High Throughput Assessment of Multicomponent Alloy Materials

Submitted in partial fulfillment of the requirements for

the degree of

Doctor of Philosophy

in

Chemical Engineering

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May, 2018

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Acknowledgements

First of all, I would like to express my sincere gratitude to my advisor Prof. Andrew Gellman for the continuous support of my five years of PhD study. Without his guidance, it would not be possible to write of this thesis. Besides my advisor, I would like to thank the rest of my thesis committee, Prof. Jonathan Malen, Prof. Dennis Prieve, Prof. Zachary Ulissi, and Prof. John Kitchin for their valuable time to give insightful comments on my research.

I would like to thank my colleagues in Prof. Andrew Gellman's lab, who have been really supportive to my research. Without them, my last five years of student's life could not be successful and enjoyable. In particular, I am grateful to Dr. Matthew Payne for his patience to teach me how to operate every instruments in our laboratory and enlighten me the first glance of research. I also want to thank Dr. Petro Kondratyuk and Dr. Chunrong Yin for helping me resolve research problems. It is my pleasure to collaborate with Prof. Jonathan Malen, and his student Justin Freedman, Dipanjan Saha, and Minyoung Jeong and Prof. Jeff Weldon and his student Mohamed Darwish for all of efforts to make our research moving forwards. I want to thank all my labmates in Catalysis group who has been working consistently and closely with me during last five years, like Jianfeng Liu, Irem Sen, Jacob Boes, Aaron Reinicher, Gamze Gumuslu, Yongju Yun, Burcu Karagoz, Soham Dutta, Sasimas katanyutanon, Daniel Lee, Nicholas Golio, Micheal Radetic, Zhongyu Piao, and Zhitao Guo. Again, I would like to thank my family, who supports me spiritually throughout last five years.

Lastly, I want to acknowledge the Department of Chemical Engineering at Carnegie Mellon University, Seagate Technology LLC and National Science Foundation under grant number CHE1704871 for financial supporting and continuously funding my research.

Abstract

Multicomponent metal alloys play an essential role in many technologies and their properties must be optimized by rational selection of the alloy's components and its fractional composition of each. High-throughput materials synthesis allows us to prepare Composition Spread Alloy Films (CSAFs), sample libraries that contains all possible compositions of a binary or ternary alloy. In our lab, a Rotatable Shadow Mask (RSM) – CSAF deposition tool has been developed for the creation of CSAFs. Such CSAFs can be prepared with composition gradients and/or thickness gradients in arbitrarily controlled directions and on a variety of substrates.

Once prepared, the CSAF libraries can be characterized thoroughly using a variety of highthroughput spectroscopic methods. Their bulk composition is mapped across the library using Energy Dispersive X-ray spectroscopy (EDX). The near-surface compositions are mapped across composition space using X-ray Photoemission Spectroscopy (XPS). Finally, the electronic structure can be mapped using UV photoemission spectroscopy (UPS) and valence band XPS. Once characterized, these CSAFs are being used for high-throughput studies of alloy catalysis and thermal properties of the alloys and of alloy-substrate interfaces.

First of all, $Pd_zCu_{1-z}CSAF$ was prepared to show that alloy nanoparticles (aNPs) and thin films can adopt phases that differ from those of the corresponding bulk alloy. The mapping of XPS-derived core level binding energy shifts across $Pd_zCu_{1-z}SCSNaP$ library shows a promising result that the FCC phase can be dimensionally stabilized over the composition range where B2 phase exists in the bulk. This observation can potentially improve the performance of $Pd_zCu_{1-z}NP$ catalysts in H₂ separation. Secondly, the relationship between catalyst activity-electronic structure-composition has been investigated. A high throughput characterization of electronic structure (valence band energy) of binary Pd_xAg_{1-x} and ternary Pd_xCu_yAu_{1-x-y} CSAFs were performed by XPS. This XPS-derived valence band center is compared with UPS-derived data across Pd_xCu_yAu_{1-x-y} CSAFs. In addition, H₂-D₂ exchange reaction was studied on Pd_xAg_{1-x} CASF. A higher HD formation rate is experimentally observed but cannot be predicted by the Langmuir-Hinshelwood model when the surface coverage is saturated. However, the proposed H₂-D₂ exchange mechanism (breakthrough model) involved with surface and subsurface hydrogen reaction is investigated to produce a same reaction order as Langmuir-Hinshelwood mechanism, which cannot explain the experimental observation.

Furthermore, the thermal interface conductance (*G*) was studied as a function of metal alloy composition. A high-throughput approach to preparation, characterization, and measurement of *G* was also demonstrated to study the thermal property of alloyed materials. Our result in studying the *G* across the Au_xY_{1-x} (Y = Pd and Cu) CSAFs-dielectric interfaces has shown a linear relationship with alloy composition, which monotonically increases with decreasing Au (at. %). Lastly, the effect of interdiffusion in metal films on *G* at metal-dielectric interface was also examined. The XPS depth profiling was designed to experimentally determine the temperature effect on compositional profiles in the Au-Cu system, and how to further influence *G*. This study provides fundamental understanding of stability of adhesion layer of Cu and the effect of interdiffusion in Cu-Au alloy on the heat dissipation.

All in all, the key value to these CSAF libraries is that they enable measurement of important alloy properties across entire binary or ternary alloy composition spaces, without the need to prepare and characterize numerous discrete composition samples.

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Chapter 1 Introduction

1.1 High throughput method of material design across multidimensional continua

Multicomponent metal alloys play important roles in many novel applications including catalysts, optics and sensors. ¹⁻⁵ The major challenge to developing alloy materials for various applications is to screen the desired functional properties over multiple structural degrees of freedom and a large set of other parameters. Because the properties of alloy materials are strongly influenced by the alloy components and alloy composition, the experimental approach to search for the optimal composition for a desired property can be time-consuming, requiring the preparation and characterization of a large set of discrete samples. Furthermore, it will be further complicated by the nanomaterial descriptors include size, shape and morphology.

Comprehensive study of the properties of alloy materials can be accelerated by use of high

throughput methods based on materials libraries. High-throughput methods have evolved rapidly during the last decade, allowing a systematic approach to preparation, characterization, and measurement of functional properties on different materials libraries in a rapid and efficient fashion. ⁶⁻⁸ Composition spread alloy films (CSAFs) are material libraries based on thin alloy films that have lateral composition gradients allowing one to span all possible compositions of a binary alloy (A_xB_{1-x}, $x = 0 \rightarrow$



Figure 1. 1. Ternary $A_xB_yC_{1-x-y}$ composition spread alloy film (CSAF) with a composition gradient that spans the entire composition space but at constant thickness.

1) or ternary alloy $(A_xB_yC_{1-x-y}, x = 0 \rightarrow 1 \text{ and } y = 0 \rightarrow 1-x)$ in a single film. In this study, we make use of a variant on the CSAF which spans both alloy composition and film thickness, in order to study the properties of alloy materials spanning nanoscale dimensions. Figure 1.1 displays a graphical representation of a ternary $A_xB_yC_{1-x-y}$ composition spread alloy film (CSAF) with a composition gradient that spans the entire composition space with a constant film thickness. ⁹⁻¹¹

In this work, a comprehensive high-throughput study of the catalytic and thermal properties of multicomponent alloy materials (e.g. Pd, Cu, Au, and Ag) will be conducted through material libraries that span various parameter spaces including composition, size, and morphology.

1.2 Electronic structure for alloy catalysts

Multicomponent alloys are used as catalysts in many applications because they can possess catalytic properties superior to their pure components. ^{1, 5} The activity of alloy catalysts can be optimized by searching for different combinations of alloy components across the composition space, which leads to modifying the phase and electronic structures of the alloy materials. To understand the relationships between alloy composition, phase, electronic structure and catalytic reactivity, both experimental and computational approaches are required to measure and model the properties of alloys across the composition space. Here, the interaction between electronic structures of individual components of alloy material has been described as ligand effect, which can result in a shift in the position and width of *d*-band center.¹² More important, this shift of position of *d*-band center relative to the Fermi level can influence the energy barrier of a reaction occurring on the metal surface.¹³⁻¹⁵ This ligand effects of alloy can be experimentally measured using both x-ray photoelectron spectroscopy (XPS) and UV photoelectron spectroscopy (UPS).¹.

¹⁶ The average energy of the *d*-band (ε_d) as an important parameter can be estimated to predict the reactivity of the alloy metal.¹⁴ In our study, an experimental approach to measure the filled states of the valence band (*v*-band) energy across Pd_xAg_{1-x} and Pd_xCu_yAu_{1-x-y}CSAFs was proposed, which can be used to benchmark *d*-band energy in the density functional theory (DFT) calculation.

1.3 Alloy membranes for hydrogen purification

High throughput techniques can be used to improve membrane materials used for industrial separation of hydrogen.^{17, 18} Hydrogen plays a significant role in advanced energy systems, such as fuel cells. ^{11, 19, 20} In general, hydrogen production are from a CO_2 -rich mixture by methods such as pressure swing adsorption or cryogenic distillation, both of which require large capital expenditure and energy consumption. ³⁷ In contrast, membrane separation is a greener alternative for hydrogen purification, because it is less energy intensive and allows continuous operation.

Among the materials for designing hydrogen purification membrane, palladium is known to have high permeability for H atoms, high H₂ selectivity and reasonable cost. ^{18, 21, 22} However, pure Pd usually encounters problems, such as hydrogen embrittlement and surface poisoning by sulfur.²³⁻²⁵ In order to resolve these problems, Pd is often alloyed with other metallic components (e.g. Cu, Au, and Ag) to improve the mechanical strength and impart tolerance to sulfur containing compounds in gas streams.²³⁻²⁸

The reaction mechanisms to separate H₂ from other gases by Pd alloy membranes consist of three major elementary steps, which has been investigated through the kinetics study of catalytic H₂-D₂ exchange reaction on Pd_xCu_{1-x} catalysts.²⁴ First, H₂ dissociatively adsorbs on the membrane surface, then H atoms diffuse through the membrane, finally H₂ recombinatively desorbs from the opposite side the membrane surface. However, the understanding of adsorption and desorption kinetics on the surface of Pd-based alloys is lacking. Thus, the study of the H₂-D₂ exchange (H₂ + D₂ \rightarrow 2HD) reaction can provide critical information about the kinetic descriptors for these steps. In this work, we demonstrate a high throughput approach to examine the catalytic activity for H_2 - D_2 exchange reaction on Pd_xAg_{1-x} and Cu_xAu_yPd_{1-x-y} CSAFs across a continuous composition space. The reaction mechanisms for H_2 - D_2 exchange has been examine on both Langmuir-Hinshelwood model and breakthrough model.

For Pd_zCu_{1-z} binary system, Priyadarshini *et al.* mapped the bulk phase diagram by electron backscatter diffraction (EBSD), there exhibits a large composition range, 0.35 < z < 0.55, where a B2 phase (ordered body centered cubic, CsCl structure) is formed at temperatures of < 873 K, although pure Pd and Cu both have face centered cubic (FCC) bulk crystal structures.^{29, 30} However, the Pd_{0.47}Cu_{0.53} alloy can also adopt a metastable FCC phase after annealing above 873K and quenching rapidly.²⁴ Based on our previous work, it has been demonstrated that the kinetics of H₂ dissociation on the bulk Pd_{0.47}Cu_{0.53} alloy are much faster on the FCC phase than on the B2 phase.²⁴ If the FCC phase can be stabilized at the nanoscale at T < 873 K, the performance of Pd_zCu_{1-z} NP catalysts can be greatly improved over the activity of the bulk alloy. Interestingly, alloy nanoparticles (aNPs) and thin films can adopt phases that differ from those of the corresponding bulk alloy. ³⁸⁻⁴¹ This observation provides an opportunity to design materials with properties that cannot be obtained from their bulk counterparts. In this study, spatially resolved XPS was used to map the Cu 2*p*_{3/2} core level shifts (CLS) for a Pd-Cu CSAF as a function of both composition and film thickness.

