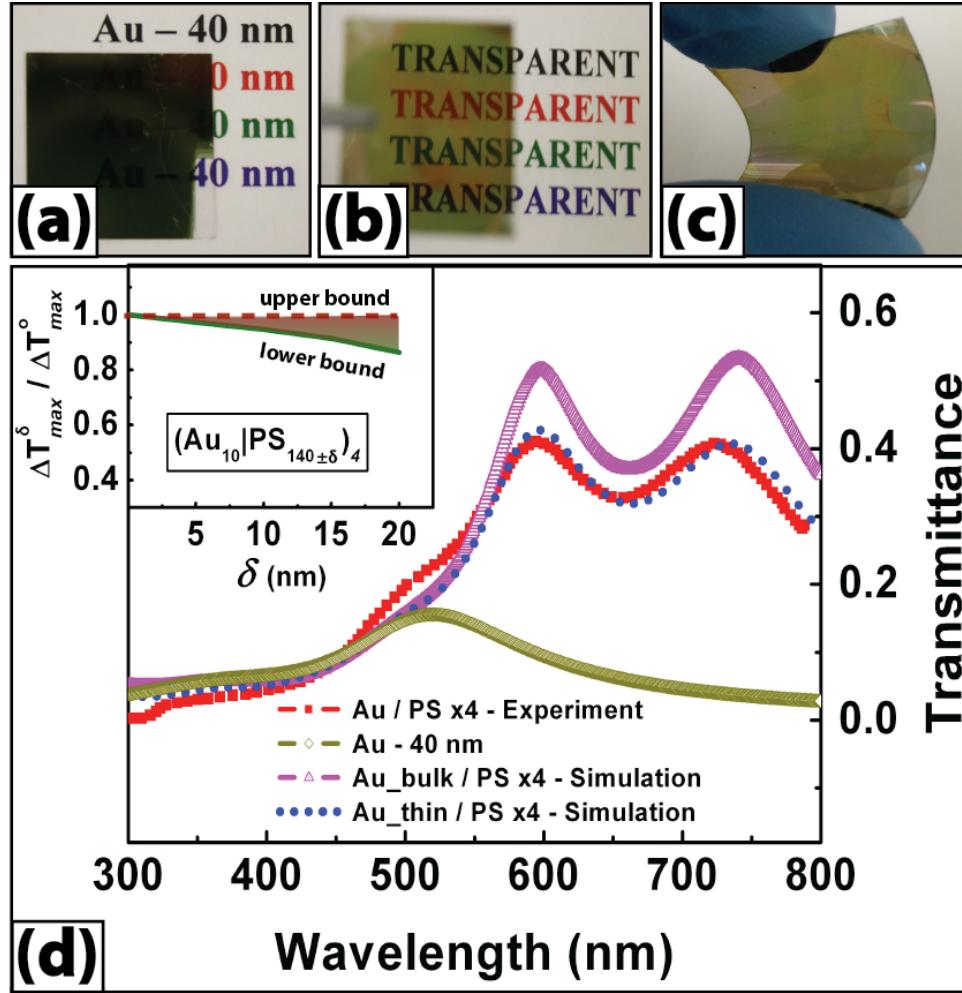


Figure 4.7: Optical characterization of $(\text{Au}_{10}|\text{PS}_{140})_4$ resonant structures. Pictures of (a) monolithic Au film ($d_{\text{Au}} = 40$ nm) deposited on PET substrate, (b) $(\text{Au}_{10}|\text{PS}_{140})_4$ laminate film deposited on PET substrate and (c) the $(\text{Au}_{10}|\text{PS}_{140})_4$ resonant structure demonstrating film flexibility; (d) Optical transmission spectra of $(\text{Au}_{10}|\text{PS}_{140})_4$ laminate compared with its predicted transmission and that of the monolithic Au film. Reproduced from [9] © 2013 American Chemical Society.

To quantify the increase in transmission that is facilitated by resonant tunneling the film absorption was determined using optical spectroscopy. Figure 5d confirms the increase in optical transmission at $\lambda = 520$ nm by almost 100% (and up to $\sim 500\%$ over certain wavelengths in the visible spectrum) as compared to the monolithic film. This increase in transmission is consistent with the predicted increase of the field amplitude $|E|^2$ in the resonant structure that is depicted in Figure 1a and 1b. The experimental transmission data of the resonant structure (red line) is in close

agreement with the predicted values based on the TMM simulation (assuming optical constants corresponding to the experimental data of thin films reported in Figure 4.6), thus providing further evidence for the tunneling mechanism. It is to be noted that the agreement between the experimental and calculated values sensitively depends on the proper choice of optical constants according to the film thickness. This is illustrated by comparison with the calculated transmission values assuming bulk values for the optical constants of gold (pink curve) that significantly overestimate attainable film transparencies [19]. The good agreement between calculations for an idealized uniform geometry and the experimental system that necessarily includes minor variability of layer thickness due to the film fabrication procedure can be interpreted as an indicator for the robustness of the optical resonant tunneling effect with regard to structural defects.

To understand the effect of random PS-layer thickness variation on the films' optical properties, the transmission spectra of different realizations of four-layer stacks were calculated assuming a fluctuating thickness of each PS layer according to $d_{PS} = 140 \pm \delta$ nm (where δ denotes the respective thickness variation) under the constraint of constant average layer thickness $\langle d_{PS} \rangle = 140$ nm. The maximum reduction of the films optical transmittance (and thus the lower bound for optical transmission) due to the non-uniformity of the PS layer thickness was subsequently determined by comparison of the maximum transmittance values of the ideal (uniform) stack with the corresponding four layer variable stack $(\text{Au}_{10}|\text{PS}_{140\pm\delta})_4$ that exhibits the lowest optical transmittance. The inset of Figure 4.7d depicts the effect of a random thickness variation (of the PS layer) on the film's maximum attainable transmittance and reveals that ΔT (or equivalently the lower bound of T_{max}) remains within 10% of the optimum value (that corresponds to the uniform reference structure) for thickness fluctuations up to $\delta = 10$ nm. It must however be noted that this is not inconsistent

with Figure 4.4a where the overall maximum transmittance remains within 10% of the maximum value when the PS layer thickness is varied within the range $80 \text{ nm} < d_{PS} < 180 \text{ nm}$, despite there being a rapid decrease in transmittance at $\lambda = 520 \text{ nm}$. This robustness of the optical resonant tunneling effect can be expected to greatly benefit the applicability of this approach for the fabrication of polymer/metal composite structures with reduced optical absorption since it enables the use of rapid processing techniques such as spin-coating.

4.7 Conclusion

In conclusion, it has been shown that optical resonant tunneling in periodic metal/polymer composite structures provides a means to significantly reduce optical absorption losses in polymer-based metallodielectric composite structures while retaining the advantageous (mechanical) properties of the polymer matrix. For the particular case of a 1D periodic (laminate) structure it is shown that a suitable strategy for the design of resonant structures is to align the lower band edge of the 1D periodic (photonic crystal) structure with the plasma absorption frequency of the metal component. For the particular case of gold/polystyrene laminate structures an increase of the optical transmission by about 500% is realized by the appropriate design of a four-layer structure. The resulting flexible and (near) transparent polymer/metal composite structures could provide a robust material platform for the fabrication of flexible transparent conductors that play a central role in the development of ‘organic flexible electronics’. We note that for the latter application it is not the ‘absolute transparency’ but rather the ratio of transparency and resistance that is used as metric to classify the performance of transparent conductors. The high conductivity that is imparted by the metal component (in our case the in-plane conductivity was determined to be $\sigma \simeq 10^6 \Omega^{-1} \text{ cm}^{-1}$) should benefit the application of resonant metal/polymer composite structures as transparent conductors.

Furthermore, the sensitivity of resonant tunneling to variations in the optical properties of the constituents could render these material systems interesting for a range of responsive material applications in which a minor change to one of the layers gives rise to an amplified collective response of the stack. Strategies to further enhance the optical transparency of resonant metal/polymer composite structures should focus on the use of metals such as Ag with a plasma frequency outside the visible range. Furthermore, the self-assembly of polymer/nanoparticle composite systems into laminate structures could be explored as a more efficient and scalable fabrication methodology for resonant metal/polymer composite structures.[20–22]

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Chapter 5

Transparent, Conducting, Flexible Ag-NW/Polymer Composite Films

The contents of this chapter are being submitted for publication in a slightly modified form –

S. Narayanan, J. R. Hajzus, C. E. Treacy, M. R. Bockstaller, and L. M. Porter:
“Polymer Embedded Metal-Nanowire Network Structures – A Platform For The
Facile Fabrication of Flexible Transparent Conductors”, *Under submission*.

5.1 Introduction

As has been discussed in an earlier section (Section 2.5), random networked films of Ag-NWs provide a viable and promising alternative to conventional oxide-based TC materials in terms of their comparable FoMs and performance when used in photovoltaic devices.[1–5]. However, processing of films from solution to yield high uniformity in network morphology as well as good mechanical flexibility, has remained an issue. One possible and elegant solution to address this issue is to embed the NWs in polymer matrices so as to not only stabilize them in dispersion but also to translate this stability into uniformity in network morphology of cast films.[5–7]

It is to be noted that by the term “uniformity” here, we refer to a reduction in or absence of aggregation/bundling of Ag-NWs in dispersion as well as in thin film morphology.

The objective of this contribution is to elucidate the role of polymeric embedding media on the structure formation and optical and electronic properties of Ag-NW network structures, and to evaluate their ability to withstand cyclic deformation processes as in typical flexible TC applications. Our observations suggest that embedding Ag-NW network structures in semicrystalline polymers (such as PVA and PEDOT:PSS) facilitate fabrication of mechanically robust TCs with optimal electrical and optical properties and having low batch-to-batch variability.

The structure of this chapter of the thesis is as follows: first, we evaluate the effect of polymer additives on the uniformity of morphology in pristine and polymer embedded Ag-NW films. Subsequently, we present an image analysis procedure that allows for the quantitative correlation between film microstructure and electrical properties of Ag-NW network structures. The materials in this study are comprised of Ag-NWs dispersed in isopropyl alcohol (IPA) as well as in deionized water (DI water) and in polymer solutions of poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), NaPSS (sodium salt of PSS), poly(vinyl alcohol) (PVA), and poly(acrylic acid) (PAA). Polymer matrices have been chosen to systematically test the role of physical properties such as electrical conductivity (PEDOT:PSS), mechanical toughness (PVA) or polymer-AgNW interaction (PAA, PSS). We find that the best overall performance as a flexible TC is realized with semi-crystalline embedding polymers such as PVA or PEDOT:PSS, while glassy amorphous polymers display more rapid wear under cyclic loading conditions. Furthermore, the ideal candidate material system for TC applications in our study was found to be PVA-

embedded Ag-NW structures that exhibit the most favorable combination of electro-optical FoM and mechanical durability and stability. This insight is particularly important in the context of disadvantages associated with PEDOT:PSS such as corrosion and reduced lifetime of photovoltaic cells.[8, 9]

5.2 Experimental methods

5.2.1 Transparent conducting flexible Metal-NW/polymer composite films

Solution processed silver nanowire (Ag-NW) thin films

Ag-NWs were purchased from Blue Nano, Inc. The NWs had diameters of ~ 90 nm and lengths ranging from $10\text{ }\mu\text{m}$ - $30\text{ }\mu\text{m}$. The nanowires as supplied were dispersed in isopropyl alcohol (IPA) at a concentration of 10 mg/mL. To obtain films of varying densities (or areal coverages), portions of the solution were taken out and diluted to desired (lower) concentrations in IPA. The resulting solutions were then spun cast over glass substrates after they were sequentially cleaned by ultrasonication in deionized water, acetone and IPA, in that order. Following deposition, the Ag-NW films were annealed in an oven maintained at a temperature between 180–200 °C for 30-40 minutes under rough vacuum (~ 1 Torr). The annealing step evaporates the solvent and mobilizes the thin monolayer coating of poly(vinyl pyrrolidone) (PVP) on the surface of the NW (a remnant of the synthesis process) leading to more effective contact between NWs.

Transparent polymer thin films

Transparent conducting polymer thin films were fabricated using PEDOT:PSS (high conductivity grade Clevios PH 1000) purchased from Heraeus. Since PEDOT:PSS on its own is not very conductive; as described in an earlier section the use of an additive like DMSO brings about an almost thousand-fold increase in conductivity [10]. To prepare a solution of conductive PEDOT:PSS, 5% (v/v solution) of DMSO

was added, followed by small amounts ($\sim 0.5\%$ v/v solution) of a surfactant (Dynol-604 from Air Products, Inc.) along with $\sim 10\%$ (v/v solution) of IPA, to improve adhesion on glass. This solution was then spun cast (between 2000-3000 rpm for 30 seconds) over over 1 cm x 1 cm cover slip glass substrates from Corning, Inc and HP transparency sheets (poly(ethylene terephthalate)-PET base). The resulting films were annealed in air at $140\text{ }^{\circ}\text{C}$ for 20 minutes. Films with different thicknesses can be obtained by repeating the same process of spinning solution and annealing until a film of desired thickness is achieved.