1.4 Thermal interface conductance of alloy materials

Recent development of electronic devices have been scaled downwards to the nanoscale, at which the length scales of materials are comparable to the energy carrier (phonons and electrons) mean free paths.³¹⁻³³ At this characterization length scale, it is critical to understand the thermal conduction of electronic devices, which is controlled by the thermal interface conductance (*G*) across metal-dielectric interfaces. Although *G* has been measured across the interfaces between pure metal and dielectric, the alloy composition effect on *G* across the alloy-dielectric interfaces is not well understood. Nonetheless it is important to development of alloy materials for application, e.g. heat-assisted magnetic recording (HAMR).³⁴

HAMR is a magnetic data storage technology, which uses a gold near field transducer (NFT) to generate plasmons that locally heat the magnetic media.³⁵ However, low *G* across the Audielectric interface contributes to be a large thermal interface resistance and drives a temperature raise in the Au NFT.³⁵ In order to stabilize the Au-dielectric interface, alloying Au with other metallic components (e.g. Cu and Pd) with relative high Debye temperatures can optimize the thermal and plasmonic properties of the metal-dielectric interface across the composition space. In this study, *G* across Au_xY_{1-x}-sapphire (Al₂O₃) interfaces, where Y = Pd and Cu, will be measured by spanning the entire composition space.

In order to dissipate heat across the Au-dielectric interface, a metal adhesion layer can also enhance *G*. Jeong at el. found that a thickness of 1.5 nm of the adhesion layer for metals (e.g. Cu and Cr) can increase *G* between Au and sapphire by factors of 2 and 4 respectively³⁶. However, when the adhesion layer operates at high temperatures, the metal adhesion layer can diffuse into the Au. Thus, it is critical to determine the stability of the adhesion layer (e.g. Cu), and measure the diffusion of Cu into Au as a function of temperature and time by XPS depth profiling. Furthermore, the effect of interdiffusion of Cu-Au on the heat dissipation in terms of G was studied.

1.5 Scope of research thesis

This research will contribute the high-throughput study of catalytic and thermal properties of multicomponent alloy materials including different combination of Pd, Cu, Au and Ag through material libraries that span parameter spaces such as composition, size, and morphology. We have successfully developed the fabrication and characterization methodologies to advance the design and development of complex materials, and detail descriptions can be found in Chapter 2.

In Chapter 3, Pd_zCu_{1-z}CSAF was prepared to show that alloy nanoparticles (aNPs) and thin films can adopt phases that differ from those of the corresponding bulk alloy. In the bulk, Pd_zCu_{1z} adopts a B2 phase (CsCl structure) for 0.35 < z < 0.55, in spite of the fact that pure Pd and Cu both have FCC bulk crystal structures. Spatially resolved x-ray photoemission spectroscopy (XPS) was used to map the Cu $2p_{3/2}$ core level shifts for a Pd_zCu_{1-z} composition spread alloy film (CSAF) as a function of both composition and film thickness. In the FCC phase, the Cu $2p_{3/2}$ binding energy decreases monotonically across the range $z = 0 \rightarrow 1$. At T < 873 K, there is an additional discontinuous CLS over the composition range 0.35 < z < 0.55, where the B2 phase forms as a results of a disorder-order transition. Thus, the Cu $2p_{3/2}$ CLS can be used to distinguish between the B2 and FCC phases. After annealing the Pd_zCu_{1-z} CSAF to 700 K, the bulk B2 phase was observed at film thicknesses >6 nm. However, at film thicknesses in the range 4 - 6 nm, only the FCC phase was observed. Because the FCC phase is more densely packed than the B2 phase, surface tension in this nanoscale regime drives a conversion from the B2 phase to the FCC phase in the thinnest films. At film thicknesses < 4 nm, the B2 phase reappears as a result of film dewetting and thickening to > 6 nm.

In Chapter 4, we focused on establishing a correlation between catalytic activity, alloy composition and electronic structure on binary Pd_xAg_{1-x} and ternary $Pd_xCu_yAu_{1-x-y}$ CSAFs. The composition and electronic structure were characterized by XPS. The XPS-derived valence band center is compared with UPS-derived data across $Pd_xCu_yAu_{1-x-y}$ CSAFs. These results have shown a good agreement with DFT calculation but an offset of ~1.5 eV has been observed from XPS-derived data. In addition, we have shown that the H₂-D₂ exchange mechanism (breakthrough model) involved surface and subsurface hydrogen produce the same reaction order as the classic Langmuir Hinshelwood model.

In Chapter 5, we present the first measurements of thermal interface conductance as a function of metal alloy composition across interfaces between dielectrics and metallic alloys. Composition spread alloy films of Au_xCu_{1-x} and Au_xPd_{1-x} solid solutions were deposited on single crystal sapphire substrates via electron-beam evaporation. High throughput measurements of thermal interface conductance across the alloy-sapphire interfaces were made by positional scanning of frequency domain thermoreflectance measurements (FDTR) to sample a continuum of Au atomic fractions (x ~ 0 \rightarrow 1). At a temperature of 300 K, the thermal interface conductance at the Au_xCu_{1-x} -sapphire interface monotonically decreased from 197 ± 40 MW/m²-K to 75 ± 15 MW/m²-K for 0 ≤ x ≤ 0.95 ± 0.02 and at the Au_xPd_{1-x} -sapphire interface from 173 ± 34 MW/m²-K to 69 ± 13 MW/m²-K for 0.025 ≤ x ≤ 0.97 ± 0.02.

In Chapter 6, Thermal conductance across the interface between a multilayer metal film and a dielectric has been measured for Au-Cu-Al₂O₃. The effect of interdiffusion between the Au and Cu layers has been probed by annealing at various temperatures and for various lengths of time. XPS depth profiling measurements following vacuum annealing at 320, 440, 460, 480, and 520 K, were used to determine the temperature dependence of the Au-Cu composition profiles. These depth profiles reveal that once a metal atom crosses the Au-Cu interface, it uniformly redistributes itself in the other layer. We derive an analytical model to describe the depth profile as a function of time, the permeability of the Au-Cu interface to each species, and initial thicknesses of the Au and Cu layers.

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Chapter 2 Experimental methodology

2.1 Rotatable shadow mask deposition tool

A rotatable shadow mask (RSM)-CSAF deposition tool has been developed for the creation of CSAFs as shown in Figure 2.1.¹ Four water-cooled electron beam evaporators (Mantis Deposition, Inc.) are integrated within the RSM-CSAF deposition tool. It allows us to co-deposit up to four metallic components at the same time. The deposition tool is mounted at the bottom of a stainless steel ultra-high vacuum (UHV) chamber. The RSM is located between the wideaperture electron beam evaporation source and the substrate. Herein, due to the geometry of the deposition tool, the flux from each source can form a spatially varying flux gradients and deposits a wedge with a linear thickness gradient (~7 mm band) across the substrate. The orientation of the RSM for each source can be used to control the direction of the flux gradient so that a complex composition spread can be generated. The UHV chamber can be evacuated to an operating pressure of 10⁻⁹ Torr using turbomolecular pump. Additional equipment attached on the UHV chamber includes a Varian ionization gauge for pressure measurement, a PHI model sputter ion

gun for sputtering cleaning the substrate with Ar^+ , and a Maxtek quartz crystal microbalance (QCM) for measurement of physical vapor deposition rates from each metal source. Inside the chamber, an *xyz*-manipulator is used to position the substrate. The substrate was mounted on the sample holder with a thermally conductive paste and retained by four spring-tension screws. The sample holder can be heated





resistively up to 900 K. A type-K thermocouple spotted welded to the backside of the sample holder was used to monitor the temperature of sample.

2.2 Experimental procedure for CSAF preparation

Once each of the four e-beam sources (Pd, Cu, Au, or Ag) was aligned on the deposition substrate, the deposition profile that creates a roughly linear thickness gradient across ~7mm can be made from any of the four sources. In this study, different types of CSAF samples were prepared including a Pd_zCu_{1-z} CSAF on Mo, a Pd_xCu_yAu_{1-x-y} CSAF on Mo, a Pd_xAg_{1-x} CSAF on Mo, a Au_xCu_{1-x} CSAF on sapphire (Al₂O₃), a Au_xPd_{1-x} CSAF on sapphire (Al₂O₃), a two layered Au-Cu on Mo and a two layered Au-Cu on sapphire (Al₂O₃). Using these the properties of complex materials can be studied across various spaces (e.g. composition, size, and morphology). Two types of substrates were used including a $14 \times 14 \times 2.5$ mm³ polycrystalline Mo substrate polished with a roughness < 3 nm (Valley Design Corp) and an [0001]-oriented (c-plane cut) $14 \times 14 \times 1$ mm³ single crystal sapphire wafer polished with a roughness < 0.3 nm (University Wafer). Mo substrate was used because it is a conductive material required for XPS measurements. Metal (e.g. Pd, Cu, Au, or Ag) will not interdiffuse with Mo at an elevated temperature.²⁻⁴ The sapphire wafer (Al₂O₃) was selected for the dielectric substrate in thermal interface conductance measurements because there are several prior measurements of interface conductance with sapphire for comparison.^{5, 6} The standard operating procedure for deposition of CSAFs was as following.

The substrate was cleaned by an isopropanol rinse and dried in air. After loading the substrate, the UHV chamber was sealed and evacuated with a mechanical pump and then with the turbomolecular pump. The deposition of CSAF was carried out at pressure of approximate 10^{-9} Torr. The substrate was sputter cleaned by 2 kV Ar⁺ beam with ~10 mA emission current for 20

min to remove any contaminants or oxide and then annealed at 700 K for 1 h. After cooling to room temperature, each of the e-beam sources incorporated with the RSM-CASF deposition tool was brought to a constant flux of 0.2 nm per min, which was calibrated by a *Maxtek* quartz crystal microbalance (QCM). Deposition rate from each component was controlled by filament heating power and measured using a QCM. The substrate was moved to the deposition position by the manipulator arm. The orientation of the shadow mask for each e-beam source was adjusted to deposit either binary or ternary CSAFs.

Taking the binary Pd_zCu_{1-z} CSAF as an example, the flux gradients of e-beam sources of Pd and Cu were orientated at 90° from one another by rotating the orientations of the shadow masks. After 20 min deposition, the Mo substrate was annealed for 30 min at 700 K to crystallize the CSAF.^{2, 3} The sample was achieved with a thickness gradient from $d = 0 \rightarrow 8$ nm and a composition gradient from pure Cu to pure Pd. Similar operating procedure was performed for fabricating other CSAFs and details are described in the Table 1. In addition, two layered samples of Cu and Au were prepared by first depositing the Cu wedge on either Mo or sapphire substrate, then take out the RSM for the Au source. A uniform thickness of Au film can deposited on top of the Cu wedge and a consistent temperature of 300 K. Finally, the chamber was vented to remove the sample for composition and thickness vs. position analysis.

Sample	Substrate	Shadow Mask Orientation (deg)	Deposition Time (min)	Deposition Rate (nm/min)	Annealing Temperatur e (K)
PdzCu1-z CSAF	Мо	90	30	0.2	700
Pd _x Cu _y Au _{1-x-y} CSAF	Мо	120	500	0.2	800
Pd _x Ag _{1-x} CSAF	Мо	180	500	0.2	800
Au _x Cu _{1-x} CSAF	sapphire	90	250	0.2	800
Au _x Pd _{1-x} CSAF	sapphire	90	250	0.2	800

Table 1. Operating parameters for fabrication of CSAFs

2.3 EDX mapping of composition and thickness gradient on CSAFs

The bulk composition and thickness of the CSAF can be mapped by a Tescan Vega 3 scanning electron microscope (SEM) with an Oxford Instruments X-mas 80 mm² detector for energy dispersive X-ray spectroscopy (EDX) analysis. The sample was characterized at a specific characterization grid by INCA Energy software. For instance, the sample was measured at 169 points on a 1 mm² grid of total 12×12 mm² area centered on the 14×14 mm². At each measuring point, a 20 kV SEM electron beam was rastered across at a 50 × 50 µm² area to obtain an EDX spectrum from 0-10 keV. The thickness of the CSAF was <100 nm, but the characterization depth of SEM beam on sample is >300 nm.⁷ Assuming that the sampled volume consists of a homogenous CSAF on an infinitely thick substrate (Mo/sapphire), the INCA ThinFilmID software was used to quantify the concentrations of each component at each analysis point and to determine the thickness of the CSAF layer.

2.4 XPS mapping of near surface composition and electronic structure on CSAFs

The sample can be characterized using spatially resolved X-ray photoemission spectra (XPS) in ThetaProbe surface analysis system (ThermoFisher Scientific Inc.). Al K α radiation from a monochromatic X-ray source (1486.6 eV) was focused to a 200 µm diameter spot size. The XP spectra can be obtained at a specific characterization grid as an example in previous Section 2.3. They were collected at binding energies with 10 eV ranges centered on Pd 3*d*_{3/2}, Ag 3*p*_{3/2}, Cu 2*p*3/2, Au 4*f*7/2 peaks, which were used for quantifying the composition. The *v*-band spectra were also scanned at binding energies in the range from 0 to 25 with analyzer pass energy of 40 eV. These scans were gathered at analyzer pass energy of 100 eV with a 0.01 eV step size. The peak area of XP spectra were determined by performing the Thermo "Smart" background subtraction and peaking fitting with a fixed 30% Lorentzian and Gaussian line shape in Thermo Advantage Processing software. The relative atomic composition at each point was calculated by applying Thermo sensitivity factors to adjust the peak areas.

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Chapter 3 A dimensionally stabilized phase: Nanoscale stabilization of FCC Pd_zCu_{1-z} across $z = 0 \rightarrow 1$

3.1 Introduction

One of the most exciting characteristics of alloy nanoparticles (aNPs) is that they possess properties that can be superior to those of pure component NPs and, in some cases, properties that are quite different from those of the alloy in its bulk phase. In particular, they can adopt phases that are different from those of the bulk alloy at the same composition. For instance, bimetallic alloys such as AgNi, AgPt and AuPt, with compositions that phase separate in the bulk can form solid solutions at the nanoscale regime.¹⁻⁴ Herein, we refer to these as dimensionally stabilized phases (DSPs), where the phases of multicomponent aNP materials, A_zB_{1-z}, are determined by both composition, z, and size, d. These dimensionally stabilized alloy phases can serve as the basis for design of materials with properties that could not be predicted or obtained from bulk alloys. The experimental approach to determining the phase behavior of materials across composition and size space, (z, d), can be time-consuming, requiring the preparation and characterization of a large set of samples with discrete size and composition. Herein, we demonstrate the use of Size and Composition Spread NanoParticle (SCSNaP) films as high-throughput materials libraries, coupled with a novel application of XPS-derived core level binding energy shifts, to identify a new DSP based on Cu_zPd_{1-z} alloys.

Comprehensive study of the properties of nanoscale alloy materials can be accelerated by use of high-throughput methods based on materials libraries that span both size and composition



Figure 3. 1. Left. Binary A_zB_{1-z} CSAF with a linear thickness gradient in the horizontal direction and a composition gradient along the vertical direction. Right. By annealing to induce dewetting of the CSAF from the substrate, aNPs are formed with a size distribution that is dictated by the original thickness gradient. This is a Size and Composition Spread NanoParticle (SCSNaP) film.

space. Composition spread alloy films (CSAFs) are material libraries based on thin alloy films that have lateral composition gradients allowing one to create all possible compositions of a binary alloy (A_zB_{1-z} , $z = 0 \rightarrow 1$) or ternary alloy ($A_zB_yC_{1-z-y}$, $z = 0 \rightarrow 1$ and $y = 0 \rightarrow 1-z$) in a single film. Over the past decade, CSAFs have been used frequently as libraries for high-throughput studies of alloy properties.⁵⁻⁷ In this work, we demonstrate the use of a variant on the CSAF which spans both alloy composition and film thickness, in order to study alloy nanomaterials. Figure 3.1 displays a graphical representation of a binary A_zB_{1-z} CSAF with a composition gradient along the vertical direction and a linear thickness gradient in the horizontal direction. If the film is not too thick, annealing this A_zB_{1-z} CSAF at high temperature can induce dewetting of the film to form aNPs. The result is a Size and Composition Spread NanoParticle (SCSNaP) library with aNPs whose size varies continuously along the horizontal while their composition varies continuously along the vertical.⁸⁻¹⁰

3.1.1 Pd_zCu_{1-z} bulk phase diagram

Pd membranes are used in a number of applications that require separation or purification of hydrogen.¹¹ Pd is alloyed with second components such as Cu and Ag to provide mechanism

stability and sulfur tolerance during operation.¹²⁻¹⁹ Both Pd and Cu have FCC bulk structures. However, at temperatures < 873 K, the Pd_zCu_{1-z} bulk phase diagram exhibits a B2 phase (ordered BCC lattice with Pd and Cu in a CsCl structure) across a broad composition range of 0.35 < z < 0.55.^{16, 20} This B2 phase impacts the performance of Pd_zCu_{1-z} alloy membranes used for hydrogen purification and in membrane reactors for hydrogenation catalysis. It has been determined that the bulk hydrogen permeance of Pd_zCu_{1-z} in this composition range is roughly an order of magnitude higher in the B2 phase than in the FCC phase.²¹ If the formation of the B2 phases were suppressed in ultrathin Pd_zCu_{1-z} alloy membranes, this advantage would be lost.²² It has also been shown that the rate of H₂ dissociation on the Pd_{0.47}Cu_{0.53} surface is much faster on the FCC phase than on the B2 phase.^{23, 24} If the FCC phase can be stabilized in Pd_zCu_{1-z} aNPs at T < 873 K, the performance of nanoparticulate Pd_zCu_{1-z} hydrogenation catalysts could be greatly improved over the activity of larger particles of the same composition.

An experimental methodology based on the use of Cu $2p_{3/2}$ core level binding energies as measured using x-ray photoemission spectroscopy (XPS) has been developed recently for determining the phase behavior of Pd_zCu_{1-z} aNPs.^{24, 25} This makes use of a high-throughput approach using spatially resolved XPS on a Pd_zCu_{1-z} CSAF to map the Cu $2p_{3/2}$ core level shifts (CLS) in binding energy relative to the $2p_{3/2}$ binding energy in pure Cu, $\Delta E_{CLS}^{Cu}(z) = E_{2p}^{Cu}(z) - E_{2p}^{Cu}(0)$. The CLS is sensitive to the alloy phase, exhibiting a discontinuous shift across the FCC-B2-FCC phase boundaries because these are order-disorder transitions.²⁴ DFT calculations showed that the Cu $2p_{3/2}$ binding energy is sensitive to the number of Cu atoms in the nearest neighbor shell of the Cu atom from which the electron is photoemitted. The CLS shifts discontinuously across the phase boundary because the FCC phase is a random solid solution in which Cu atoms can be nearest neighbors while Cu atoms in the ordered B2 phase have no Cu atoms in their nearest neighbor shell. Thus, the Cu $2p_{3/2}$ CLS can be used to distinguish between the ordered B2 phase and disordered FCC phase. One of the interesting advantages of using XPS for phase analysis is that it allows determination of the structure/phase in nanomaterials and in the near surface (1-2 nm) regions of bulk alloys.

The work described herein uses Cu $2p_{3/2}$ CLS measurements to study the phases present in ultra-thin (< 8 nm) Cu_zPd_{1-z} CSAFs before and after dewetting to form aNPs. In continuous films that are < 6 nm thick the B2 phase disappears. This is attributed to the fact that surface tension acts to densify the film and stabilizes the high density FCC phase. Once dewetted from the Mo substrate surface, the B2 phase reappears due to local thickening of the film.

3.2 Experimental methods

3.2.1 XPS mapping of composition and phase analysis

The Pd_zCu_{1-z} CSAF library was transferred to a ThetaProbe surface analysis system (ThermoFisher Scientific Inc.) for spatially resolved XPS measurements after heating to temperatures of 300, 600 and 700 K in a vacuum of ~10⁻⁹ Torr. Detailed procedure to collect and analyze the near surface composition of Pd_zCu_{1-z} CSAF can be found in Section 2.4.

3.2.2 Composition distribution model and thickness gradient of Pd_zCu_{1-z} CSAF

A Concentration Distribution Model (CDM) has been developed based on the deposition geometry of the RSM-CSAF deposition tool, and assuming that each alloy component is deposited

as a wedge in real space starting from zero along one line across the substrate and increasing linearly to a plateau value along a parallel line.²⁶ After determining the thicknesss distribution parameters of the Pd and Cu wedges (zero-line orientation, wedge width and maximum molar thickness of each component) by fitting to 169 XPS-measured compositions collected on a 1 mm² grid of points spanning a 12×12 mm² area, the composition and component thickness at all real space locations on the CSAF can be predicted using the CDM. The best-fit CDM was defined by the set of thickness distribution parameters for each component which minimized the difference between the CDM-predicted composition and XPS-measured composition for all 169 points measured on the surface of the Pd_zCu_{1-z} CSAF. The CDM then serves as the map for estimation of composition and component thickness at any point on the CSAF.

3.3 Results and discussion

3.3.1 Composition and thickness map for Pd_zCu_{1-z} CSAF

A combination of XPS and energy dispersive x-ray spectroscopy (EDX) measurements was used to determine the composition map, z(x, y), and thickness map, t(x, y), across the physical dimensions of the Pd_zCu_{1-z} CSAF. The Pd and Cu compositions (at%) were mapped at each point using the Pd 3 $d_{3/2}$ and Cu 2 $p_{3/2}$ XPS peaks (Figure 3.2a). Prior work has shown that XPS provides a good estimate of the bulk composition of Pd_zCu_{1-z} CSAFs.^{6,16} For each alloy component i = Pdor Cu, the molar areal concentrations, c_i , at the thickest portions of the wedges were determined using EDX to be $c_{Pd}^{max} = 446 \pm 3 \ \mu mol/m^2$ and $c_{Cu}^{max} = 545 \pm 3 \ \mu mol/m^2$. The physical thicknesses, t_i , at the thickest portions of the wedge were calculated to be $t_{Pd}^{max} = 3.95 \pm 0.03$ nm and $t_{Cu}^{max} = 3.87 \pm 0.02$ nm based on equation (1):



Figure 3. 2. Contour maps of Pd composition, z(x, y), across the Pd_zCu_{1-z} CSAF library. a) Measured directly using XPS analysis at the 169 points indicated by the black dots. b) Composition distribution model fit to the XPS data.

$$t_i = \frac{c_i \times M_i}{\rho_i} \tag{1}$$

where M_i and ρ_i are the molar masses and volumetric mass densities of each component, respectively. The maximum thicknesses, t_{Pd}^{max} and t_{Cu}^{max} , and the composition map, z(x, y), were then used to parameterize a concentration distribution model (CDM) which describes the physical distribution of each component across the CSAF as a wedge with a maximum thickness plateau at one edge and a linear decrease to a zero thickness at the other edge (Figure 3.3a & 3.3b).²⁶ This is consistent with the expected distribution based on the film deposition method and with EDXbased composition measurements made on thicker CSAFs.^{16, 26, 27} The map of Pd composition determined from the CDM is illustrated in Figure 3.2b. The difference between the CDM predicted



Figure 3. 3. 3D plots of a) Pd thickness and b) Cu thickness across the Pd_zCu_{1-z} CSAF. (c) Contours of Pd_zCu_{1-z} total thickness versus position across the CSAF library. Black dots represent the positions at which the local compositions were determined using XPS. Component thicknesses were derived from the CDM.

Pd compositions and those determined from XPS measurements ($\varepsilon_{Pd} = z_{Pd}^{CDM} - z_{Pd}^{XPS}$) is 1.1 ± 1.0 at.% where the uncertainty represents one standard deviation. The error arising from the surface segregation after annealing at 700 K is within 1.5 at.% of the bulk composition over the entire composition range of the Pd_zCu_{1-z}CSAF.¹⁶ The thickness maps for each alloy component can be determined from equation (1) using the concentrations predicted from the CDM as shown in Figure 3.3a and 3.3b. Figure 3.3c illustrates the map of total film thickness, t(x, y), spanning the range 1.3 to 7.8 nm.