The other polymers used in this study were poly-vinyl alcohol (PVA) from Sigma Aldrich (MW = 130,000 g/mol), sodium salt of poly-styrene sulfonate (NaPSS) (MW = 70,000 g/mol) and poly-acrylic acid (PAA) from Alfa Aesar (MW = 240,000 g/mol, 25 wt% solution in water). Solutions of PVA and PSS were prepared in water in appropriate weight percent values (2 wt% in the case of PVA and 5 wt% for NaPSS) and spun cast (between 2000-3000 rpm for 30 seconds) over glass and PET substrates so as to obtain films ~ 90 nm thick. The films were subsequently annealed in air at $150\text{--}180\text{ }^{\circ}\text{C}$ for 20 minutes. Solutions of PAA, meanwhile, were primarily used for comparing dispersion characteristics of Ag-NWs in such polymer solutions (Section 3.4).

Ag-NW/polymer composite thin films

Dispersions of Ag-NWs in polymers were prepared by centrifuging a desired concentration of Ag-NWs in IPA at 5000 rpm for 30 minutes using a VWR Clinical 200 centrifuge and re-dispersing the NWs in the various polymers after decanting/pipetting the supernatant. Composites of Ag-NWs with PEDOT:PSS were spun cast as in the case of pristine PEDOT:PSS films. For films of Ag-NW/PVA and Ag-NW/PSS, hexamethyldisilazane (HMDS) from Sigma Aldrich was used as an adhesion promoter before spinning the composite dispersions.

5.3 Results: Role of polymer additives on Ag-NW dispersion stability

The effect of polymer additives on the structure formation of Ag-NW network structures was evaluated by image analysis of thin films cast from dilute dispersions on glass and PET substrates. Figure 5.1 shows SEM micrographs comparing the morphology of cast films in the pristine (Figure 5.1(a)) and composite state (Figure 5.1(b)) with PEDOT:PSS, for example. The extent of non-uniformity of NW coverage across the pristine NW films is apparent from the presence of regions with aggregated clusters of NWs and those with little or no NW coverage. Figure 5.1(b) shows an SEM micrograph of an area of a thin film cast from an Ag-NW/PEDOT:PSS composite dispersion, having a similar NW areal density. Visual inspection of both micrographs reveals dramatic improvements in the distribution of NWs within the film with little to no visible aggregate structures. Such an observation was consistent over multiple samples of pristine and polymer-composite Ag-NW films having varying Ag-NW areal densities, wherein aggregation was seen to be more prominent with pristine Ag-NW films in comparison to the polymer-composites.

We attribute the increase in uniformity, in part, to the improvement of the NW dispersion stability that is facilitated by the polymer additive, as supported by a quantitative evaluation of the stability of Ag-NW dispersions under equivalent conditions using optical absorption spectroscopy. The transmittance spectra for all of the Ag-NW dispersions were measured at various intervals of time, and the specific transmittances at the characteristic plasma frequency of Ag (~ 320 nm [11]) were extracted. The normalized transmittances (with respect to absorption of the dispersant) for the Ag-NW dispersions were then converted to an absorbance equivalent at time t using $A(t) = 1 - T(t)/T(0)$, where $T(0)$ is the transmittance of the bare solvent, and $T(t)$ is the transmittance of the Ag-NWs dispersed in the

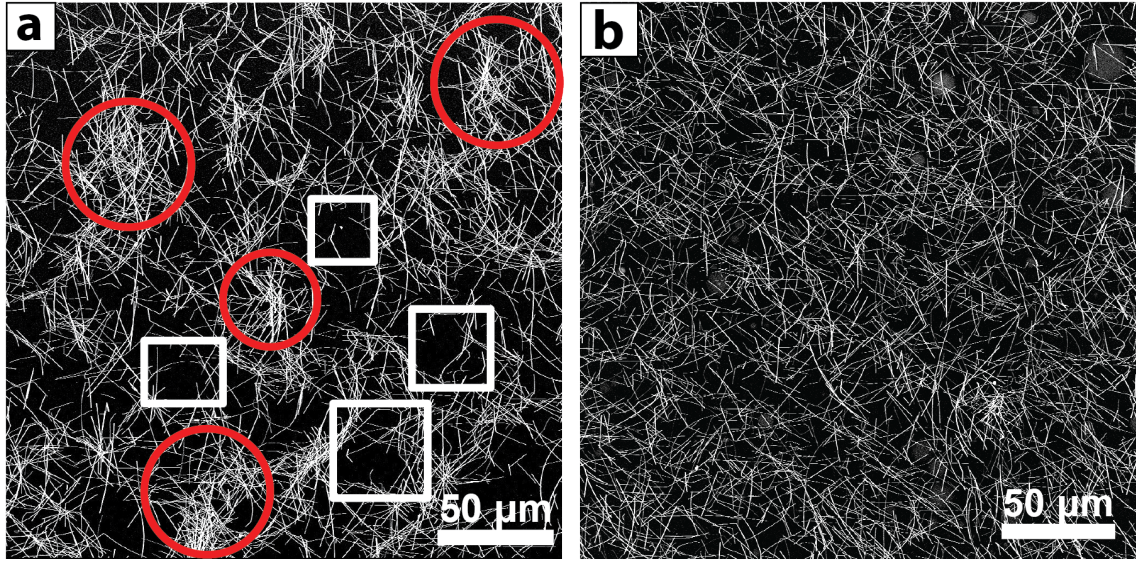


Figure 5.1: Scanning electron micrographs of Ag-NW films having NW areal fraction $A_f = 14\%$. (a) A pristine Ag-NW film spun-cast from a dispersion in IPA, showing the extent of non-uniformity in NW coverage. Red circles and white squares indicate aggregated regions and areas completely devoid of NWs, respectively. (b) An Ag-NW/PEDOT:PSS composite film showing high uniformity and negligible aggregation.

particular solvent at time t .

The plots of normalized absorbance (Figure 5.2) reveal a marked difference in the sedimentation behavior of the Ag-NWs as dispersed in common reagents like IPA and DI water in comparison to NWs in polymeric dispersants. The faster decay in absorption values for NWs in IPA and DI water implies a more rapid sedimentation and thus highlights the reduced stability of the NW dispersions in these media. In contrast, NWs dispersed in polymers such as PEDOT:PSS, NaPSS, PVA and PAA remained dispersed in solution for longer time periods, as is indicated by the absence of any appreciable change in absorption during 4 hours of observation. We note that the origin for the improved dispersion stability of Ag-NWs in polymer solutions is not fully understood and likely involves the cumulative effect of charge and steric stabilization of the NWs. The latter is corroborated by previous studies by Tadd *et al.* [12] as well as Andrew *et al.* [13], who have observed stabilization of metallic

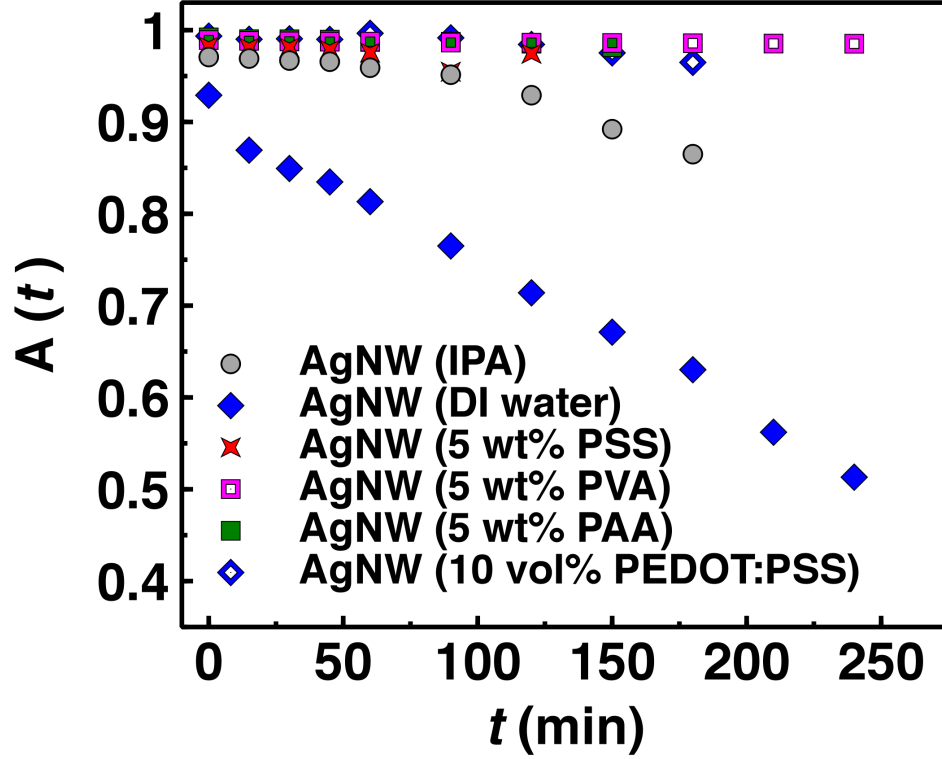


Figure 5.2: Normalized absorbance equivalent, $A(t)$, of the various Ag-NW dispersions as a function of time, at $\lambda = 320$ nm. Rapid decline in absorbance over time indicates more rapid sedimentation of the NWs from dispersion, as in the case of dispersions in IPA and D.I. water. In contrast, the absorbances in aqueous dispersions of Ag-NWs in PEDOT:PSS, PSS, PVA and PAA remain unchanged even over large periods of time indicating greater stability.

nanostructures by long chain polymer surface adsorption or functionalization.

In addition to measuring the absorption of the various Ag-NW dispersions, electrophoretic (zeta potential) and dynamic light scattering (size distribution profile) measurements were also conducted on the same using a Malvern Zetasizer Nano ZS instrument with the dispersions in a disposable capillary cell. The dispersions in this case were diluted further to 0.05 mg/mL since the zetasizer is very sensitive to the size of the particles being tested.

Zeta potential: For dispersions of Ag-NWs in IPA and DI water, the ZP was found to be ~ -35 mV, indicating good stability as per estimations for generic colloidal systems (Section 2.5.6). However, since the standard models to calculate

electrophoretic mobility and ZP apply only to spherical systems or at best low-aspect ratio elliptical colloids, the ZP values obtained thus cannot be compared directly to the stability criteria mentioned in earlier discussions.

ZP values for dispersions of Ag-NWs in polymeric dispersants such as PEDOT:PSS, NaPSS, PVA and PAA were found to be much lower than -100 mV (and beyond voltage-sweep limits of the instrument), further indicating the deviation from standard spherical colloidal dispersions. Moreover, the polyelectrolytic nature of polymers such as PSS and PAA also complicate such measurements since the effect of the polymers cannot be decoupled from the effective electrical state of the NWs in the dispersion in a straightforward manner.

Size distribution profile: To circumvent complications in determining the absolute electrical state of the NW system arising out of zeta potential measurements for the Ag-NW dispersions, alternatively, the size distribution profile of the various dispersions were also obtained by dynamic light scattering. However, as in the case of ZP measurements, size distributions of NWs can also be inconsistent owing to the use of models for spherical colloids for such large-aspect ratio dispersions, aggregation of NWs, their multiple degrees of rotational freedom and also varying polymer chain-lengths. Nevertheless, while size distribution profiles may not be an ideal representation of the NW dispersion, correlation functions of scattered-light intensities can provide a picture that is more representative of the nature of the dispersion. Of particular interest here is the dependence of relaxation times as well as widths of the distribution in sizes that help make a conclusion of the nature of the dispersion.

For standard colloidal systems, the autocorrelation function can be fit to a single

exponential decay as per Equation 2.16 that can be rewritten as –

$$g_1(t) = A \exp \left[-\frac{t}{\tau} \right] \quad (5.1)$$

where A is the correlation function intercept and τ the relaxation time. Typically for a monodisperse colloidal system, the relaxation time, τ , is indicative of the size of the particle distribution.

For polydisperse colloidal systems, as described in Section 2.5.6, owing to the wide range of particle size distributions, the relaxation mechanisms in these systems are more complicated. Such disordered systems are said to evolve over multiple independent relaxation times, with the broadening in relaxation often being described using a “stretched exponential decay” (also known as the Kohlrausch-Williams-Watts function or the KWW function) in the simplest of approximations, which is of the form –

$$g_1(t) = B \exp \left[-\left(\frac{t}{\tau} \right)^\beta \right] \quad (5.2)$$

where B is the autocorrelation function intercept and the parameter β (when < 1) describes the degree of polydispersity in the system ($\beta = 1$ is the case of a monodisperse colloidal system as per Equation 5.1).[14, 15]

The various Ag-NW dispersions were fit to stretched exponential decay functions as per Equation 5.2 and are shown in Figure 5.3 with Table 5.1 listing values of curve fitting parameters.