3.3.2 Pd_zCu_{1-z} film dewetting from Mo substrate

After the composition and thickness of the Pd_zCu_{1-z} CSAF were characterized at room temperature, it was annealed at 600 K and 700 K for 30 mins. For CSAF that are ~100 nm thick, annealing at temperatures in this range is sufficient to achieve crystalline films that have phases identical to those of the bulk phase diagram.^{16, 24} This does not cause dewetting of Pd_zCu_{1-z} films with thickness ~100 nm. However, over-annealing of thinner films can result in dewetting from



Figure 3. 4. a) Mo $3d_{5/2}$ peak area measured as a function of CSAF thickness and b) backgroundsubtracted Mo $3d_{5/2}$ peak spectra at a film thickness of 2.5 nm at 300 K, and after annealing for 30 mins at 600 K, and 700 K. The discontinuous increases in Mo $3d_{5/2}$ peak area at 3.5 and 3.8 nm after heating to 600 and 700 K, are clear evidence of CSAF dewetting from the Mo substrate.

the substrate, driven by lowering of the total free energy of the surfaces and interfaces of the film and substrate.⁹ Dewetting of thinner films occurs at lower temperatures and shorter times than dewetting of thick films. These issues limit the temperatures at which the CSAFs can be used.

Herein, dewetting of Pd_zCu_{1-z} CSAFs is detected by the appearance of the substrate Mo $3d_{5/2}$ XPS signals after annealing. The evidence for Pd_zCu_{1-z} film dewetting from the Mo substrate is provided in Figure 3.4a, where the Mo $3d_{5/2}$ peak area is plotted as a function of initial film thickness as deposited at 300 K and after annealing at 600 K and 700 K for 30 mins. The Mo $3d_{5/2}$ XP spectra (binding energy = 227.9 eV) collected from a point with an initial film thickness of 2.5 nm are illustrated in Figure 3.4b. Figure 3.4a shows that no Mo $3d_{5/2}$ signal was observed at initial Pd_zCu_{1-z} CSAF thicknesses > 1.7 nm as deposited at 300 K. After annealing at 600 K for 30 min there is a discontinuous appearance of the Mo $3d_{5/2}$ signal at an initial CSAF thickness of 3.5 nm, followed by an increase in the signal with decreasing initial thickness. After annealing at 700 K


Figure 3. 5. SEM images (17.5 keV electron beam energy) of the topography of the Pd_zCu_{1-z} CSAF after annealing at 700 K for 30 min. (a) A dewetted region of the Pd_zCu_{1-z} CSAF with z = 0.45 and an initial thickness of 2.2 nm. (b) A region of continuous Pd_zCu_{1-z} film with z = 0.48 and an initial thickness of 5.2 nm.

for 30 min, the onset of Mo $3d_{5/2}$ signal occurs at an initial thickness of 3.8 nm and the Mo $3d_{5/2}$ signal at < 3.5 nm increases by ~20% over its intensity following the 600 K anneal. These data provide clear evidence of CSAF dewetting as a result of annealing, but only at low initial film thicknesses.

Further evidence of CSAF dewetting in regions with an initial thickness < 4 nm is revealed by the SEM images shown in Figure 3.5. These are from regions of the CSAF with similar compositions, Pd_{0.45}Cu_{0.55} and Pd_{0.48}Cu_{0.52}, but different initial thicknesses, 2.2 and 5.2 nm, after annealing at 700 K for 30 min. The micrograph of the 2.2 nm film in Figure 3.5a reveals contrast variation across the image whereas the image of the thicker film in Figure 3.5b reveals virtually no contrast. Coupled with the appearance of the Mo $3d_{5/2}$ XPS signal (Figure 3.4a), this indicates that heating to 700 K for 30 min has resulted in dewetting of the 2.2 nm thick CSAF and the formation of structures with length scale on the order of 10 nm separated by darker regions that presumably expose the Mo substrate. The image in Figure 3.5a is representative of those obtained from all regions of the CSAF with thickness < 4 nm after annealing at 700 K for 30 min. In contrast, the featureless micrograph of the 5.2 nm thick region in Figure 3.5b is representative of those from parts of the CSAF with initial thickness > 4 nm. The lack of contrast, coupled with the lack of Mo $3d_{5/2}$ XPS signal (Figure 3.4) indicates that heating to 700 K for 30 min has not resulted in dewetting of the CSAF with initial thicknesses > 4 nm.

3.3.3 Thickness-dependent phases of Pd_zCu_{1-z} thin films

Mapping the Cu $2p_{3/2}$ CLS across Pd_zCu_{1-z} CSAFs has been used to map compositiondependent phase behavior in thick Pd_zCu_{1-z} and CuAuPd alloys.^{24, 25} Across a ~100 nm thick Pd_zCu_{1-z} CSAF annealed at 700 K, the Cu $2p_{3/2}$ CLS relative to that of pure Cu, $\Delta E_{CLS}^{Cu}(z) = E_{2p}^{Cu}(z) - E_{2p}^{Cu}(0)$, decreases monotonically with increasing *z* while the alloy is in the FCC phase. However there is an additional discontinuous CLS over the composition range 0.35 < z < 0.55, in which the alloy adopts the B2 phase. Because XPS can detect signal from materials of < 1 nm thickness, the Cu $2p_{3/2}$ CLS is ideal for detecting the FCC-B2 phase transition in Pd_zCu_{1-z} aNPs and ultra-thin alloy films; alloy morphologies whose phases can be difficult to determined using other methods.

The key result of this work is that XPS has shown that Pd_zCu_{1-z} films in the thickness range 4-6 nm do not exhibit the B2 phase observed in thicker films and in the bulk. In other words, the FCC phase of Pd_zCu_{1-z} with 0.35 < z < 0.55 is dimensionally stabilized for thicknesses < 6 nm. Figure 3.6a shows the Cu $2p_{3/2}$ CLS versus *z* at film thickness < 4 nm, in the range 4-6 nm and > 6 nm after the Pd_zCu_{1-z} CSAF was annealed at 700 K. The additional CLS associated with the B2 phase is observed over the composition range 0.35 < z < 0.55 for film thickness > 6 nm.^{16, 24} When the film thickness falls in the range 4 – 6 nm, the Cu $2p_{3/2}$ binding energy decreases monotonically



Figure 3. 6. Left) Cu $2p_{3/2}$ binding energy measured versus Pd (at.%) after annealing the CSAF at 700 K for 30 min. Binding energies are grouped by film thickness: < 4 nm, 4 – 6 nm, and > 6 nm. Right) Illustration of the thickness dependent phase behavior implied for Pd_{0.40}Cu_{0.60}. Films that are < 4 nm have dewetted and the Cu $2p_{3/2}$ peak exhibits the discontinuous CLS with composition that is indicative of the B2 phase. In the range 4 – 6 nm the CLS is absent, indicative of the FCC phase at all compositions. At > 6 nm the CLS associated with the B2 phase is evident.

with increasing *z*, indicating the presence of only the FCC phase for Pd_zCu_{1-z} alloy films in this thickness range. Note that at these thicknesses the Pd_zCu_{1-z} CSAFs are continuous films and stable against dewetting. This thickness dependent phase behavior of the Pd_zCu_{1-z} CSAF is illustrated in Figure 3.6b. Because the FCC structure is more densely packed than the B2 structure, surface tension may cause the stabilization of the FCC phase relative to the B2 phase because of the increased surface-to-volume ratio for these thin films.

An additional feature of our XPS data is that it indicates that for film morphologies generated by dewetting, the B2 phase is restabilized for compositions in the range 0.35 < z < 0.55. Figure 3.6a reveals that the CLS associated with the B2 phase over the composition range 0.35 < z < 0.55 reappears at a film thickness < 4 nm, the thickness below which the Mo $3d_{5/2}$ XPS signal reveals that the Pd_zCu_{1-z} CSAF has dewetted from the Mo substrate. It is likely that dewetting allows the film to thicken locally to > 6 nm, at which the B2 phase is still stable (Figure 3.6b).

3.4 Conclusion

High-throughput synthesis and characterization methodologies were implemented to determine the phase behavior of Pd_zCu_{1-z} alloy films spanning both composition and thickness. This approach has served to demonstrate the value of the XPS CLS as a means to explore the dimensional dependence of alloy phase diagrams and to identify a dimensionally stabilized phase of Pd_zCu_{1-z}. Spatially resolved XPS mapping of the Cu 2p_{3/2} CLS has successfully differentiated the ordered B2 and random FCC phases found over various ranges of composition and film thickness. The Cu 2p_{3/2} CLS works to differentiate these phases because the FCC-B2-FCC phase transitions are order-disorder transitions that result in discontinuous changes in the number of Cu atoms in a Cu nearest neighbor shell. In particular, at a film thickness < 6 nm, the FCC phase is stabilized over the composition range, 0.35 < z < 0.55, where the ordered B2 phase exists in bulk. We also observed that $Pd_zCu_{1-z}CSAF$ dewets the Mo substrate at a thicknesses < 4 nm, resulting in a morphology with a local thickness > 6 nm and the reappearance of the B2 phase in the composition region 0.35 < z < 0.55. These results reveal an interplay between phase change (FCC-B2) and morphology change (dewetting) in response to reduction in Pd_zCu_{1-z} film thickness. They suggest that sufficiently small Pd_zCu_{1-z} alloy NPs would have an FCC structure over the composition range 0.35 < z < 0.55.

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Chapter 4 Electronic structure of Pd_xAg_{1-x} and Pd_xCu_yAu_{1-x-y} CSAF

4.1 Introduction

One of the most exciting characteristics for multicomponent alloy catalysts is that they can possess properties superior to their pure components.^{1, 2} In other words, their activity and selectivity can be tuned by either substituting its elemental components or adjusting its composition. These modifications lead to the changes of the alloy's electronic and geometric structure, both of which determine catalytic activity.^{3,4} However, few experimental studies has correlated catalytic activity of alloys with their electronic properties over a wide range of compositions. This is mainly due to the cost and time incurred by preparation and characterization of a large number of single composition samples using conventional methods. Conventional approaches study one alloy composition at a time, limiting the scope of a feasible study to a small number of discrete alloy compositions. Compared to conventional methodologies, high throughput techniques offers great advantages in studying multicomponent systems, allowing a systematic approach to preparation, characterization, and measurement of catalytic properties on different materials libraries.⁵⁻⁹ Using CSAFs as catalyst libraries, they enable characterization of the activity of all possible alloy compositions in one single experiment.¹⁰⁻¹² By using a multichannel micro-reactor developed by our group, the catalytic activity of a CSAF catalyst library for a given reaction can be measured at 100 different alloy compositions in parallel.¹³

To understand the relationships between alloy composition, electronic structure and catalytic activity, both experimental and computational approaches are required to measure and model the properties of alloys across the composition space. Based on the density functional theory (DFT), *d*-band electrons on transition metal surfaces extensively interact with adsorbed species.^{4,14-16} The density of states (DOS) of *d*-band can be modified by substituting with different

components or composition of alloy metals.^{4, 14} Furthermore, the average energy of the *d*-band (ε_d) relative to the Fermi level is a critical indicator to predict the reactivity of the alloy metal.^{4, 14, 17} It has been shown that stronger bonding between adsorbed species and the surface occurs when ε_d shifts towards the Fermi level.¹⁴ The *v*-band energies, as an experimental proxy for *d*-band energy, can be measured using X-ray photoelectron spectroscopy (XPS) and UV photoelectron spectroscopy (UPS).¹⁸

As described in Section 1.3, Pd is often alloyed with metals such as Au, Cu, and Ag to enhance its properties. The reaction mechanisms to separate H₂ from other gases by Pd alloy membranes consist of three major elementary steps. First, H₂ dissociatively adsorbs on the membrane surface, then H atoms diffuse through the membrane, finally H₂ recombinatively desorbs from the opposite side the membrane surface.^{19, 20} The diffusion of H atoms through the bulk materials is known to be the rate limiting step, which depends on $\frac{1}{2}$ order of H₂ pressure.²¹ However, the pressure dependence increases with decreasing the thickness of membrane materials.^{22, 23} It has been shown that rate of H₂ transport through thin Pd-based membrane with thicknesses < 500 nm has the 1st order dependence on H₂ pressure across a temperature range from 373 K to 523 K.²³ Therefore, the rate of H₂ transport through thin Pd-based membrane is also controlled by the adsorption and desorption steps at the membrane surface. Nevertheless, the kinetic processes of adsorption and desorption are not well understood on Pd-based alloy surfaces. Thus, the study of the H₂ - D₂ exchange (H₂ + D₂ \rightarrow 2HD) reaction can bring critical insight into the reaction mechanism at the Pd-based alloy membrane surface.