It is to be noted, however, that such light scattering measurements on a polydisperse system like that of Ag-NWs presents several challenges that are difficult to avoid given the material and instrumental constraints. Some of these challenges include -

- Absorption of light by Ag-NWs that can lead to convection and lens effects that

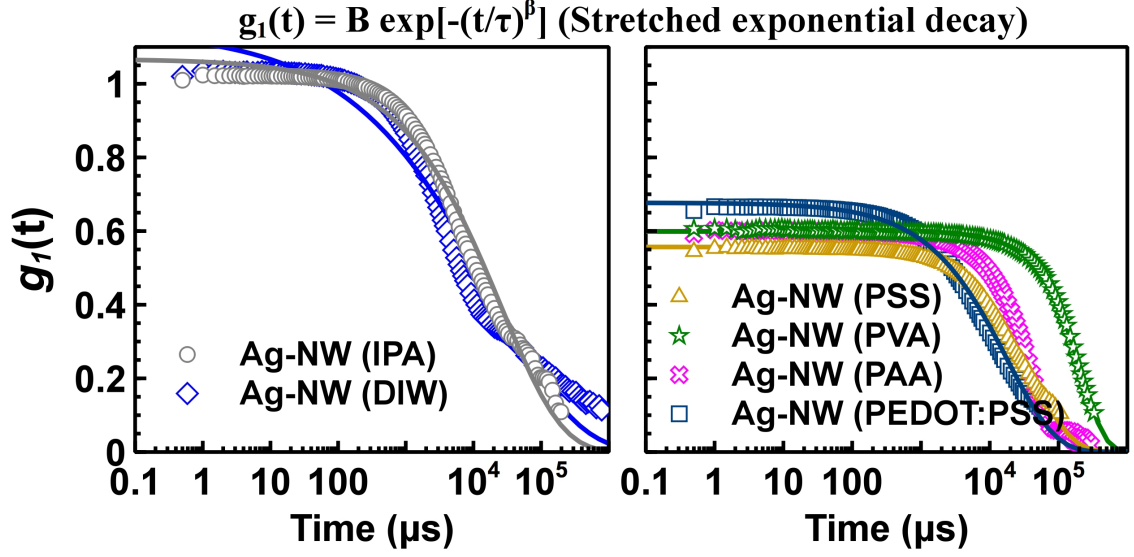


Figure 5.3: Autocorrelation functions of Ag-NW dispersions as a function of time (μs) with the curves fit to a stretched exponential decay. Curve-fit parameters are listed in Table 5.1.

Table 5.1: Curve-fit parameters for DLS correlation functions of Ag-NW dispersions in Figure 5.3 assuming a stretched exponential (KWW) decay relaxation as per Equation 5.2.

Dispersion System	Curve-fit Parameter			R_{fit}^2
	A	τ (μs)	β	
Ag-NW (IPA)	1.0670	26060	0.49	0.99
Ag-NW (DI water)	1.1450	19880	0.35	0.97
Ag-NW (PEDOT:PSS)	0.6768	18220	0.63	0.99
Ag-NW (PSS)	0.5568	42170	0.75	0.99
Ag-NW (PVA)	0.6021	228100	1.04	0.99
Ag-NW (PAA)	0.5989	41050	1.08	0.99

in turn affect measurement of scattered light

- The large size of the NWs used and their anisotropy in shape lead to several complications; in addition to translational degrees of freedom, the NWs also possess rotational motion that scatter light differently, the contributions of which cannot be easily separated out from the measured apparent diffusion coefficients
- Shape anisotropy also leads to change in polarization of incident light during

scattering. An instrument ill-equipped in depolarizing scattered light would be unsuitable in interpreting light-scattering data

- Viscosities of the Ag-NW/polymer dispersions are not known and not easy to measure either and hence the effect of viscosity on the diffusion coefficient is difficult to determine

Keeping these challenges in mind, the focus of this work was primarily on the dependence of the stretched exponential parameter, β , which provides a reasonable indication of the widths or size distribution of the scatterers, rather than the relaxation times, τ , which are dependent on several factors as noted above.

The goodness of fit to stretched exponentials as indicated by $R_{fit}^2 \sim 1$ justifies the use of such a function to physically describe the system. As indicated in Table 5.1, dispersions of Ag-NWs in IPA and DI water have $\beta \ll 1$ whereas those dispersed in polymers such as PEDOT:PSS^a, PSS, PVA and PAA have $\beta \sim 1$, further reiterating the high degree of polydispersity in the case of Ag-NWs in IPA and DI water while suggesting greater monodispersity and dispersion stability for the NWs dispersed in polymeric media. We attribute the differences in the values for absolute relaxation times, τ , which in turn vary size distribution profiles of the Ag-NW dispersions, to the effect of the polymer themselves on the effective hydrodynamic radius of the system and also to the deviation from ideal colloidal nature of these high aspect ratio NW dispersions.

^aSince light scattering experiments for Ag-NWs dispersed in PEDOT:PSS were conducted using well-diluted PEDOT:PSS solutions owing to the absorptive nature of PEDOT:PSS, β for this system was estimated to be ~ 0.7 ; judging by trends in dispersions with other polymers, β for Ag-NWs in undiluted PEDOT:PSS can be assumed to be closer to 1

5.4 Results: Role of polymer additives on uniformity of Ag-NW networks

A critical requisite for maximizing the FoM of Ag-NW network-based TCs is the minimization of the percolation threshold of the system. Since the latter is accomplished by maximizing film uniformity, or in other words NW aggregation, understanding the effect of process conditions on the network microstructure is particularly important. A variety of statistical methods to analyze the uniformity of network structures have been proposed that most commonly involve spatial statistical image analysis.[16–18] A particularly convenient and suitable method to quantify uniformity of a random network of linear segments is described by Stoyan et al.,[19] which has been applied to a network of CNTs by Pegel et al.[16] by the use of morphological image processing tools on electron micrographs.

In this method, the 2D network of NWs is treated as a “random closed set” Ξ , for which the areal fraction $A_f(r)$ of the segments is calculated after dilating the image with a disc of radius r as a structuring element (also known as Minkowski-Addition). As the disc radius increases, $A_f(r)$ correspondingly increases before eventually saturating. The rate of convergence of this areal fraction provides a measure for the uniformity of the network, since more uniform networks converge faster than non-uniform ones. Further, the calculated $A_f(r)$ can be related to an empirical spherical contact distribution function (SCDF), $H_S(r)$, which represents the probability of a point lying completely outside the set Ξ , and hence describes the proximity of the NW segments to each other:

$$1 - H_S(r) = \frac{1 - A_f(r)}{1 - p} \quad (5.3)$$

where ‘ p ’ refers to the areal fraction of the undiluted image. Based on the Boolean

“fibre process” model [16, 19], $H_S(r)$ can be written as

$$H_S(r) = 1 - e^{-\gamma r(2m + \pi r)} \quad (5.4)$$

Here γ represents the number of segments per unit area and m denotes the mean length of segments.

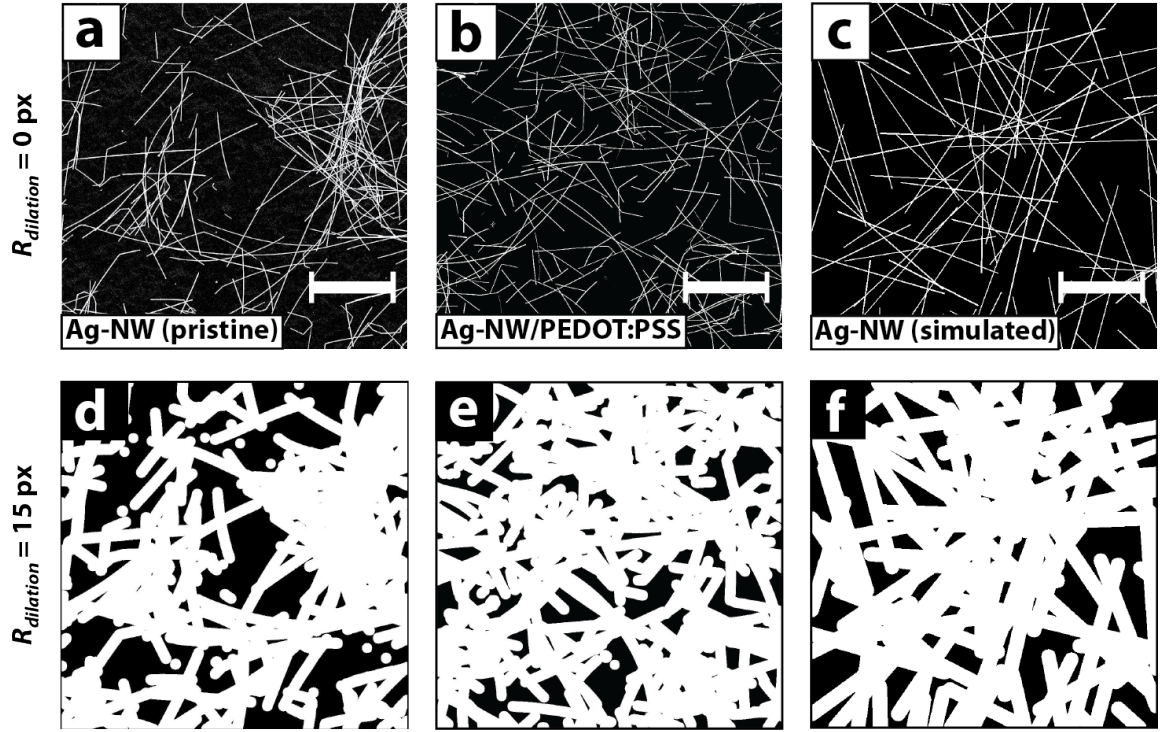


Figure 5.4: Illustration of the process of quantifying the uniformity of Ag-NW-based thin films. Scanning electron micrographs images of (a) pristine Ag-NW film and (b) Ag-NW/PEDOT:PSS composite, along with (c) simulated network of Ag-NW, all with $A_f \sim 9\%$. (d-f) The morphed counterparts of (a-c) generated by dilation of the original image with a structuring disc element of radius 15 pixels. For a homogeneous film the network remains well “connected” post-processing as in the case of the composite and the simulated image, while the pristine NW film remains sparsely connected. Scale bar = $20 \mu\text{m}$.

The process above is illustrated in Figures 5.4 and 5.5, which shows the image processing sequence for a pristine Ag-NW and a Ag-NW/PEDOT:PSS composite with similar NW areal fractions. To better interpret observed trends, experimental data was compared to predicted data for an ideal random network structure of equivalent

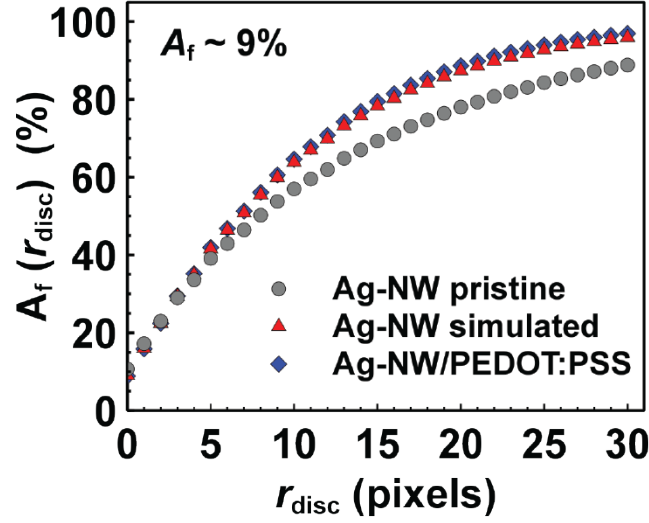


Figure 5.5: Variation of Ag-NW areal fraction as a function of dilation disc radii extracted from images as in Figure 5.4 – faster convergence to 100% implies greater homogeneity.

Ag-NWs that was obtained using simulations (see Experimental Section 3.7 for more details). Figures 5.4(a) and 5.4(b) show SEM images of a pristine Ag-NW film and an Ag-NW/PEDOT:PSS composite, respectively, of similar NW areal coverages. Figure 5.4(c) shows the image of a simulated Ag-NW random network of comparable NW areal density. Figures 5.4(d-f) represent the corresponding dilated images, processed with a disc element of size 15 pixels. Whereas the composite and the simulated films show uniform dilation (Figure 5.4(e) and 5.4(f)), the pristine Ag-NW film reveals non-uniform dilation (Figure 5.4(d)) even for large dilation disc sizes. This difference is graphically represented in Figure 5.5, which shows a plot of $A_f(r)$ averaged over several such images for each film, bringing out the contrast in areal coverage and corresponding film uniformity as size of the disc element, r , increases.

To quantitatively compare the morphologies of the films, the corresponding SCDFs were computed for the three films at three different NW areal fractions ($A_f = 9, 14$, and 23%) as illustrated in Figure 5.6(a-c).

Just as in Figure 5.5, $H_S(r)$ for the polymer composite and the simulated Ag-NW

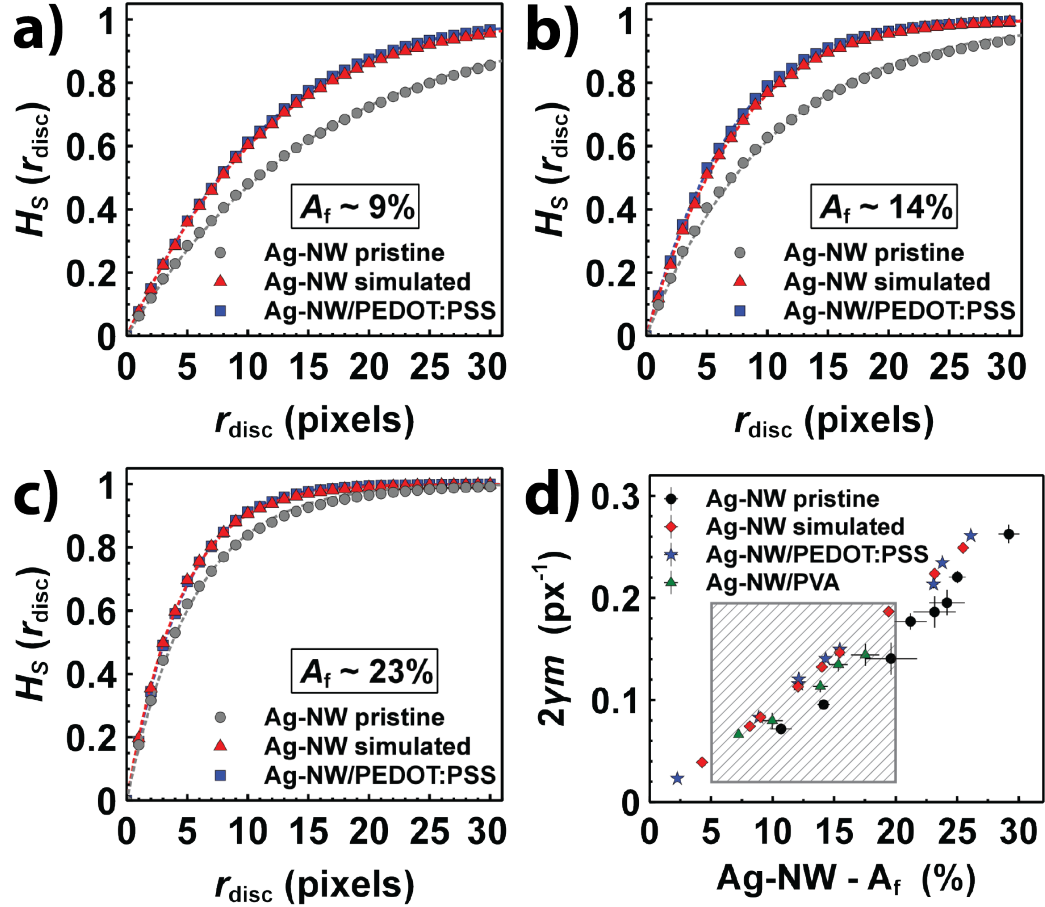


Figure 5.6: (a-c) Comparison of spherical point contact distribution functions $H_S(r)$ as a function of dilation disc radii for films of pristine Ag-NWs (grey circles), simulated Ag-NW networks (red triangles) and Ag-NW/PEDOT:PSS composites (blue diamonds) for different Ag-NW areal fractions each averaged over a large set of images, where in (a) $A_f = 9\%$, (b) $A_f = 14\%$, (c) $A_f = 23\%$. The dashed curves represent fits to $H_S(r)$ as per Equation 5.4. Faster convergence of $H_S(r)$ to one implies greater uniformity in film. (d) Variation of the product of dilation fit parameters, γ and m ($2\gamma m$), with the Ag-NW areal fraction. Higher values indicate faster convergence of $H_S(r)$ to one and hence greater uniformity (box highlights range of A_f corresponding to Ag-NW network structures within the percolative regime).

network shows faster convergence to one, than for pristine Ag-NWs. The dotted lines in Figure 5.6(a-c) represent fits by the Boolean model (Equation 5.3). A quantitative picture of the contrast in uniformity can be inferred from the gradient of the SCDF curves at small ‘r’, denoted by the term ‘ $2\gamma m$ ’ (i.e. equivalent to number of segments per unit length of the film). Figure 5.6(d) compares values of ‘ $2\gamma m$ ’ for the pristine and simulated Ag-NW networks as well as composites of Ag-NWs with PEDOT:PSS, PSS and PVA, confirming that polymer-embedded Ag-NW network structures exhibit

a uniformity close to the ideal random reference state. The shaded box in Figure 5.6(d) highlights this difference for a particular range of Ag-NW areal density that is relevant for device applications. Note that only in the limit of large values of A_f at which optical absorption is significant do pristine Ag-NW films compare well with the simulated networks and composite films, thus revealing a major challenge for the application of pristine Ag-NW networks as TCs. A second important observation in Figure 5.6(d) is the presence of large error bars (exceeding 10% of the average value) on both the fit exponents and the calculated areal fractions for pristine Ag-NW structures, thus indicating large variability in batch-to-batch processed systems of pristine Ag-NWs.

5.5 Results: Optical and electrical characteristics

The optical transmittances (specifically at $\lambda = 550$ nm, corresponding to the wavelength at which incoming solar radiation, AM1.5G spectrum, is at its maximum intensity) and sheet resistances for both pristine Ag-NW and Ag-NW/polymer composite films are shown in Figure 5.7(a). Measured values (closed markers) are compared to theoretical models corresponding to bulk (dashed curves, Equation 2.4) and percolation behavior (short dashed curves, Equation 2.5). Figure 5.7(b) depicts the variation of average sheet conductance, σ_{Sheet} ($1/R_{\text{Sheet}}$)^b as a function of corresponding Ag-NW areal fraction A_f obtained from SEM micrographs and averaged over several images. The figure reveals a typical percolative trend in the conductivity of the system, with $\sigma_{\text{Sheet}} \propto (\phi - \phi_C)^n$, similar to previous reports for networked conductors in the literature.[20] Percolative transitions are also observed

^bThe term sheet conductance (σ_{Sheet}) is introduced here which is a thickness-independent term describing the electrical conductivity of the system, since, for such networked conducting tubes, a “thickness” has no meaning, unless an “average thickness” is defined taking into account the inhomogeneity in the morphology of the networked structure. Such a treatment has been left out of this work owing to the involved complications.

for Ag-NW/polymer composite films where the polymer is non-conductive. Note that the Ag-NW/PEDOT:PSS composites deviate from exponentially rapid decay in conductance at low NW areal fractions, owing to the conductive nature of the PEDOT:PSS matrix. In this case, it is hypothesized that the increase in conductance even at low Ag-NW content is due to a combined contribution of both PEDOT and the Ag-NWs in providing electrical pathways and also due to a lowering of the interfacial resistance between the NWs. The Ag-NW/PEDOT:PSS composite system thus offers the added benefit of retaining electrical conductivity even at low Ag-NW content in the films. However, this benefit does come at the cost of reduced transmittance as demonstrated in Figure 5.7(a).

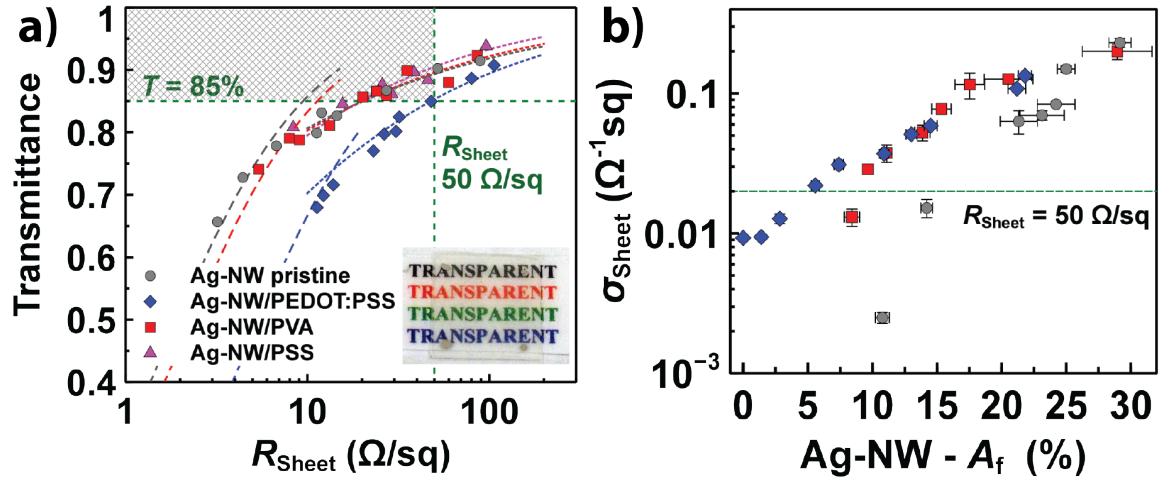


Figure 5.7: (a) Plot of transmittance T vs. sheet resistance R_{Sheet} showing an apparent transition in T for $R_{\text{Sheet}} < 10 \Omega/\text{sq}$, characteristic of a shift in the optical and electrical properties from percolative to a bulk-like regime. The shaded box represents the region for which $R_{\text{Sheet}} < 50 \Omega/\text{sq}$ and $T > 85\%$, a typical criterion for good transparent conductors in photovoltaic applications. Inset shows a picture of an Ag-NW film on glass, demonstrating transparency; (b) sheet conductivity, σ_{Sheet} , as a function of Ag-NW areal fraction, The green dashed line corresponds to $R_{\text{Sheet}} = 50 \Omega/\text{sq}$, which the composite films can be seen to achieve at lower NW A_f in comparison to pristine Ag-NWs, indicative of lowered percolation thresholds.

Figure 5.7(b) depicts the dependence of the films sheet conductivity on the NW areal coverage, revealing that the benefit of direct polymer processing is most dominant in the limit of small NW coverage where an order of magnitude increase in σ_{Sheet} as compared to pristine systems, is realized. The trend depicted in Figure 5.7(b)

confirms previous reports that have determined polymer composites to exhibit lower corresponding values for percolation thresholds.[20–22]

A quantitative assessment of the advantages of polymeric embedding media for the purpose of TC applications can be made by comparing FoMs of the different systems in both bulk-like (vis-à-vis thick bulk films of Ag, as is commonly reported in literature) and percolation-like regimes that were determined using the values displayed in Figure 5.7(a) using Equations 1 and 2, with those specified in previous reports.[23] Table 5.2 summarizes both the bulk and percolative FoMs for all systems used in the present study, extracted from fitting T – vs. – R_{Sheet} curves, as well as reference values from literature. The bulk-like FoM ($\sigma_{\text{DC,B}}/\sigma_{\text{op}}$) for all Ag-NW systems is found to exceed 35 (which is an oft-cited threshold value for TCs in PV applications). We note that the differences between the present systems and literature values are expected and can be attributed to the distinct NW characteristics (such as aspect ratios).[24, 25] The percolative FoM (Π) that evaluates the distinct structural characteristics of Ag-NW films reveals superior properties of the Ag-NW/PVA and Ag-NW/PSS composite-networks in comparison to the pristine NW systems.

Table 5.2: FoM parameters - $\sigma_{\text{DC,B}}/\sigma_{\text{op}}$, Π , and n extracted from fits to T – vs. – R_{Sheet} curves in Figure 5.7(a)

Sample	Bulk-like	Percolation-like	
	$\sigma_{\text{DC}}/\sigma_{\text{Op}}$	Π	n
Ag-NW pristine (literature[23])	415	31.7	1.9
Ag-NW pristine	245	40	1.4
Ag-NW/PEDOT:PSS	84	35	0.9
Ag-NW/PSS	228	57.7	0.86
Ag-NW/PVA	197	43.6	1.24

Whereas a higher Π is directly indicative of improved electrical and optical properties

as a consequence of higher uniformity, the value of n has been known to vary widely between 0.6 and 6.5; the ideal value for a 2-D film (drawing a comparison with conventional oxide-based 2-D thin film TCs) from computational predictions is 1.3.[23] Since n is related to the true percolation exponent in such networks, a reduction in n suggests a lowering of the percolation threshold in the polymer-composite networks. Incidentally, for Ag-NW/PVA composites the exponent n attains a value close to the predicted value for ideal 2-D films, making them comparable to 2-D thin film TCs from a percolation standpoint. Thus Ag-NW/polymer composites can achieve electrical conductivities similar to that of pristine networks, with lower Ag-NW content (Figure 5.7(b)), and correspondingly higher transmittances.

It has to be noted, however, that the observed reduction in percolation threshold in this study is understood to most likely be a consequence of a reduction in the aggregation of Ag-NWs. To arrive at a more comprehensive understanding of the nature of this observation, other contributing factors such as excluded volume effect of polymers, filler aspect ratios, etc. need to be considered as well.[26] The differentiation of contribution of these various factors in determining the percolation properties are beyond the scope of this thesis.

Consistent with the data reported in Figure 5.7(b) is the decrease of standard errors in measurements of R_{Sheet} and A_f in the case of nanocomposite films. This is an important aspect that relates to the expected reproducibility of material performance in batch-to-batch processes that is critical to the viability of the material in TC applications. We attribute the improved reproducibility of sample characteristics to the improved stability of polymer/Ag-NW dispersions and the reduced influence of aggregation and flocculation phenomena on the film fabrication process.