In this chapter, we demonstrate a high throughput approach to experimentally measure the filled states of the valence band (*v*-band) energy across Pd_xAg_{1-x} and Pd_xCu_yAu_{1-x-y}CSAFs, which can be used to benchmark *d*-band energy in the density functional theory (DFT) calculation. The

electronic structure was measured by XPS on both Pd_xAg_{1-x} and Pd_xCu_yAu_{1-x-y}CSAFs. The center of the *v*-band has been compared with experimental data from XPS and UPS on Pd_xCu_yAu_{1-x-y}CSAF.

The kinetic data of H_2 -D₂ exchange reaction have also been measured by other group members on $Pd_xAg_{1-x}CSAFs$. H₂-D₂ exchange reaction is a simple and ideal reaction for studying the mechanism that can be used to correlate the fundamental kinetic parameters with alloy composition and electronic structure. The most commonly described mechanisms for H_2 - D_2 exchange is a Langmuir-Hinshelwood mechanism in which the only two relevant rate constants are those for dissociative adsorption, k_{ads} , of H_2 , HD, and D_2 and for recombinative adsorption, k_{des} , of H and D atoms. Furthermore, the reaction barriers (dissociative adsorption and recombinative desorption) can be estimated. Recently, Savara et al. have experimentally observed a higher HD formation rate (or reaction order) than the value predicted by the Langmuir-Hinshelwood simulation under low temperature reaction conditions where the surface coverage is saturated.²⁴ Based on this observation, they developed a mechanism for the involvement of subsurface hydrogen species in the hydrogen surface adsorption and desorption processes.²⁴ Specifically, H_2 - D_2 exchange on the *Pd*-*Ag* surface is considered to undergo two reaction paths. One is the surface reaction path described in Langmuir-Hinshelwood model. The second path described as the breakthrough model, considers HD formation by recombination of one surface H atom and one subsurface H atom. However, after investigating Savara's model, we produce the same reaction order for H_2 - D_2 exchange reaction as classic Langmuir-Hinshelwood mechanism, which cannot explain the experimental observation. Thus, there is still a question what other mechanisms may involve on the transition metals to resolve this discrepancy.

4.2 Results and discussion

4.2.1 Characterization of Pd_xCu_yAu_{1-x-y}CSAF composition

The Pd_xCu_yAu_{1-x-y} near surface composition was mapped using XPS at 169 points on a 13 × 13 characterization grid with 1 mm spacing as described in Section 2.4. Figure 4.1 shows the contours of atomic fraction of ternary atomic fraction of Pd (Pd $3d_{3/2}$), Cu (Cu $2p_{3/2}$), and Au (Au $4f_{7/2}$) across the Pd_xCu_yAu_{1-x-y} CSAF in the real space. In the ternary composition diagram, the evenly distributed compositions almost span entire ternary alloy composition space, because the continuous composition gradients were generated through the CSAF deposition.



Figure 4. 1. Contour plots of the $Pd_xCu_yAu_{1-x-y}$ composition as measured by XPS (Cu $2p_{3/2}$, Pd $3d_{3/2}$ and Au $4f_{7/2}$) at 169 points indicated by black dots in the real space. The ternary composition of $Pd_xCu_yAu_{1-x-y}$ CSAF.

4.2.2 XPS-derived average energy characterization on Pd_xCu_yAu_{1-x-y}CSAF

In this study, XPS was used to map the v-band electronic structure at 169 points of the characterization grids on Pd_xCu_yAu_{1-x-y} CSAF. The background subtracted v-band spectra are plotted as functions of energy relative to the Fermi level (ε) as shown in Figure 4.2. To better understand the characteristic of v-band structures, we selected three XPS spectra for pure Pd, Cu,



and Au component as shown in Figure 4.3. Clearly, Pd has a broader *v*-band than Au or Cu, but more filled states are closer to the Fermi level. As the Pd at.% increases, the density of states shifts towards the Fermi level. However, as Cu and Au composition increase, the density of states shifts

to the Fermi level of 169 points on a Pd_xCu_vAu_{1-x-v} CSAF across the composition space.

away from the Fermi level. Interestingly, the density state of Au (blue peak) has a unique peak feature at \sim -8 eV. The intensity of this peak increases with Au atomic fraction.

The XPS-derived average energy of the filled v-band (ε_v) were calculated from the background subtracted v-band spectra obtained from ternary PdxCuyAu1-x-y CSAF based on Equation 2.

$$\varepsilon_{v} = \frac{\int N(\varepsilon)\varepsilon \,d\varepsilon}{\int N(\varepsilon) \,d\varepsilon} \qquad \qquad Equation 2$$

 ε : Energy of filled state in the valence band relative to the Fermi level. ε_v : Average energy of the valence band. N(ε): Density of filled states at the energy, ε . The density of filled states N(ε) is assumed to be proportional to the intensity of *v*-band spectrum. The features of measured spectra (e.g. peak locations or heights) were changed significantly over the energy range of -10 to 0, where 0 eV was chosen to be the Fermi level, by varying Pd_xCu_yAu_{1-x-y} alloy composition as shown in Figure 4.2. The integration was performed over this energy range of *v*-band spectra. The XPS-



derived average energy of the filled valence band relative to the Fermi level of a Pd_xCu_yAu_{1-x-y} alloy CSAF over ternary composition are illustrated in Figure 4.4 (a). The average energy of *v*-band shifts towards the Fermi level from -6 to -3 eV as the composition changes from the Au–Cu rich region to the Pd-Cu rich region.

4.2.3 Comparison of XPS-derived and UPS-derived average energy on PdxCuyAu1-x-y CSAF

The ultraviolet photoelectron spectroscopy (UPS) was also used to measure the *v*-band spectra by former group member and the detailed experimental method has been described elsewhere.¹⁸ The background subtraction method described by Li et al. was used to remove the low energy secondary electron contributions to the UP spectra.²⁵ UPS-derived average energy of



Figure 4. 4. (a) XPS-derived average energy of valence band relative to the Fermi level of 169 points on a $Pd_xCu_yAu_{1-x-y}$ CSAF across the ternary composition space. Black dots indicate each measured XPS composition at ternary composition space. (b) XPS-derived average energy of valence band was interpolated by the Thin Plate Spline algorithm from Origin software with 164 points where UPS was used to measure the v-band spectra on ternary composition space. (c) UPS-derived average energy of v-band relative to the Fermi level of 164 points on $Pd_xCu_yAu_{1-x-y}$ alloy CSAF across the ternary composition space. (d) A parity plot comparison of interpolated XPS & UPS-derived average energy of v-band.

the filled *v*-band were also calculated from the background subtracted *v*-band spectra obtained from ternary $Pd_xCu_yAu_{1-x-y}$ CSAF based on Equation 1. Figure 4.4 (c) shows the UPS-derived average energy of the filled valence band relative to the Fermi-Level of a $Pd_xCu_yAu_{1-x-y}$ alloy CSAF over ternary composition. The average energy of *v*-band shifts towards the Fermi level from -5 to -2 eV as the composition changes from the Au–Cu rich region to the Pd-Cu rich region. This result is consistent with the average energy calculated from XPS *v*-band spectra, but the most significant difference is that XPS-derived average energy is about 1.5 eV lower than those measured values from UPS. In Figure 4.4 (b), the 169 points of calculated average energy based on XPS measured *v*-band were interpolated using the Thin Plate Spline algorithm from Origin software to generate 164 data points in the ternary composition space, where *v*-band spectra were measured using UPS. A parity plot has shown the comparison of the XPS-derived and UPSderived average energy of *v*-band for all compositions of $Pd_xCu_yAu_{1-x-y}$ CSAF in Figure 4.4 (d). However, there is an offset can be clearly seen from Figure 4.5 that demonstrates the comparison



Figure 4. 5. XPS-derived (blue) and UPS-derived (red) average energy of the filled v-band relative to the Fermi level measured at Pd-Cu binary region on Pd_xCu_yAu_{1-x-y} CSAF versus Cu (at. %) compositions. DFT d-band (black square) and v-band (empty square) are also calculated as function of Cu (at. %) compositions.

between XPS-derived (blue circle) and UPS-derived (red circle) average energy of the filled v-band relative to the Fermi level measured at Pd-Cu binary region on $Pd_xCu_yAu_{1-x-y}CSAF$ as a function of Cu (at. %) compositions. Both measured *v*band centers are fairly flat at low Cu concentration (< 50 at. %), but they shifts linearly away from the Fermi level as the Cu at. % increases. The *d*-band centers were also calculated based on their electronic structures. DFT was also used to calculate the *d*band (black square) and *v*-band (empty square) centers across a wide range composition of Cu as shown in Figure 4.5. The DFT prediction matches well with our measurements from UPS-derived *v*-band centers. However, an offset of about 1.5 eV has been observed from XPS-derived *v*-band centers. This offset between the *v*-band center measured from XPS and those calculated from DFT can result from an incomplete background subtraction arisen from inelastic scattering of secondary electrons that originated at higher kinetic energies. Another reason that causes the differences of *v*-band centers can be due to the selection of the integration boundaries for binding energies. We can conclude that UPS-derived and XPS-derived *v*-band average energy mapping across a wide composition range agree well with DFT calculations, although an offset of XPS-derived data has been observed.

The average value for *d*-band for each pure metal component (Pd, Cu, and Au) was also reported. The energy of *d*-band center for Pd ranges from -2.64 to -2.02 eV, Cu ranges from -3.6 to -2.53 eV and Au ranges from -4.45 to -2.5 eV. $^{4, 15-17, 26-29}$ These existing data have shown a strong agreement with our UPS experimental results, but an offset relative to the XPS data. More importantly, this mapping of electronic structure can both benchmark *d*-band energy in the DFT calculation, and also correlate with the experimental results of reaction barriers for both adsorption and desorption of H₂ across the composition space of the ternary Pd_xCu_yAu_{1-x-y}CSAF.

4.2.4 Characterization of Pd_xAg_{1-x} composition

The composition of Pd and Ag in real space on the Pd_xAg_{1-x} CSAF was mapped by using the spatial resolved XPS. Figure 4.6 displays the contour of atomic fraction of Pd (Pd 3d3/2) across a 12×12 mm² area centered on the 14×14 mm² Pd_xAg_{1-x} CSAF. The contours are fit to



169 XPS composition measurements taken on a 13 \times 13 characterization grid, because the continuous composition gradients are present on the Pd_xAg_{1-x} CSAF, where 0 < x < 100.

4.2.5 XPS-derived average energy characterization of Pd_xAg_{1-x} CSAF

XPS was also used to map the *v*-band electronic structure at the same points of the characterization grids on Pd_xAg_{1-x} CSAF. The

XPS-derived average energy of the filled *v*-band (ε_v) were calculated from the background subtracted *v*-band spectra obtained from Pd_xAg_{1-x} CSAF based on Equation 2. Figure 4.7 (a) demonstrates the "Smart" background subtracted *v*-band spectra mapped at 169 discrete locations across the Pd_xAg_{1-x} CSAF. The density of filled states was mapped as a function of energy with respect to the Fermi level, which is located at zero on the energy scale, across different Pd_xAg_{1-x} compositions. It can be clearly seen that the density of states shifts towards the Fermi level as the Pd (at. %) composition increases. Figure 4.7 (b) shows that the average energy of Pd_xAg_{1-x} *v*-band is plotted as a function of Pd composition (at. %). As the Pd at. % increases, the average energy of Pd_xAg_{1-x} *v*-band shifts linearly towards the Fermi level, which is consistent with the observations from Figure 4.7 (a). The *d*-band centers for Pd and Ag were also reported based on



Figure 4. 7. (a) Background subtracted XP spectra of 169 different Pd_xAg_{1-x} composition across the entire composition space. (b) XPS-derived average energy of the filled v-band relative to the Fermi level of Pd_xAg_{1-x} CSAF versus Pd (at. %) compositions.

electronic structure calculations. The dband center for Pd ranges from -2.64 to -2.02 eV, and Ag ranges from -5.28 to -4.28 eV. 14, 15, 30, 31 These values are comparable to our measurements where $\varepsilon_v^{Pd} = -3.4 \ eV$ and $\varepsilon_v^{Ag} = -6.2 \ eV$, which ~1 eV offset for both Pd and Ag were observed. This offset between the v-band center measured from XPS and those from literature can result from an incomplete background subtraction arisen from inelastic secondary electrons that originated at higher kinetic energies. Another reason that causes the differences of *v*-band centers can be due the selection of the integration to boundaries for binding energies. Lastly, this offset can also be resulted from the fact that photoelectrons ejected from the

s- and *p*-bands will be counted for *v*-band measurements compared to the calculated *d*-band center. However, since our goal in measuring v-band center by XPS is to correlate with the experimental results of activation barriers for both adsorption and desorption of H_2 across the composition space of the ternary Pd_xCu_yAu_{1-x-y} CSAF, this offset between XPS-derived estimation of *v*-band energy and DFT calculated d-band center is not critical to the observation that *v*-band shifts linearly across composition space.

4.2.6 Derivation of H₂-D₂ exchange mechanism for breakthrough microkinetic model

The kinetic data of H₂-D₂ exchange reaction have been measured on Pd_xAg_{1-x} CSAFs, which has been conducted by other colleagues in the lab. H₂ conversions were collected at 100 channels over a temperature range from 300 to 593 K with 20 K increments and at 14 different inlet flow conditions with H₂ ranging from 0.9 to 9 mL/min and D₂ partial pressures ranging from 0.01 to 9 mL/min. Figure 4.8 display the experimental *HD* production rate on five different *Pd* compositions at 593 K as a function of H_2 or D_2 partial pressure with a) H_2 partial pressure (P_{H_2}) held constant at 30.39 kPa and a variable D_2 partial pressure (P_{D_2}), and b) D_2 partial pressure held constant at 0.03 kPa and a variable P_{H_2} . For Case 1, a positive dependence of the *HD* production rate was observed on the growing P_{D_2} from a very low partial pressure while P_{H_2} remaining constant at a relative high pressure. In contrast, for Case 2, a zero slope was detected on the growing P_{H_2} to a relative high partial pressure while P_{D_2} held constant at a very low partial pressure.

The mechanisms for $H_2 - D_2$ exchange is often described by the classic Langmuir-Hinshelwood model in which the only two relevant rate constants are those for dissociative adsorption, k_{ads} , of H_2 , HD, and D_2 and for recombinative adsorption, k_{des} , of H and D atoms. The reaction orders for previous described cases can be derived analytically using Langmuir-Hinshelwood model as shown in Appendix. For Case 1, the reaction order measured experimentally agrees with the value derived from model. However, for Case 2, as the total coverage of H and D becomes saturated, a negative dependence of HD rate is expected on P_{H_2} . In



other words, as P_{H_2} increases, surface coverage of D decreases because of competitive effect between H and D atoms. As a result, Langmuir Hinshelwood model predicts the reaction order to be -1, where our observation of zero reaction order from experimental results cannot be explained.

Recently, instead of only considering the surface species in the reaction model, Savara, et al. have developed a mechanism for the involvement of subsurface hydrogen species in the hydrogen surface adsorption and desorption processes.²⁴ H_2 - D_2 exchange on the Pd - Ag surface is considered to undergo two reaction paths. One is the surface reaction path described in Langmuir-Hinshelwood model. The second path described as the breakthrough model, considers HD formation by recombination of one surface H atom and one subsurface H

atom. However, we have investigated and proved Savara's model should produce the same reaction order for H_2 - D_2 exchange reaction as the classic Langmuir-Hinshelwood mechanism. The proof can be found in the Appendix. Based on our previous experimental observations, the

Langmuir-Hinshelwood mechanism does not properly explain the reaction mechanism when the surface coverage of H/D is saturated at low temperature. However, there is still ongoing debate on the possibility of involving with other mechanisms on the transition metals (e.g. subsurface hydrogen reaction and hydrogen diffusion to bulk) which may be described this discrepancy.

4.2.7 Correlation of reaction barriers and election structure across Pd_xAg_{1-x} composition space

Based on the previous discussion, we can concluded that the Langmuir-Hinshelwood model didn't predict the correct reaction order under high surface coverages. However, when the $H_2 - D_2$ exchange reaction takes place at high temperature, the surface coverages become low and model matches the experimental results.^{18,35} The kinetic data collected at which the surface coverage of H and D species is close to zero, were used to fit the



reaction barriers (dissociative adsorption and recombinative desorption) across the composition space based on the Langmuir-Hinshelwood mechanism.⁴⁰ The correlation of XPS-derived *v*-band average energy (ε_v) and reaction barriers ($\Delta E_{ads}^{\ddagger}$ and $\Delta E_{des}^{\ddagger}$) as shown in Figure 4.9. We observed that both reaction barriers decrease linearly as ε_v moves toward the Fermi level. More importantly, we are the first to correlate the electronic structure (*v*-band) with these fundamental kinetic parameters ($\Delta E_{ads}^{\ddagger}$ and $\Delta E_{des}^{\ddagger}$) for the H₂-D₂ exchange reaction over Ag_xPd_{*l*-x} alloys.

4.3 Conclusions

In this chapter, we have prepared Pd_xAg_{1-x} and $Pd_xCu_yAu_{1-x-y}CSAFs$ using rotating shadow mask deposition tools. A high throughput approach was used to characterize compositions and the filled states of the valence band (v-band) energy across Pd_xAg_{1-x} and $Pd_xCu_yAu_{1-x-y}CSAFs$. The electronic structure was measured by XPS on both Pd_xAg_{1-x} and Pd_xCu_yAu_{1-x-y}CSAFs. The catalytic reactivity of H₂-D₂ exchange reaction has been measured on both Pd_xCu_yAu_{1-x-y} and Pd_xAg_{1-x} CSAFs using the multichannel microreactor system by other group members. The relationship of composition - electronic structure - catalytic activity has been investigated through these high throughput techniques on both Pd_xCu_yAu_{1-x-y} and Pd_xAg_{1-x} CSAFs. For Pd_xCu_yAu_{1-x-y} CSAF, the center of the v-band has been compared with experimental data from both XPS and UPS. The results have shown a good agreement with DFT calculations. For Pd_xAg_{1-x} CSAF, a zero reaction order of H₂-D₂ exchange reaction has been observed from experiments while P_{D_2} held constant at a very low partial pressure by varying P_{H_2} at a relative high partial pressure. This observation agrees with Savara's experimental results at the high surface coverage. However, we have shown that the mechanism involved surface and subsurface hydrogen in H₂-D₂ exchange reaction produce the same reaction order as the classic Langmuir Hinshelwood model, which could not explain the experimental observation. Other mechanisms may also contribute to this experimental observation. More importantly, we have successfully correlate the electronic structure of Pd_xAg_{1-x} alloy with both adsorption and desorption barriers from low surface coverage kinetic data of the H₂-D₂ exchange reaction, which shows a linear relationship.

Reference:

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Appendix:

The H_2 - D_2 exchange on Pd-Ag surface is considered to undergo two reaction paths. One is the surface reaction path described in Langmuir Hinshelwood model:

$$H_2 + 2 * \leftrightarrow 2H *$$
$$D_2 + 2 * \leftrightarrow 2D *$$
$$H * + D * \leftrightarrow HD + 2 *$$

where * denotes empty surface site, and H * and D * represent surface species of H and D respectively.

The second one is the subsurface reaction path described as breakthrough model, which considers *HD* can also be produced via recombination of one surface and one subsurface species:

 $H_2 + * + *' \leftrightarrow H * + H * '$ $D_2 + * + *' \leftrightarrow D * + D * '$ $H * + D *' \leftrightarrow HD + * + * '$ $D * + H *' \leftrightarrow HD + * + * '$

where the superscript ' indicates the corresponding species is subsurface species.

Based on the two reaction paths above, the steady state time dependence of the surface and subsurface species (H *, D *, H * ', D * ') can be obtained,

$$\begin{aligned} \frac{d\theta_H}{dt} &= 0 = 2k_a P_{H_2}(1-\theta)^2 - 2k_d \theta_H^2 + k_a P_{HD}(1-\theta)^2 - 2k_d \theta_H \theta_D + k'_a P_{H_2}(1-\theta)(1-\theta') \\ &- k'_d \theta_H \theta'_H + \frac{1}{2}k'_a P_{HD}(1-\theta)(1-\theta') - k'_d \theta_H \theta'_D \quad (Eqn. 1) \\ \\ \frac{d\theta_H'}{dt} &= 0 = k_a' P_{H_2}(1-\theta)(1-\theta') - k'_d \theta_H \theta'_H + \frac{1}{2}k'_a P_{HD}(1-\theta)(1-\theta') \\ &- k'_d \theta_H' \theta_D \quad (Eqn. 2) \end{aligned}$$

$$\begin{aligned} \frac{d\theta_D}{dt} &= 0 = 2k_a P_{D_2}(1-\theta)^2 - 2k_d \theta_D^2 + k_a P_{HD}(1-\theta)^2 - 2k_d \theta_H \theta_D + k'_a P_{D_2}(1-\theta)(1-\theta') \\ &- k'_d \theta_D \theta'_D + \frac{1}{2}k'_a P_{HD}(1-\theta)(1-\theta') - k'_d \theta_H' \theta_D \quad (Eqn. 3) \end{aligned}$$

$$\begin{aligned} \frac{d\theta_D'}{dt} &= 0 = k_a' P_{D_2}(1-\theta)(1-\theta') - k'_d \theta_D \theta'_D + \frac{1}{2}k'_a P_{HD}(1-\theta)(1-\theta') \end{aligned}$$

$$-k'_d \theta_H \theta'_D$$
 (Eqn. 4)

where θ_i is the coverage of species i, P_i is the partial pressure of gas i, θ and θ' are the total surface and subsurface coverage respectively, C_H and C_D are the bulk concentration of H and D respectively, where

$$\theta = \theta_H + \theta_D$$
 (Eqn. 5)
 $\theta' = \theta'_H + \theta'_D$ (Eqn. 6)

 k_a and k_d are rate constants for surface adsorption and desorption respectively, k_a' and k_d' are rate constants for breakthrough adsorption and desorption respectively.

We define x as the fraction of hydrogen in the inlet H_2 - D_2 mixture flux.

$$P_{H_2}^{in} = x P_H^{tot} = P_{H_2} + \frac{1}{2} P_{HD}$$
$$P_{D_2}^{in} = (1 - x) P_H^{tot} = P_{D_2} + \frac{1}{2} P_{HD}$$
$$P_H^{tot} = P_{H_2}^{in} + P_{D_2}^{in} = P_{H_2} + P_{D_2} + P_{HD}$$

where P_H^{tot} is the pressure of all hydrogen isotopes molecules.

Eqn.1 - Eqn.2, we have

$$2k_a P_{H_2}(1-\theta)^2 + k_a P_{HD}(1-\theta)^2 = 2k_d \theta_H(\theta_H + \theta_D)$$
 (Eqn. 1.1)

Substitute Eqn.5 into Eqn.1.1, we have

$$k_a P_{H_2}^{in} (1-\theta)^2 = k_d \theta_H \theta \quad \text{(Eqn. 1.2)}$$

Eqn.3 - Eqn.4, we have

$$2k_a P_{H_2}(1-\theta)^2 + k_a P_{HD}(1-\theta)^2 = 2k_d \theta_H(\theta_H + \theta_D)$$
 (Eqn. 3.1)

Substitute Eqn.5 into Eqn.3.1, we have

$$k_a P_{D_2}^{in} (1-\theta)^2 = k_d \theta_D \theta \quad \text{(Eqn. 3.2)}$$

Eqn.1.2 + Eqn.3.2, we have

$$k_a (P_{H_2}^{in} + P_{D_2}^{in})(1 - \theta)^2 = k_d (\theta_H + \theta_D)\theta$$
 (Eqn. 1.3)

Therefore,

$$\theta = \frac{\sqrt{KP_H^{tot}}}{1 + \sqrt{KP_H^{tot}}}$$

where $K = k_a/k_d$.