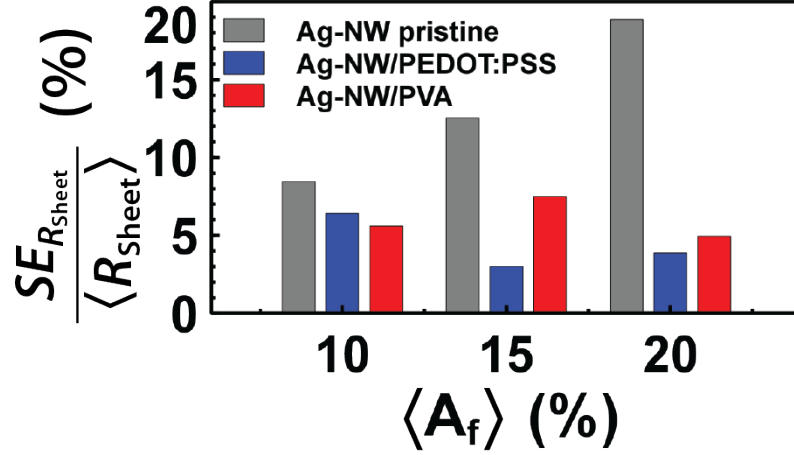


Figure 5.8: Reproducibility of electrical properties for Ag-NW films and composites determined by analysis of > 10 samples for each areal fraction. Plot depicts standard errors in R_{Sheet} values for pristine Ag-NW films (grey bars), Ag-NW/PEDOT:PSS (blue bars) and Ag-NW/PVA (red bars) composites for different Ag-NW densities $\langle A_f \rangle$, normalized to $\langle R_{\text{Sheet}} \rangle$ and represented as a percentage. The standard deviation in sheet resistance is significantly lowered in case of polymer composite systems thus indicating higher reproducibility in batch-processed films.

Figure 5.8 displays the standard errors in measurements for R_{Sheet} (represented as a percentage of the average value $\langle R_{\text{Sheet}} \rangle$) as a function of $\langle A_f \rangle$ for the pristine NWs and composite systems of Ag-NW/PEDOT:PSS and Ag-NW/PVA. This comparison further demonstrates the advantage of the polymer-solution processing of Ag-NWs in the fabrication of films with $< 5\%$ error in critical parameters.

5.6 Results: Flexibility studies of Ag-NW and Ag-NW/polymer composite films

As a measure of the mechanical performance, pristine Ag-NW films and their composite homologues were cast on flexible PET substrates and subjected to repeated bending up to an angle of $\sim 130^\circ$. During each cycle, the films' electrical conductivities were evaluated at three different curvatures ($C = 0, 2$ and 3 cm^{-1}). The films were then relaxed to their original unbent state ($C = 0$) before repeating the bending cycle. The setup and process of deformation are illustrated in Figure 5.9. Figure 5.10 depicts the electrical resistance of the pristine and composite films at curvatures $C = 0, 2$ and 3 cm^{-1} . The figure reveals that the electrical conductivity

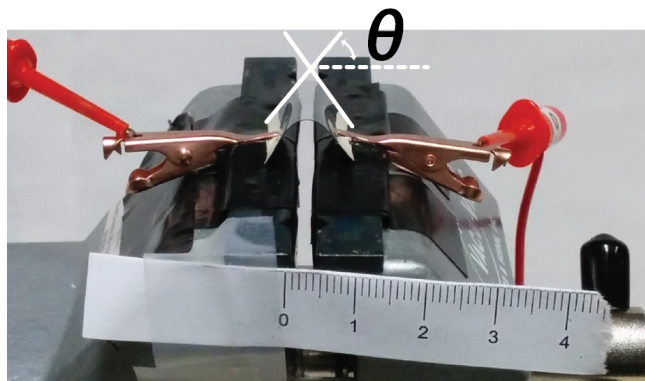


Figure 5.9: Photograph of the film bending apparatus, where θ denotes the bending angle. Curvature of bending is calculated using θ , length of sample and distance between electrodes during bending.

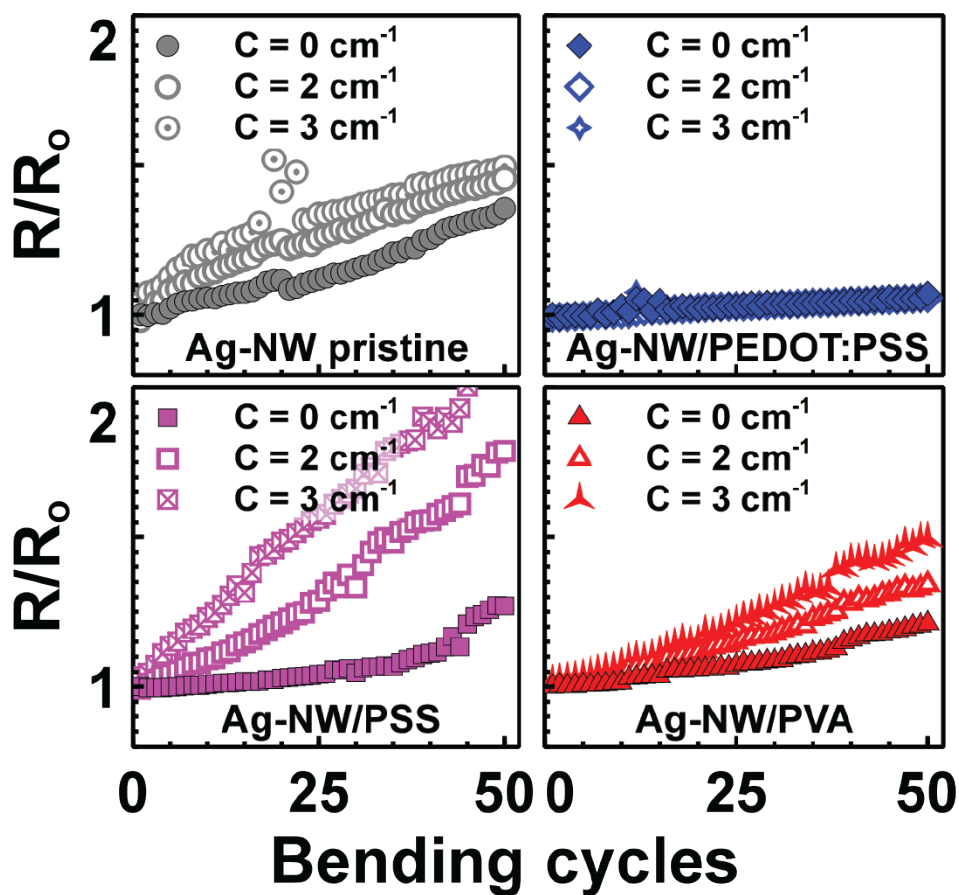


Figure 5.10: Bending studies on pristine Ag-NW films and Ag-NW/polymer composite films. Plot legend: Grey circles – Ag-NW pristine, Blue diamonds – Ag-NW/PEDOT:PSS composite films, Magenta squares – Ag-NW/PSS composite films, Red triangles – Ag-NW/PVA composite films. Variation of R/R_0 with bending cycles at different curvatures for pristine Ag-NW films and composite films with PEDOT:PSS, PSS and PVA.

of pristine Ag-NW films systematically degrades with increasing bending cycle, the degradation being more pronounced at larger curvatures. A marked improvement can be observed in PEDOT:PSS and PVA matrices that display reduced degradation – in the case of PEDOT:PSS no appreciable degradation is observed under any bending situation within the tested range. We attribute this improved resilience to mechanical degradation to the semicrystalline nature of PEDOT:PSS and PVA, a property that is generally expected to raise the toughness of polymer materials and hence their resistance to fracture during deformation. In contrast, films of Ag-NWs in NaPSS display significantly larger increases in electrical resistance during bend deformation. SEM analysis of films after deformation (Figure 5.11) confirmed fracture of PSS-composite films. This is consistent with the brittle nature of NaPSS, which is a glassy polymer with a high softening temperature ($T_g \sim 150$ °C for PSS[27] while $T_g \sim 85$ °C for PVA[22]). We attribute the rapid increase in resistance (up to 3 times for PSS composites and up to 5 times for PVA composites) that is observed at very large curvatures ($C \sim 3$ cm⁻¹) to microfracture processes within the polymer film (possibly supported by substrate-film interactions).

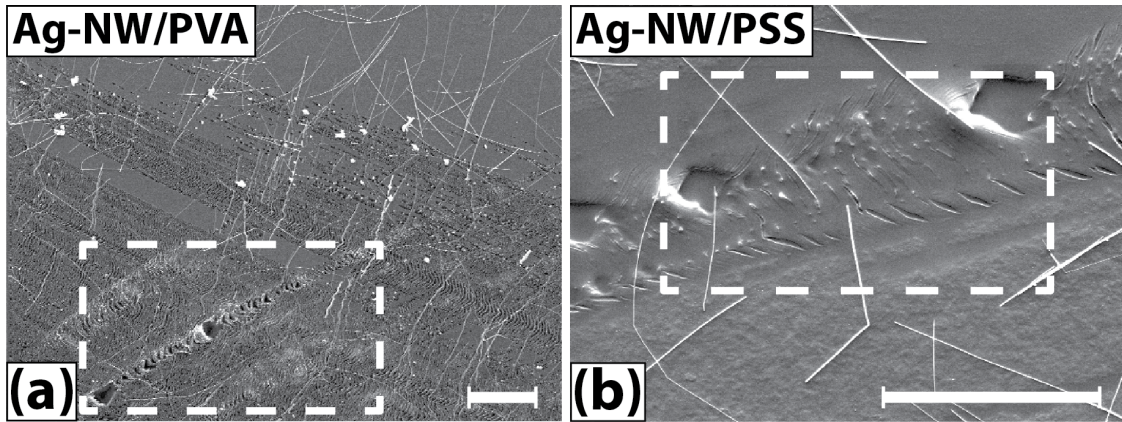


Figure 5.11: SEM images show surface defects on polymer thin films generated from bending stresses in (a) Ag-NW/PVA and (b) Ag-NW/PSS composite films on PET substrates (indicated by dashed box). Scale bar = 20 μ m.

5.7 Conclusion

The processing of Ag-NW network structures from polymer solutions has been shown to provide a path to fabricating transparent and flexible films with improved structural uniformity and figure of merits as compared to analogous pristine Ag-NW network structures. For NWs processed with PEDOT:PSS and PVA solutions the structural uniformity is found to approximately correspond to the values predicted for idealized (i.e. non-aggregated) NW network structures. The use of polymeric embedding media furthermore is found to substantially decrease batch-to-batch variation of film characteristics that have been a widely cited challenge associated with the application of Ag-NW network structures as transparent conductors. Semicrystalline polymer matrices (such as PVA or PEDOT:PSS) are found to substantially increase the resilience of electronic properties of films during cyclic bending tests, an aspect that is of critical importance to the design of transparent conductors for flexible electronic applications.

In this context, our results suggest that PVA could be a viable alternative for PEDOT:PSS (the most widely studied system to date) for realizing Ag-NW/polymer composite TCs. It was found that PVA retains or improves many of the benefits (in terms of reproducibility and figure of merit) while being a more benign and non-corrosive material, which should be beneficial for device applications. Further studies need to be carried out to gauge the extent to which the physical properties of the polymer-composite networks can be affected by the nature of the polymer used, i.e. its molecular weight, viscosity, film forming characteristics, optical absorption, metal-polymer interactions and the solvent involved, among various other factors. Such studies on the polymer used is necessitated by the fact that the mechanical behavior of these polymer-embedded networked films is closely associated with the thermo-mechanical properties of the polymer used as well as the nature of substrate-film

interactions. Additionally, integration of these composites into devices such as solar cells or LEDs is necessary to demonstrate the effectiveness of the system proposed in this study over existing Ag-NW network based device architectures.

5.8 References

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Chapter 6

Ag-NW Transparent Conductors in Organic Solar Cells

A manuscript for publishing the contents of this chapter in a slightly modified form is under preparation –

S. Narayanan, E. D. Weiss, T. Kowalewski, M. R. Bockstaller, and L. M. Porter:
“Polymer Embedded Metal-Nanowire Network Structures as Solution-Processable
Transparent Anodes in Organic Solar Cells”, *Manuscript under preparation*.

6.1 Introduction

Transparent conductors (TCs) are integral components in novel thin-film photovoltaic device technologies and even more so in the case of organic photovoltaics where device efficiencies are critically dependent on the performance of the TCs.

6.1.1 TCOs as electrodes in organic photovoltaics

In current state-of-the-art and in most commercial applications, transparent conducting oxides (TCOs) are the materials of choice owing to their easy processability, high figure-of-merits in terms of optical transparency and electrical

conductivity, thermal and chemical stabilities. TCOs also have a range of work-functions, which allows for tuning of device open-circuit voltages.[1] In particular, degenerately doped oxides based on In, Sn and Zn have work functions ranging between $\sim 4.5\text{--}5.0$ eV, and transmittances $T > 85\%$ in the visible spectrum for conductivities $\sim 10^4$ S cm $^{-1}$. With ITO as the TC electrode, record efficiencies of organic/polymer solar cells have evolved from $\sim 2.5\%$ in 2001 to over 10%, with potential to increase up to 15% and thus to a point where these can compete with other thin-film solar cell technologies using materials such as CdTe, Cu(In $_x$ Ge $_{1-x}$)Se $_2$ (CIGS), etc where cell efficiencies $\sim 20\%$ have been reported.[2–4] The use of other oxides, such as Al-doped zinc oxide (AZO) and F-doped tin oxide (FTO) have also yielded solar cells but with lower power conversion efficiencies ($\sim 5\text{--}8\%$) in organic solar cells (OSCs).[5, 6] The expensive processing, dwindling indium resources and brittle nature limit the use of ITO as a TC for low-cost, flexible, plastic solar cells, because of which alternative material systems are constantly being sought that could effectively replace ITO for such applications.

6.1.2 Ag-NWs as electrodes in organic photovoltaics

As discussed earlier in Section 2.3 Ag-NWs emulate the properties of commercially used TCOs like ITO.[7, 8] Such versatility in electrical, optical and mechanical properties has been effectively utilized in realizing optoelectronic and photovoltaic devices; Ag-NWs, either in pristine or in composite form have been employed in various device structures with different organic material systems to demonstrate their applicability as highly transparent, conducting and flexible TCs in organic solar cells[9–14] and also organic LEDs.[15–17] In this study we investigate the application of Ag-NWs and Ag-NW/polymer composites on the performance of OSCs.

6.2 Experimental Methods

The materials used in the fabrication of organic solar cells in this work were -

Substrate: Microscope slide glass of thickness 1 mm from Fisher Scientific, cut to dimensions as mentioned in Figure 3.11

Transparent anodes: ITO, Ag-NW pristine, Ag-NW/PEDOT:PSS and Ag-NW/PVA

Hole transport layer: PEDOT:PSS – brandnames Clevios™ P VP AI 4083 ($\rho = 500 - 5000 \, \Omega \, \text{cm}$) and Clevios™ PH 1000 ($\rho \sim 0.001 \, \Omega \, \text{cm}$), purchased from Heraeus, Inc.

Bulk heterojunction: P3HT:PCBM (1.5:1) blend: P3HT, brandname Plextronics OS 2100 from Plextronics, Inc., and PCBM purchased from Nano-C, Inc.

Cathode: Al, evaporated from a 99.999% pure elemental source purchased from Kurt J. Lesker, Inc.

The devices were fabricated using a procedure outlined in the following section.

6.2.1 Fabrication procedure for OSC devices

Before depositing the various layers of the solar cell, the glass substrates were thoroughly cleaned by sonicating in acetone, IPA and DI water. The substrates were then patterned with photoresist using photolithography based on the pattern described in Figure 3.11 in Section 3.8.3. For ITO-based OSCs, glass substrates pre-patterned with ITO electrodes (having nominal sheet resistance of $10 \, \Omega/\square$) from Luminescence Technology Corp. Taiwan, were used.

The various Ag-NW based TC electrodes were deposited on the patterned glass substrates by spin coating. The NW dispersions contained NW concentrations that resulted in film sheet resistances of $\sim 5\text{-}15\ \Omega/\square$ (see Section 5.5 for details about the effect of NW concentration on sheet resistance). The specific electrode patterns were then obtained by soaking the substrates in acetone to allow for liftoff of unwanted electrode material. Following this step, metal electrode contacts (Ti-5 nm/Au-50 nm) over a portion of the NW electrodes were deposited by electron beam evaporation using a shadow mask (Figure 6.1). The metal overlayers provide direct electrical contact to the underlying Ag-NW based electrode and make it accessible for measuring J - V characteristics after deposition of the various organic layers on the top. The metal contacts also ensure isolation of these portions of the NW electrodes from the organic PV materials that could otherwise contribute to stray resistances and capacitances in the resulting device.

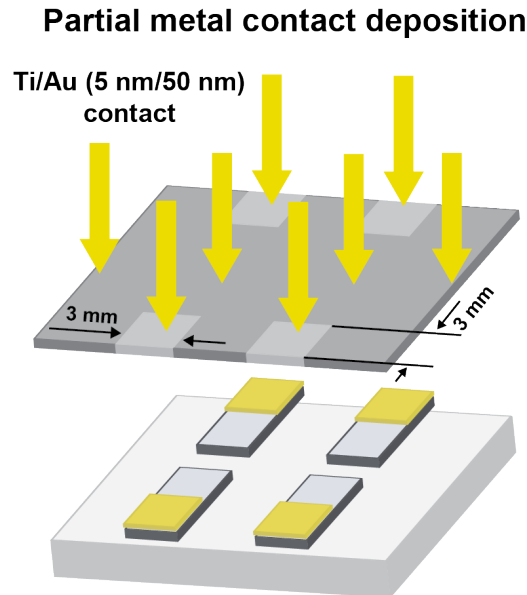


Figure 6.1: Schematic of deposition of partial Ti/Au contacts to Ag-NW TCs prior to deposition of active organic layers. The Ti/Au contacts provide direct electrical contact and easy access to the underlying electrodes, while at the same time isolating them from interfacing with the active layers that may bring about stray resistances and capacitances in the resulting device.

Following electrode patterning and depositions, the steps for OSC device fabrication

are detailed thus -

Step 1: Plasma cleaning: The pre-patterned ITO electrodes were cleaned in a PE-50 Plasma etch system from Plasma Etch, Inc., first in an O₂ atmosphere for 5 minutes followed by a second etch in an Ar atmosphere for 5 minutes. The O₂ plasma etch has been known to increase the work function of ITO electrodes and is thus considered beneficial in OSC fabrication processes since it allows for better matching of work functions with the hole transport layers as well as typical donor materials.[18, 19] Substrates patterned with Ag-NWs and NW-based composite electrodes were etched only in Ar for 5 minutes since an O₂ plasma would oxidize the Ag. Such a plasma etching step also increases hydrophilicity of the surfaces, enabling deposition of more uniform PEDOT:PSS HTL layers.

Step 2: HTL deposition: A thin layer of PEDOT:PSS (25–40 nm) was then deposited by spin coating to enable more efficient injection of holes from the active layers to the TC electrodes. The HTL was deposited by spin coating inside an N₂ glovebox. The spin conditions for the two grades of PEDOT:PSS used are mentioned in Table 6.1. In the spin-coating process described in the

Table 6.1: Spin conditions for PEDOT:PSS HTL deposition

Spin Speed (rpm)	
Clevios™ P VP AI 4083	Clevios™ PH 1000
Step 1: 300 (4 sec)	Step 1: 400 (10 sec)
Step 2: 700 (1 min 30 sec)	Step 2: 4000 (1 min)
Step 3: 2000 (5 sec)	

table, the first step enables spreading of the solution evenly over the entire surface while the second step determines the thickness of the film deposited. An additional third step (as in the case of Clevios™ P VP AI 4083 ink), typically

a high-speed spin-step removes excess ink at the edges of the substrate surface. The deposited films were then annealed at 150 °C for 30 minutes before further processing.

Step 3: Active layer deposition: The prepared P3HT:PCBM blend was then spin-coated on HTL-coated ITO and Ag-NW TCs as well as on bare pre-patterned ITO substrates. Conditions for the spinning process (a multistep one, as in the case of deposition of the HTL, discussed earlier) used were -

Step 1: 350 rpm (5 sec)

Step 2: 375 rpm (4 min)

Step 3: 2000 rpm (5 sec)

The samples were then annealed at 175 °C for 30 minutes before further processing. All spin-coating and corresponding thermal annealing steps were conducted within the N₂ glovebox.

Step 4: Al cathode deposition: The samples were then taken out of the glovebox and transferred into a bell-jar apparatus (see Figure 3.1), which was evacuated by a diffusion pump. An Al sheet with a thickness of 100 nm was thermally evaporated at a pressure of $\sim 7-8 \times 10^{-6}$ torr, through a shadow mask with a pattern perpendicular to that of the electrode pattern. The final device consisted of four identical solar cells each of area 0.09 cm² (schematically depicted in Figures 3.11 and 6.2). The samples were then annealed again on a hotplate at 150 °C for 5 minutes, since such an annealing step has been shown to improve the metal-organic contact at the interface.[20]

Step 5: Device *J-V* characterization: The fabricated devices were then transferred to another glovebox housing the *J-V* measurement apparatus (see Figure 3.12) for device characterizations. Prior to device measurement, a small

portion of the device corresponding to the side of the ITO and Ag-NW TC electrodes were soaked in acetone to enable slow dissolution of organic layers (away from the designated cell-areas) and expose the underlying electrode contact; mild scraping of the layers using a Q-tip helped in quick removal of the organic matter. To ensure good electrical contact between the electrode pins of the test-device enclosure and the fabricated OSC device electrodes, quick-drying Ag paste was applied on the latter. The devices were then inverted and inserted into the enclosure such that light from the solar simulator could enter into the active cell area from the glass side. $J-V$ measurements were subsequently conducted using a source-measure unit that is USB-interfaced to a computer through a custom MATLAB script. The $J-V$ characteristics of the devices were measured both under illumination and under the dark so as to effectively extract device-specific parameters for further analysis.

A pictorial schematic of the device fabrication process is shown in Figure 6.2.

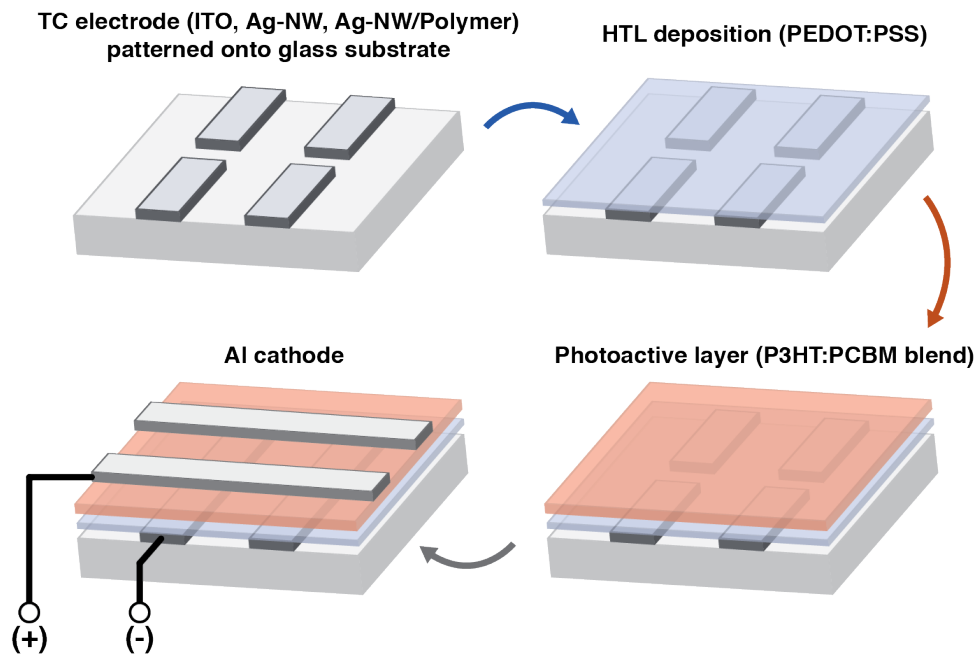


Figure 6.2: Schematic illustration of process flow for fabrication of organic solar cells in this study

6.2.2 Extraction of device parameters from J - V characteristics

The J - V characteristics of a solar cell contain a wealth of information pertaining not only to open-circuit voltages, short-circuit currents, fill factors and power conversion efficiencies derivable from these, but also other parameters such as R_{shunt} , R_{series} , ideality factor, etc. of the diode that help understand better the factors (be it material or structural) affecting the performance of the device. In this manner, the device performances can be tuned in a much more systematic manner.

These parameters can be extracted from the experimentally obtained solar cell J - V curves (in the dark and under illumination) by manipulating the lumped-circuit model J - V Equation 2.32 (with J_{S} , R_{shunt} and R_{series} as variables) as per the steps outlined by Hegedus and Shafarman in [21]. In a nutshell, the steps involved are as follows -

- (a) A plot of the derivative of J with respect to V , $g(V) \equiv dJ/dV$, in the vicinity of J_{SC} is ideally flat and gives an estimate of the shunt conductance, G_{shunt} .
- (b) The derivative of V with respect to J , $r(J) \equiv dV/dJ$, can then be taken, which when plotted against the term $(J + J_{\text{SC}})^{-1}$ contains R_{series} as the intercept of a linear fit to the data, since

$$r(J) \equiv dV/dJ = R_{\text{series}} + \frac{nk_{\text{B}}T}{q} (J + J_{\text{L}})^{-1} \quad (6.1)$$

Generally, during such analyses, $J_{\text{L}} = J_{\text{SC}}$. From the slope of the same plot, n , the ideality factor can be calculated as well.

- (c) Using R_{series} as calculated above, the effective voltage across the load is $V - R_{\text{series}}J$. By plotting $J + J_{\text{SC}}$ as a function of $V - R_{\text{series}}J$ on a semilogarithmic plot, the intercept of the linear region then gives the value for J_{S} and a slope

that is equal to $q/nk_{\text{B}}T$, from which the value of n can again be calculated and compared with that obtained in the previous step.

6.3 Results: Effect of hole transport layer on OSCs

As has been mentioned earlier, the presence of a hole transport layer (HTL) in an organic solar cell (OSC) contributes towards efficient injection of holes from the organic layer to the transparent electrode, while ensuring complete blockage of electrons at the same interface; injection of electrons across the same interface would lead to large losses in current due to recombination. The effect of the presence and absence of an HTL particularly in the case of ITO-based OSC devices was tested. Two different HTLs were used: a semiconducting grade PEDOT:PSS (Clevios™ P VP AI 4083), and a high-conductivity grade PEDOT:PSS (Clevios™ PH 1000).

The J - V curves for ITO-based OSCs with and without these two HTLs (see Figure 6.3) show an expected trend. The short-circuit current in these devices jumped from $\sim 8 \text{ mA/cm}^2$ without an HTL to 15 mA/cm^2 when the high-conductivity HTL was used, almost a two-fold increase. The corresponding power conversion efficiencies also increased from a meagre 0.5% to 3.4%. The performance with the semiconductor-grade HTL was better than that without an HTL but not as good as the performance with the high-conductivity HTL. This result could be attributed to the conductivity difference as well as the better film uniformity of the PH 1000 PEDOT:PSS. All subsequent OSC devices were fabricated with PH 1000 as the HTL.