Substitute Eqn.5 into Eqn.2, we have

$$k'_a P_{H_2}^{in}(1-\theta)(1-\theta') = k'_d \theta'_H \theta \quad \text{(Eqn. 2.1)}$$

Substitute Eqn.5 into Eqn.4, we have

$$k'_{a}P^{in}_{D_{2}}(1-\theta)(1-\theta') = k'_{d}\theta'_{D}\theta$$
 (Eqn. 4.1)

Eqn.2.1 + Eqn.4.1, we have

$$k'_{a} (P^{in}_{H_{2}} + P^{in}_{D_{2}})(1 - \theta)(1 - \theta') = k'_{a} (\theta'_{H} + \theta'_{D})\theta$$
 (Eqn. 2.2)

Substitute Eqn.6 into Eqn.2.2, we have

$$K'P_{H}^{tot}(1-\theta)(1-\theta') = \theta'\theta \text{ (Eqn. 2.3)}$$

where $K' = k_a'/k_d'$.

Substitute θ into Eqn.2.3, we have

$$\theta' = \frac{K' P_H^{tot}}{K' P_H^{tot} + \sqrt{K P_H^{tot}}}$$

Summary:

$$\theta = \frac{\sqrt{KP_H^{tot}}}{1 + \sqrt{KP_H^{tot}}} \quad (\text{Eqn. 1.4})$$

$$\theta' = \frac{K' P_H^{tot}}{K' P_H^{tot} + \sqrt{K P_H^{tot}}}$$
(Eqn. 2.3)

$$\theta_D = KP_{D_2}^{in} \frac{(1-\theta)^2}{\theta} \quad (\text{Eqn. 3.2})$$

$$\theta'_D = K' P_{D_2}^{in} \frac{(1-\theta)(1-\theta')}{\theta} \quad (\text{Eqn. 4.1})$$

$$\theta = \theta_H + \theta_D$$
 (Eqn. 5)

$$\theta' = \theta'_H + \theta'_D$$
 (Eqn. 6)

Therefore, we have

$$\theta_{D} = \frac{KP_{D_{2}}^{in}}{\sqrt{KP_{H}^{tot}(1 + \sqrt{KP_{H}^{tot}})}} \text{ (Eqn. 3.3)}$$
$$\theta_{D}' = \frac{K'P_{D_{2}}^{in}}{K'P_{H}^{tot} + \sqrt{KP_{H}^{tot}}} \text{ (Eqn. 4.2)}$$
$$\theta_{H} = \frac{KP_{H_{2}}^{in}}{\sqrt{KP_{H}^{tot}(1 + \sqrt{KP_{H}^{tot}})}} \text{ (Eqn. 5.1)}$$
$$\theta_{H}' = \frac{K'P_{H_{2}}^{in}}{K'P_{H}^{tot} + \sqrt{KP_{H}^{tot}}} \text{ (Eqn. 6.1)}$$

Now, we can derive an analytical expression for the production rate of *HD*.

$$\begin{aligned} r_{HD} &= 2k_{d}\theta_{H}\theta_{D} - k_{a}P_{HD}(1-\theta)^{2} + \left[k_{d}'\theta_{H}\theta_{D}' - \frac{1}{2}k_{a}'P_{HD}(1-\theta)(1-\theta')\right] \\ &+ \left[k_{d}'\theta_{D}\theta_{H}' - \frac{1}{2}k_{a}'P_{HD}(1-\theta)(1-\theta')\right] \end{aligned}$$

$$r_{HD} = 2k_d\theta_H\theta_D + k'_d(\theta_H\theta'_D + \theta_D\theta'_H) - \frac{F_{HD}P^{tot}}{F^{tot}}[k_a(1-\theta)^2 + k'_a(1-\theta)(1-\theta')]$$

where F_i is the molar flow rate of species I, and P^{tot} is the total pressure of the inlet gas flux

$$P^{tot} = P_H^{tot} + P^{buffer}$$

where P^{buffer} is the partial pressure of the inert gas in the gas flux.

Then, the outlet flow rate of HD can be calculated by solving the following integral

$$\mathbf{A} = \int_{0}^{F_{HD}^{out}} \frac{dF_{HD}}{r_{HD}}$$

Define

$$\alpha = 2k_d\theta_H\theta_D + k'_d(\theta_H\theta'_D + \theta_D\theta'_H)$$

$$\beta = \frac{P^{tot}}{F^{tot}} [k_a (1-\theta)^2 + k_a' (1-\theta)(1-\theta')]$$

Then,

$$F_{HD}^{out} = \frac{\alpha}{\beta} [1 - \exp(-\beta A)]$$

Therefore,

$$P_{HD}^{out} = \frac{2k_d \theta_H \theta_D + k'_d (\theta_H \theta'_D + \theta_D \theta'_H)}{k_a (1 - \theta)^2 + k'_a (1 - \theta)(1 - \theta')} [1 - \exp(-\frac{P^{tot}A}{F^{tot}} (k_a (1 - \theta)^2 + k'_a (1 - \theta)(1 - \theta')))]$$

Kinetic measurements must be made at low conversion,

$$-\frac{P^{tot}A}{F^{tot}}(k_a(1-\theta)^2+k_a'(1-\theta)(1-\theta'))\ll 1$$

and thus

$$P_{HD}^{out} = \frac{2k_d\theta_H\theta_D + k_d'(\theta_H\theta_D' + \theta_D\theta_H')}{k_a(1-\theta)^2 + k_a'(1-\theta)(1-\theta')} \frac{P^{tot}A}{F^{tot}} [k_a(1-\theta)^2 + k_a'(1-\theta)(1-\theta')]$$

$$P_{HD}^{out} = \left[2k_d\theta_H\theta_D + k_d'(\theta_H\theta_D' + \theta_D\theta_H')\right] \frac{P^{tot}A}{F^{tot}}$$

$$P_{HD}^{out} = \left[\frac{2k_d K^2 P_{H_2}^{in} P_{D_2}^{in}}{KP_H^{tot} (1 + \sqrt{KP_H^{tot}})^2} + \frac{2k_d' K' K P_{H_2}^{in} P_{D_2}^{in}}{\sqrt{KP_H^{tot}} (1 + \sqrt{KP_H^{tot}}) (K' P_H^{tot} + \sqrt{KP_H^{tot}})}\right] \frac{P^{tot} A}{F^{tot}}$$

$$P_{HD}^{out} = \frac{2KP_{H_2}^{in}P_{D_2}^{in}}{(KP_{H}^{tot} + \sqrt{KP_{H}^{tot}})} \left[\frac{k_d K}{(KP_{H}^{tot} + \sqrt{KP_{H}^{tot}})} + \frac{k_d' K'}{(K'P_{H}^{tot} + \sqrt{KP_{H}^{tot}})}\right] \frac{P^{tot}A}{F^{tot}}$$

Case1: Langmuir-Hinshelwood model, where K' = 0

$$P_{HD}^{out} = \frac{2k_d K^2 P_{H_2}^{in} P_{D_2}^{in}}{K P_H^{tot} (1 + \sqrt{K P_H^{tot}})^2} \frac{P^{tot} A}{F^{tot}}$$

When temperature is high, θ is low so that $\sqrt{KP_H^{tot}} \ll 1$

$$P_{HD}^{out} \propto \frac{P_{H_2}^{in} P_{D_2}^{in}}{P_H^{tot}}$$

For $P_{H_2}^{in} = \alpha P_{D_2}^{in} \approx \alpha P_H^{tot}$, varying P_H^{tot} , we have n = 1For $P_{H_2}^{in} \approx P_H^{tot}$, varying $P_{D_2}^{in}$, we have n = 1

For $P_{H_2}^{in} \approx P_H^{tot}$, varying $P_{H_2}^{in}$, we have n = 0

When temperature is low, θ is high so that $\sqrt{KP_H^{tot}} \gg 1$

$$P_{HD}^{out} \propto \frac{P_{H_2}^{in} P_{D_2}^{in}}{P_{H}^{tot^2}}$$

n is the reaction order

For $P_{H_2}^{in} = \alpha P_{D_2}^{in} \approx \alpha P_H^{tot}$, varying P_H^{tot} , we have n = 0

For $P_{H_2}^{in} \approx P_H^{tot}$, varying $P_{D_2}^{in}$, we have n = 1

For $P_{H_2}^{in} \approx P_H^{tot}$, varying $P_{H_2}^{in}$, we have n = -1

Case2: Breakthrough model,

$$P_{HD}^{out} = \frac{2k_d'K'KP_{H_2}^{in}P_{D_2}^{in}}{KP_H^{tot}(1+\sqrt{KP_H^{tot}})(1+\frac{K'}{\sqrt{K}}\sqrt{P_H^{tot}})}\frac{P^{tot}A}{F^{tot}}$$

When temperature is high, θ is low so that $\frac{\kappa'}{\sqrt{\kappa}}\sqrt{P_H^{tot}} \ll 1$

$$P_{HD}^{out} \propto rac{P_{H_2}^{in} P_{D_2}^{in}}{P_{H}^{tot}}$$

For $P_{H_2}^{in} = \alpha P_{D_2}^{in} \approx \alpha P_H^{tot}$, varying P_H^{tot} , we have n = 1

For $P_{H_2}^{in} \approx P_H^{tot}$, varying $P_{D_2}^{in}$, we have n = 1

For $P_{H_2}^{in} \approx P_H^{tot}$, varying $P_{H_2}^{in}$, we have n = 0

When temperature is low, θ is high so that $\frac{K'}{\sqrt{K}}\sqrt{P_H^{tot}} \gg 1$

$$P_{HD}^{out} \propto \frac{P_{H_2}^{in} P_{D_2}^{in}}{P_H^{tot^2}}$$

For
$$P_{H_2}^{in} = \alpha P_{D_2}^{in} \approx \alpha P_H^{tot}$$
, varying P_H^{tot} , we have $n = 0$

For $P_{H_2}^{in} \approx P_H^{tot}$, varying $P_{D_2}^{in}$, we have n = 1

For $P_{H_2}^{in} \approx P_H^{tot}$, varying $P_{H_2}^{in}$, we have n = -1

Chapter 5 Thermal interface conductance across metal alloy-dielectric interfaces

5.1 Introduction

As the length scales of electronic devices decrease and become comparable to energy carrier mean free paths, thermal conduction through electronic devices is controlled by the thermal interface conductance (*G*) across material interfaces. Metal-dielectric interfaces are a ubiquitous feature of electronic and optoelectronic applications. Presently, *G* across (pure metal)-(pure dielectric) interfaces has been extensively measured^{1,2,3,4,5,6} and modeled^{7,8,9,10}, but the effect of metal alloy composition on *G* across metal-dielectric interfaces are lack of understanding.

Metal alloy composition plays important role on *G* across a metal-dielectric interface because metal alloys may provide multifunctional and cost effective solutions to optimize thermal and non-thermal properties of metal-dielectric interfaces. For example, heat-assisted magnetic recording (HAMR) is a promising next generation data storage technology.¹¹ A Au near field transducer (NFT) is used to generate plasmons along the Au-dielectric interface that locally heat regions of the magnetic media.^{12,13} However, generated heat must be dissipated across the interface and into the surrounding dielectric.¹² Low G across the Au-dielectric interface is a major source of thermal resistance within the device and amplifies the temperature rise in the Au NFT leading to structural and thermal instability.¹² In this and other plasmonic applications the thermal properties and the plasmonic/optical properties of the metal-dielectric interface must be balanced to optimize performance. (Metal alloy)-dielectric interfaces may be ideal for such multifunctional demands. A secondary reason for studying *G* across (metal alloy)-dielectric interfaces is that interdiffusion across metal-metal interfaces may create unintentional (metal alloy)-dielectric interfaces in devices, e.g. in the case of a miscible adhesion layer. The thermal transport mechanisms that govern the relationship between G and alloy concentration are unknown, in contrast to the relationship between thermal conductivity and alloy concentration. Thermal conductivity vs. alloy concentration exhibits a characteristic "U-shape" because long energy carrier mean free paths are suppressed even at dilute concentrations due to impurity scattering. On the other hand, G across metal-dielectric interfaces is not controlled by mean free paths, but rather phonon transmission at the interface. Intriguing measurements of Gacross (pure metal)-(dielectric alloy) interfaces have exhibited non-monotonic behavior with alloy composition that is not well understood.¹⁴ Therefore, a systematic study of G across (metal alloy)dielectric interfaces is both technologically relevant and scientifically interesting.