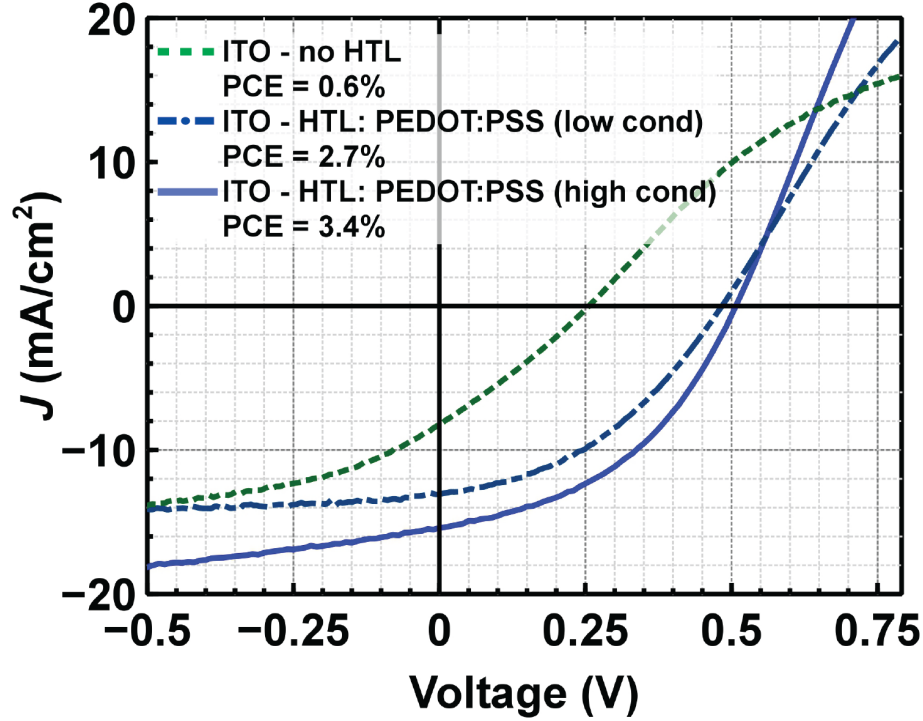


Figure 6.3: Plot of J - V data for ITO-based OSC devices (a) without an HTL (dashed curve), (b) with a semiconducting grade PEDOT:PSS (Clevios™ P VP AI 4083) (dash-dot-dashed curve) and (c) with a high-conductivity grade PEDOT:PSS (Clevios™ PH 1000) (solid curve). Devices with PH 1000 as the HTL show larger J_{SC} and V_{OC} values and thus larger fill factors and power conversion efficiencies

6.4 Results: Application of Ag-NW based TC electrodes in OSCs

Solar cell devices were also fabricated using Ag-NW based TC electrodes and tested for their J - V characteristics. The resulting data were compared to those of ITO-based devices, which were considered as “control samples”. The sheet resistances for the Ag-NW based electrodes (~ 5 – $15 \, \Omega/\square$) were closely matched to the measured sheet resistance of the ITO electrode ($\sim 10 \, \Omega/\square$). The corresponding J - V data is plotted in Figure 6.4 where devices fabricated using pristine Ag-NWs, Ag-NW/PEDOT:PSS, Ag-NW/PVA and Ag-NW/PSS composite TCs are compared to ITO control samples. The plots in Figure 6.4 show that despite its applicability in OSC devices as a TC electrode, pristine Ag-NW films still do not compare well with performances

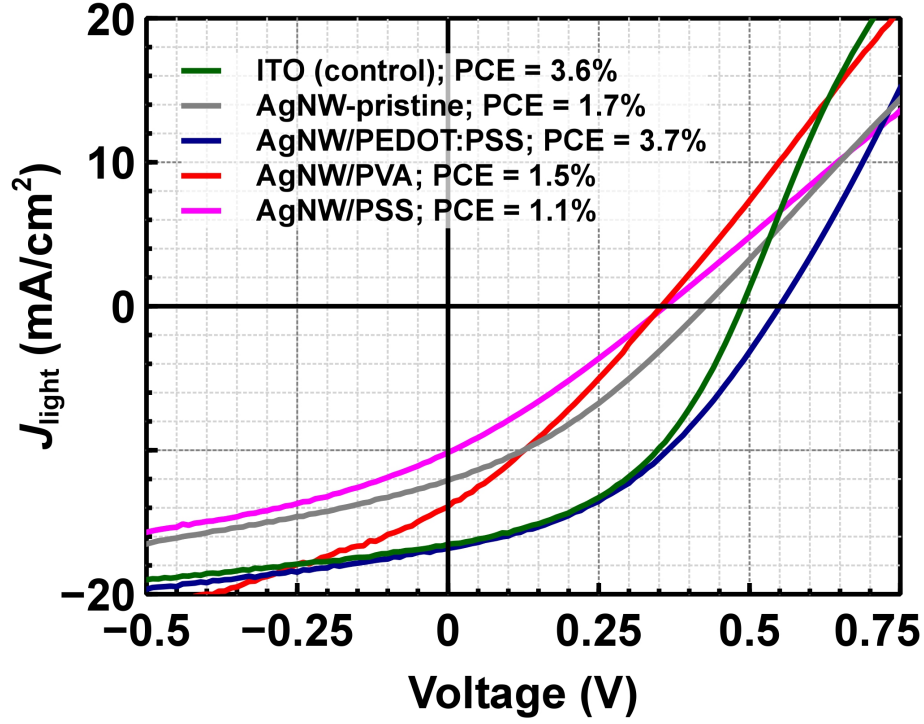


Figure 6.4: Plot of J - V data for solar cells with TC electrodes of pristine Ag-NWs, Ag-NW/PEDOT:PSS, Ag-NW/PVA and Ag-NW/PSS composites compared with that of ITO control samples. All the curves correspond to J - V characteristics for devices under illumination.

of ITO-based devices, owing to several issues including high degree of non-uniform morphologies arising out of aggregation, and also high surface roughness. While an aggregated film affects uniform transmission of light into the active organic layer resulting in lower J_{SCS} , the high surface roughness necessitates the use of an HTL sufficiently thick so as to not allow the Ag-NWs to electrically short the circuit, in the process lowering the V_{OC} values. The lower V_{OC} in these devices can also be attributed to the low work function of Ag as an electrode (~ 4.3 eV [1]).

Composites of Ag-NWs with PEDOT:PSS show marked improvement relative to the pristine Ag-NWs based OSCs. The efficiencies of the Ag-NW/PEDOT:PSS composite solar cells are comparable to, if not better than, those of the ITO-based control samples in this study, and to similar devices reported in the literature.[9, 11] This improvement in device performance can be attributed to the high uniformity

in morphologies of Ag-NW/PEDOT:PSS composite films in conjunction with lower surface roughnesses. Additionally the presence of PEDOT:PSS (commonly used also as an HTL) within the Ag-NW composite matrix provides for an electrode-HTL interface that is more efficient in transporting holes across this junction. As a consequence of this phenomenon, there is an effective reduction in recombination losses arising from a mismatch of the work function with Ag with that of the HOMO of the HTL and the P3HT active layer, which in turn increase the V_{OC} of the device.

Films of Ag-NW/PVA were also used as the TC electrode for OSC devices in order to test the effect of improvement in NW network uniformity and film morphology on cell characteristics, separate from the effect of using a conductive polymer matrix as for PEDOT:PSS. The high transparency of PVA should also, in principle, increase transmission of light through to the active organic layers. The increase in light absorption in the active layer as a result of increased light transmission through Ag-NW/PVA composite electrodes is evident from Figure 6.4 which shows an increase in J_{SC} for these cells to ~ 14 mA/cm² in comparison to that for cells with pristine Ag-NW electrodes, which is ~ 12 mA/cm². The obtained V_{OC} for Ag-NW/PVA based cells was, however, lower than that for other Ag-NWs based cells and ITO-control cells. We attributed the lower V_{OC} for the Ag-NW/PVA based cells to higher series resistances, as will be discussed further in our analysis described below. For Ag-NW/PSS based cells, both V_{OC} and J_{SC} were found to be lower than devices fabricated with pristine Ag-NWs as well as their PEDOT:PSS and PVA composite counterparts. We believe that the cause for this result is the difficulty in patterning of Ag-NW/PSS composite films primarily due to the hygroscopic nature of PSS polymer, which results in films that adhere poorly to the glass substrates.

The other device parameters such as series and shunt resistances were also extracted

Table 6.2: Device characteristics of organic solar cells based on Ag-NW TCs compared with ITO-based control samples. The HTL used in these cells was PEDOT:PSS PH 1000.

Electrode	R_{Sheet} ($\Omega/\square$)	V_{OC} (V)	J_{SC} (mA/ cm^2)	FF	η (%)	R_{series} (Ωcm^2)	R_{shunt} (Ωcm^2)	n	J_{S} (mA/ cm^2)
ITO	10	0.49	16.52	0.44	3.57	56.11	202.4	3.90	0.11
Ag-NW prist	8	0.43	12.09	0.33	1.69	168.1	112.8	4.2	0.19
Ag-NW/ PEDOT:PSS	13	0.55	16.82	0.41	3.73	75.61	174.9	3.65	0.04
Ag-NW/PVA	~ 15	0.36	13.92	0.30	1.45	127.1	66.1	3.85	0.24
Ag-NW/PSS	~ 15	0.36	10.16	0.28	1.04	160.2	89.0	4.01	0.15

as per the methodology outlined in the previous section (Section 6.2.2) and a summary of the device parameters is tabulated in Table 6.2. The computed parameter values indicate comparable J_{SC} 's with slightly higher V_{OC} for Ag-NW/PEDOT:PSS based solar cells in comparison to ITO-control cells. The calculated ideality factors for all the solar cells in this study were found to be > 3.5 , whereas typically n ranges from 1–2 in inorganic solar cells, with $n = 1$ indicating an ideal diode. Ideality factors larger than 2 are quite common in organic solar cells and are thought to arise from the various recombination processes at localized trap states in the bulk and at the donor-acceptor interface as well as low shunt resistances brought about by poor photon-capture, reflection losses and current leakage from material defects.[22, 23] Even here, the deviation from ideality is seen to be much higher (> 4) for pristine Ag-NWs based cells, which has been effectively mitigated by the use of polymer composites.

As for the series resistances, from the table of values it can be inferred that the use of polymer composites helps in reducing series resistances considerably, especially in

the case of Ag-NW/PEDOT:PSS TC electrodes. The observation of reduced R_{Series} can partly be attributed to the reduction in surface roughness of the composite films. However, the presence of a non-conducting matrix (in the case of PVA and PSS) mitigates effective contact between the Ag electrode and the HTL by reducing the surface area of the Ag-NWs available for a more efficient electrode-HTL interface. As a consequence of this, a lowering of V_{OC} is observed for Ag-NW/PVA and Ag-NW/PSS systems in comparison to the pristine Ag-NW-based devices. This can be addressed by the use of a different conductive polymer such as polyaniline or polypyrrole, which are known to protect metals from corrosion unlike PEDOT:PSS which is highly acidic and corrosive.

Using the values for device parameters in Table 6.2, J - V curves for all the devices were simulated and compared with experimental data, as in Figure 6.5(b-f). The similarity in experimental and simulated J - V curves verify the accuracy of the derived parameters in effectively describing the fabricated devices.

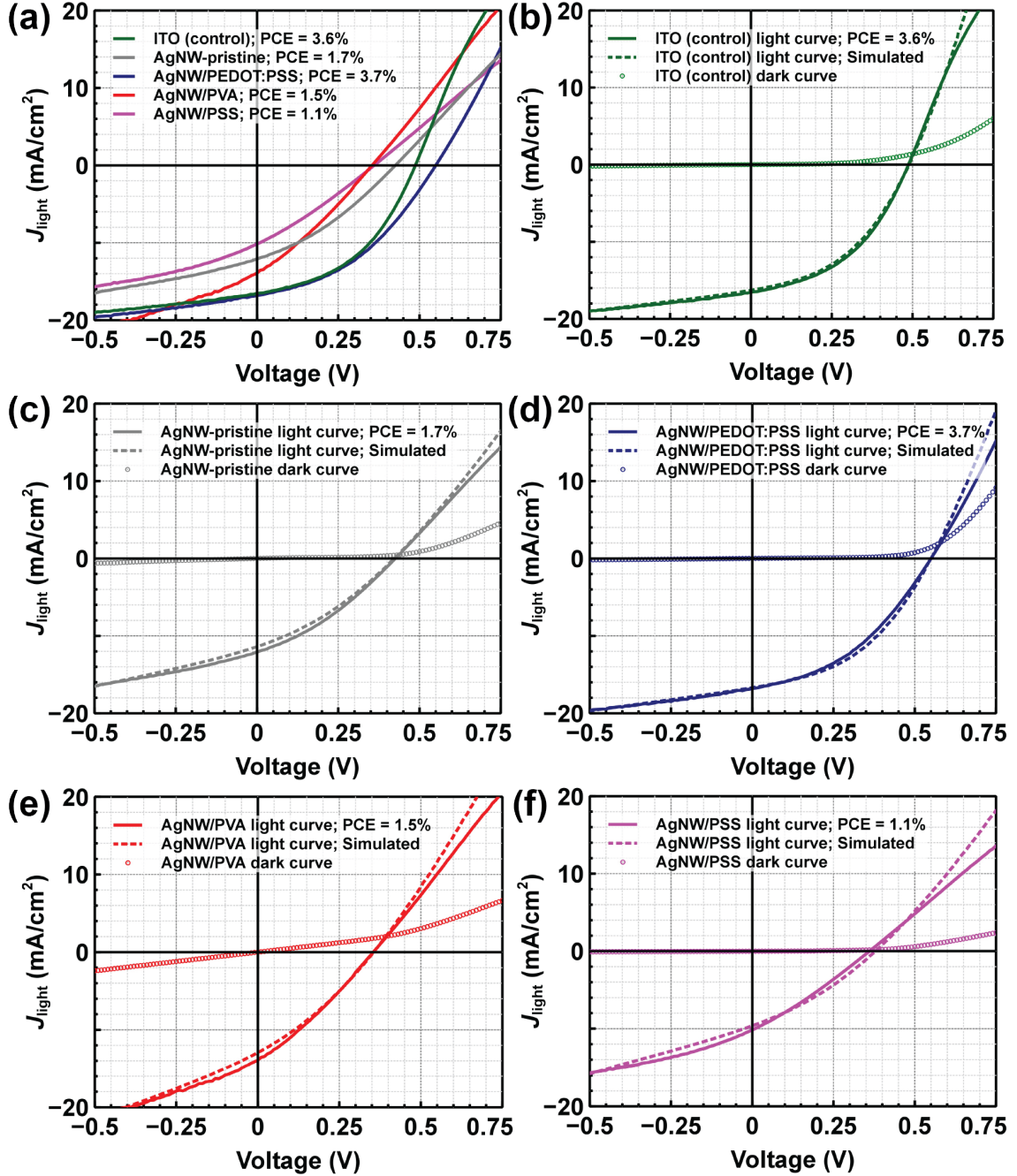


Figure 6.5: Plot of J - V data for solar cells with TC electrodes of ITO, pristine Ag-NWs, Ag-NW/PEDOT:PSS, Ag-NW/PVA and Ag-NW/PSS composites compared with J - V values simulated using device parameters in Table 6.2. The solid curves correspond to J - V characteristics for devices under illumination, the dashed curves correspond to simulated J - V curves and the open circles correspond to J - V curves for devices measured in the dark for the systems - (a) all electrodes, (b) ITO, (c) Ag-NW pristine, (d) Ag-NW/PEDOT:PSS, (e) Ag-NW/PVA and (f) Ag-NW/PSS.

6.5 Conclusion

The application of Ag-NW based transparent electrodes, in both pristine and composite form, in organic solar cells, has been demonstrated and also shown to be comparable in performance to devices fabricated using ITO, which is the electrode of choice in most commercial applications. The advantage of using Ag-NWs and their composites is in the applicability of these materials in flexible devices furthering innovation in ‘plastic’ and ‘printable’ electronics while maintaining simplicity and thus cost-effectiveness in processing. In particular, processing of these Ag-NW networked electrodes from polymer solutions has been shown to improve device performances in comparison to those processed from pristine Ag-NW dispersions demonstrating the value of such an approach.

Going forward, a systematic study of the effect of similar Ag-NW networked TCs embedded with different polymeric media on photovoltaic device performance needs to be conducted in addition to understanding better, the role of a hole transport layer in improving efficiencies. It is also necessary to study contact characteristics of the various interfaces involved, in an effort to mitigate shunt and series resistance effects and also to improve carrier transport across these interfaces.

6.6 References

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Chapter 7

Summary and Outlook

In summary, from the first part of this work it can be understood that optical resonant tunneling in periodic metal/polymer composite structures provides a means to significantly reduce optical absorption losses in polymer-based metallodielectric composite structures while retaining the advantageous (mechanical) properties of the polymer matrix. This work demonstrates promise for the use of microstructured metal-polymer composites in transparent conducting applications. For the particular case of a 1D periodic (laminate) structure, it is shown that a suitable strategy for the design of resonant structures is to align the lower band edge of the 1D periodic (photonic crystal) structure with the plasma absorption frequency of the metal component. For example, in gold/polystyrene laminate structures an increase of the optical transmission by up to 500% (at certain wavelengths) is realized by the appropriate design of a four-layer structure. The resulting flexible and (near) transparent polymer/metal composite structures could provide a robust material platform for the fabrication of flexible transparent conductors that play a central role in the development of ‘organic flexible electronics’. We note that for the latter application it is not the ‘absolute transparency’ but rather the ratio of transparency and resistance that is used as a metric to classify the performance of transparent

conductors. The high conductivity (in our case the in-plane conductivity was determined to be $\sigma \sim 10^6 \Omega^{-1}\text{cm}^{-1}$) that is imparted by the metal component should benefit the application of resonant metal/polymer composite structures as transparent conductors.

In the future,

- Strategies to further enhance the optical transparency of resonant metal/polymer composite structures need to be developed that would focus on the use of metals such as Ag with a plasma frequency outside the visible range. Preliminary results in this regard in our studies have shown great promise.
- Measurement of phononic band structure by Brillouin light scattering technique can shed more light on harnessing the potential of these metal-polymer laminates in other applications such as tunable thermal resistors.
- Furthermore, the self-assembly of polymer/nanoparticle composite systems into laminate structures could be explored as a more efficient and scalable fabrication methodology for resonant metal/polymer composite structures.

In the second part of this work, the studies conducted so far on pristine Ag-NW networks and Ag-NW/PEDOT:PSS, Ag-NW/PVA and Ag-NW/PSS composites, have proved without any doubt that these nanostructures show great promise as alternative materials to conventional oxide-based transparent conductors, especially considering their high conductivities, transmittances and even mechanical flexibilities. Networks of pristine Ag-NWs alone show transmittances of $> 90\%$ over the visible spectrum with corresponding sheet resistances consistently below $50 \Omega/\square$. Nevertheless, owing to dispersion instability, NW aggregation, non-uniform NW distribution over the film and percolation-limited conduction, more consistent and reproducible techniques of film processing are required. In this regard, we have proposed and successfully demonstrated the use of composites of Ag-NWs with

conducting polymers like PEDOT:PSS as well as insulating ones such as PSS, PVA and PAA as a means to not only stabilize the NWs in dispersion thereby preventing aggregation, but also improve network morphologies within the system in an effort to address the problem of percolation, viz. obtain the same conductivity at a lower Ag-NW concentration. In this study we have fabricated Ag-NW/PEDOT:PSS, Ag-NW/PVA and Ag-NW/PSS composite films that are $> 85\%$ transparent with sheet resistances below $50 \Omega/\square$ from films having lower Ag-NW content. The parameters extracted from curves simulating the variation of transmittance with sheet resistance corroborate the claim of lowering of the percolation threshold by the use of a polymer composite. The polymer composites were also found to have better resilience to mechanical deformation over multiple bending cycles demonstrating the ability to use these in flexible applications. In the context of solution processing of the Ag-NWs for uniform and reproducible films, the role of PEDOT:PSS and other polymeric media (electrically conducting and insulating) in stabilizing the NWs in dispersion, including mechanism for stabilization, was also studied in a systematic manner.

Furthermore, the effectiveness of the NW and composite films in a practical device like an OPV structure was optimized for, tested and compared to that of similar devices with a conventional TC (ITO), which is often used in commercial applications. The obtained power conversion efficiencies of the solar cell devices, particularly of Ag-NW/PEDOT:PSS composites compare very well with those of ITO-based control samples. Our results demonstrate not only the promise for using Ag-NW/polymer composite TCs as alternative material systems to ITO and other TCOs, but also provide an opportunity to systematically study their properties in order to effectively and efficiently incorporate these functional materials in various optoelectronic devices for commercial flexible applications.

Looking into the future,

- Specific aspects of these Ag-NW networks such as NW aspect ratios, NW-NW junction resistances and the contact resistances between the network films and other materials (used as active or as charge-transport layers in OPV devices), need to be studied and understood in greater depth, since these parameters directly impact OPV device performances.
- Functionalizing of the Ag-NWs with photoactive or other functional polymers/compounds can further open up a vast array of possibilities in utilizing these materials for other novel applications.
- Owing to the corrosive nature of PEDOT:PSS, a replacement conducting polymer also needs to be sought that can ensure long-term stability of devices containing such polymeric materials.

Appendix A

Ag-NW Network Simulation

```
%----- Stick Plot Generating Program -----%
%
% The following code generates a random network of sticks of
% specified dimensions, to simulate for a network of randomly
% distributed Ag-NWs.
%
% Created by: Colleen Treacy, Dept. of Physics, CMU
%            Sudarshan Narayanan, Dept. of MSE, CMU
%            (January, 2014)
%-----%

clear;
format long;

film_lth = 80000;           % Size of the film
                           % (length of side in nm)
                           % Size used here: 80 um
                           % (to match SEM image dimensions)

NWlength_avg = 25000;      % Average length of the NW in nm
NWlength_stddev = 10000;   % Standard deviation in length of NW

NWdiam = 90;              % Width of nanowire

totlth = 0;               % Sum of lengths of all NWs,
                           % used to calculate areal density

NumberofNWs = 150;        % Number of NWs to be generated

%% Random generation of wires based on number and average NW length %%
% Input:  Number of NWs and length/width values
```

A. Ag-NW Network Simulation

```
% Output: Randomly generated start and end points for each line,
%         stored in startx=[x-coordinate], starty=[y-coordinate],
%         endx=[x-coordinate], endy=[y-coordinate].
%         Generate random values and plot lines

hold on;
axis([0 film_lth 0 film_lth]);
axis off;

% To generate weighted random values
% (simulation of aggregated structures)

%N = 1000;
%mu = 400;          % Mean value around which random value is generated
%s = 300;           % Sigma (std deviation)

%weightarray = zeros(1,1000);

%for count = 1:N
%    weightarray(count) = exp(-(((count-mu)^2)/(2*(s^2))));
%end

for n=1:NumberofNWs;
    theta(n) = randi([-180,180]);          % Random theta value
                                           % between -pi/2 and pi/2

    lth = normrnd(NWlength_avg,NWlength_stdev); % Random lengths based
                                           % on a normal
                                           % distribution about
                                           % NWlength_avg

    totlth = totlth + lth;                  % Total length of all NWs,
                                           % used to calculate
                                           % areal density

    startx(n) = rand(1)*film_lth;           % Random startx-value for
                                           % NW stick (X)
    starty(n) = rand(1)*film_lth;           % Random starty-value for
                                           % NW stick (Y)

    startx1(n) = startx(n) - NWdiam*sind(theta(n)); % Random startx-
                                           % value for NW
                                           % stick (X1)
    starty1(n) = starty(n) + NWdiam*cosd(theta(n)); % Random starty-
                                           % value for NW
                                           % stick (Y1)

    %startx(n) = (randsample(N,1,true,weightarray)./N)*film_lth;
    % (Random weighted startx-value for NW stick)

    %starty(n) = (randsample(N,1,true,weightarray)./N)*film_lth;
    % (Random weighted starty-value for NW stick)

    endx(n) = startx(n)+lth*cosd(theta(n)); % endx-value (X') for
```

```

endy(n) = starty(n)+lth*sind(theta(n)); % stick based on theta
                                         % endy-value (Y') for
                                         % stick based on theta

endx1(n) = startx1(n)+lth*cosd(theta(n)); % endx-value (X1') for
                                         % stick based on theta
endy1(n) = starty1(n)+lth*sind(theta(n)); % endy-value (Y1') for
                                         % stick based on theta

% NW stick to be simulated for as a rectangle, using coordinates:
% (X,Y) -- (X',Y') -- (X1',Y1') -- (X1,Y1)

% Pruning edges: ensures wires are completely inside the film area

if (endx(n) < 0) % Prunes wires from the left
    endy(n) = starty(n) + (endy(n) - starty(n)) * ...
        (0 - startx(n)) / (endx(n) - startx(n));
    endx(n) = 0;

elseif (endx(n) > film_lth) % Prunes wires from the right
    endy(n) = starty(n) + (endy(n) - starty(n)) * ...
        (film_lth - startx(n)) / (endx(n) - startx(n));
    endx(n) = film_lth;

end

if (endy(n) < 0) % Prunes wires from the bottom
    endx(n) = startx(n) + (0 - starty(n)) * ...
        (endx(n) - startx(n)) / (endy(n) - starty(n));
    endy(n) = 0;

elseif (endy(n) > film_lth) % Prunes wires from the top
    endx(n) = startx(n) + (film_lth - starty(n)) * ...
        (endx(n) - startx(n)) / (endy(n) - starty(n));
    endy(n) = film_lth;

end

% Round coordinates to hundredths place
startx(n) = roundn(startx(n), -2);
endx(n) = roundn(endx(n), -2);
starty(n) = roundn(starty(n), -2);
endy(n) = roundn(endy(n), -2);

patch([startx(n) startx1(n) endx1(n) endx(n)], ...
      [starty(n) starty1(n) endy1(n) endy(n)], [0 0 0]);
% Patch command simulates for rectangle of specified dimension

end;

print(figure1, '-dpng', 'AgNW150.png')
Density = totlth * NWdiam * 100 / (film_lth)^2

```