Here, we report measurements of *G* across (Au_xCu_{1-x})-sapphire and (Au_xPd_{1-x})-sapphire interfaces as a function of Au atomic fraction (*x*). Compositionally graded metal alloy films were deposited on sapphire substrates to enable high throughput measurements of *G* over a wide range of Au atomic fractions with a single binary alloy sample. A Diffuse Mismatch Model (DMM)based prediction of *G* as a function of Au atomic fraction is presented by Freedman from Malen's group, which has shown a favorable agreement with the experimental measurements.

5.2 Experimental procedure

5.2.1 Frequency domain thermoreflectance (FDTR) measurements

To measure *G* across the metal alloys and the sapphire substrate, as a function of metal alloy composition, the samples were attached to a micromanipulator for submicron precision control of sample position. Frequency domain thermoreflectance $(FDTR)^{15,16,17}$ was used to measure *G* at various positions on the 12 mm by 12 mm compositionally mapped region of the

samples. FDTR is a non-contact optical pump-probe technique used to measure thermal transport. An electro-optic modulator intensity modulates a 488 nm wavelength continuous wave (cw) pump laser beam, which is focused onto the sample inducing a periodic heat flux at the surface. A coaligned cw 532 nm wavelength probe laser beam measures the change in temperature at the sample surface induced by the pump laser, which depends on *G* across the (metal alloy)-sapphire interface. The phase-lag between the pump and probe beams after they reflect from the sample surface is measured as a function of the pump beam's frequency (100 kHz to 5 MHz) using a lock-in amplifier. The phase-lag between the reflected pump and probe beams represents the phase difference between the temperature rise and heat flux at the sample surface. *G* is determined by fitting the measured phase-lag data to the heat diffusion equation in a layered medium, where the only unknown parameter is *G* for the interface between the metal alloy and sapphire.¹⁸ After a measurement of *G* was made via FDTR at a given position on the sample, the micromanipulator was used to translate the sample 480 μ m (Au_xCu_{1-x} sample) / 500 μ m (Au_xPd_{1-x} sample) vertically so that the co-aligned pump and probe lasers could measure *G* at different alloy compositions.
5.3 Results and discussion

5.3.1 EDX composition and thickness measurements

Figures 5.1(a) and 5.1(b) show the Cu and Pd composition in atomic fraction while Figures 5.1(c) and 5.1(d) show the CSAF thickness as a function of position on the sapphire substrate for the (a,c) Au_xCu_{1-x} and (b,d) Au_xPd_{1-x} films. The black dots in Figure 5.1 indicate the EDX measurement positions and the blue crosses represent the measured positions of *G* on the



Figure 5. 1 (a) Cu and (b) Pd atomic fraction of the Au_xCu_{1-x} and Au_xPd_{1-x} CSAFs as a function of the z and y coordinates on the sapphire substrate surface. (c) Au_xCu_{1-x} and (d) Au_xPd_{1-x} film thickness as a function of the z and y coordinates on the sapphire substrate surface. The black dots indicate EDX measurement positions and the blue crosses designate the measured positions of G on the samples.

samples. The uncertainties in the reported composition and thickness as a function of sample position are $\pm 2\%$ of the nominal values.

5.3.2 FDTR measurements of G

The measured G as a function of Au atomic fraction for Au_xCu_{1-x} -sapphire and Au_xPd_{1-x} sapphire interfaces at a temperature of 300 K are shown in Figure 5.2. Both interfaces exhibit monotonically decreasing G as a function of increasing Au atomic fraction in the metal alloys. On the left side of Figure 5.2, where nearly (pure Pd)-sapphire and (pure Cu)-sapphire interfaces were measured, the Cu-sapphire interface $(197 \pm 39 \text{ MW/m}^2\text{-K})$ exhibits a greater G than that of the Pdsapphire interface (167 \pm 35 MW/m²-K), though uncertainty weakens this distinction. The G across the Au_xCu_{1-x}-sapphire was measured to be 74 ± 11 MW/m²-K at $x = 0.95 \pm 0.02$ and the G across the Au_xPd_{1-x}-sapphire interface was measured to be 60 ± 10 MW/m²-K at $x = 0.97 \pm 0.02$, matching previous measurements of a Au-sapphire interface.² The inset in Figure 5.2 shows FDTR phase-lag data as a function of heating frequency for three Au atomic fractions in the Au_xPd_{1-x}sapphire sample and fits to the heat diffusion equation used to extract G^{18} . The distinct phase values for otherwise identical samples enable clear resolution of G across all Au fractions. The uncertainty in measured G presented in Figure 5.2 is due to the uncertainty of the (i) laser beam spot size (\pm 5%), (ii) sapphire thermal conductivity (\pm 2 Wm⁻¹ K⁻¹), (iii) thickness of the metal alloy layer (\pm 5%), (iv) heat capacity of the metal alloy layer (\pm 5%) and (v) metal alloy thermal conductivity (uncertainty ranges from the bulk value to 50% of the bulk value. To determine the size of the error bars, the FDTR-measured phase-lag vs. heating frequency data was fit to the heat diffusion equation to extract the deviations in G, where (i) through (v) were independently varied within their respective uncertainty ranges.¹⁶ The total uncertainty results from the square root of the sum of the squares of these independent deviations in G.



Figure 5. 2. Measured values of G and Diffuse Mismatch Model-based predictions across Au_xCu_{1-x} -sapphire and Au_xPd_{1-x} -sapphire interfaces as a function of Au atomic fraction, x. The inset at the top right shows FDTR phase-lag vs. heating frequency data with fits to the heat diffusion equation used to extract G for three Au atomic fractions in the Au_xPd_{1-x} -sapphire sample.

5.4 Conclusion

This chapter presents the first measurements of the influence of solid solution metal alloy composition on *G* across a metal-dielectric interface. Au_xCu_{1-x} and Au_xPd_{1-x} CSAFs were deposited on sapphire substrates allowing for high throughput measurements of *G* as a function of metal alloy composition via FDTR. For multifunctional interfaces where metal alloy composition offers unique control for optimization of thermal and nonthermal properties. This work also opens

new avenues for addressing exciting questions with regards to (metal alloy)-dielectric interfaces. For example, how do more complex binary and ternary alloys affect G? Can greater conductance than either (pure metal)-dielectric interfaces be achieved by control of alloy composition? Further examination of (metal alloy)-dielectric interfaces will provide superior understanding and control of G that is extremely valuable to nascent electronic and optoelectronic applications.

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Chapter 6 Understanding the effect of adhesion layer diffusion on thermal conductance at metal-dielectric interfaces

6.1 Introduction

Device overheating is one of the most catastrophic failure modes of electronic devices. As increasingly complex device architectures are being developed, sufficient heat dissipation through the system becomes increasingly challenging. For example, in the field of 3D integration, device stacking leads to a high density of material interfaces, each of which can contribute a significant resistance to heat transfer.¹

Among the three classes of solid materials (metals, semiconductors, and dielectrics) utilized in electronics, one of the largest thermal impedances occurs at the metalsemiconductor/dielectric interface, when the system length scale approaches the associated Kapitza length.²⁻⁶ The two types of fundamental heat carriers in solids are electrons and phonons. In semiconductors and dielectrics the free electron density is orders of magnitude lower than in metals, resulting in thermal transport across the metal- semiconductor /dielectric interface being primarily a function of phonon transmission.^{7, 8}

In order to enhance the thermal interface conductance at metal-dielectric interfaces, Jeong, *et al.* showed that thermal interface conductance (*G*) between a metal and dielectric can be significantly enhanced through the addition of select metal adhesion layers that have a higher phonon density of states overlap with the dielectric, than does the overlayer metal.⁹⁻¹² More specifically, Jeong *et al.* showed that adding as little as 1.5 nm of Cu between Au and Al₂O₃ roughly doubles the value of *G* with respect to that for Au-Al₂O₃.⁹

The enhancement of G for bilayer-dielectric interfaces can only be realized if there is no interdiffusion between the two metal films forming the bilayer. Under realistic operating

conditions, devices generate Joule heat that can result in interdiffusion between the adhesion layer and overlayer metal. This interdiffusion lowers the electrical conductivity (σ) of the metal layers causing more Joule heating, which increases the rate of interdiffusion, in a "thermal runaway" positive feedback effect.¹³⁻¹⁸ Comparatively, little is known about how interdiffusion between the metal adhesion layer and the metal overlayer affects *G*, despite its importance to mitigating thermal runaway and extending device lifetimes.

This research seeks to understand the relationship between interdiffusion in bilayer metal films and phonon transmission from the metal film into to dielectric substrates. Our experiments focus on the technologically relevant Au-Cu adhesion layer system. Au-Cu are completely miscible in their bulk phase diagram, ^{19, 20} serving as an ideal binary system for the study of interdiffusion between metal adhesion layers and metal films on dielectric substrates.

We report x-ray photoelectron spectroscopy (XPS) depth profiles and measurements of *G* for Au-Cu thin films of different Cu thicknesses that have been annealed at temperatures in the range 320 to 520 K periods of 30 - 240 min. These data reveal how such parameters affect the metal bilayer interdiffusion profiles and the thermal interface conductance. An analytical description is derived for the interdiffusion profiles as a function of time, temperature, and initial film thickness in thin Au-Cu bilayer films, and used as an input to a Diffuse Mismatch Model (DMM) to predict *G*.

6.2 Methodology

6.2.1 XPS depth profiling characterization

XPS depth profiling is a destructive technique that repeatedly measures local composition and removes material from the surface through ion sputtering. The local through-plane composition was measured at each sputtering depth with a characterization depth of ~1 nm. XPS depth profiles of layered Cu-Au samples were conducted at five selected Cu thicknesses characterized by EDX, on two similar as-deposited films in a ThetaProbe surface analysis system (ThermoFisher Scientific Inc.). Furthermore, XPS depth profiles were performed at the same Cu thicknesses of film after annealing at temperatures of 320, 360, 440 and 520 K for 30 minutes each. The XP spectra were collected at binding energies with 10 eV ranges around the Cu 2*p*_{3/2}, Au 4*f*_{7/2}, and Mo 3*p*_{3/2}d peaks, which were used for quantifying the through-plane composition as described in Section 2.4. Next, the scanned area was sputtered across an area of 1 mm² by rastering a focused Ar⁺ beam (3 keV) with a backfilled pressure of 1 × 10⁻⁵ Torr between each XPS measurement.

6.2.2 Conductance measurements

Measurements of *G* were measured as a function of Cu thickness through the noncontact optical pump/probe method, Frequency Domain Thermo-Reflectance (FDTR) as described in Section 5.2.1.^{21, 22} Then, the sample was transfer to anneal in an ultra-high vacuum environment with a base pressure of 2 ×10⁻⁸ Torr. The sample was then rescanned with FDTR. By iterating between vacuum annealing and measuring thermal interface conductance, *G* was determined as a function of Cu thickness and annealing temperature. The annealing temperatures for this sample were 360K, 440K, 460K, 480K, and 520 K with an annealing time of 30 mins per anneal.

6.3 Results

6.3.1 EDX measurements of Cu and Au thicknesses

The film thicknesses for Cu and Au layers were characterized using EDX. The sample on Mo substrates was prepared by examining the temperature effect on the interdiffusion between Cu and Au. An example has been shown in Figure 6.1 (a) where the thickness gradient of Cu adhesion layer was measured on a $10 \times 10 \text{ mm}^2$ area grid with 2 mm spacing, centered on the $14 \times 14 \text{ mm}^2$ Mo substrate. The maximum thickness of the Cu wedge reaches $25 \pm 1 \text{ nm}$ and linearly decreases with position to zero. The uniform thicknesses of Au were determined to be 39 ± 2 . Again, the



Figure 6. 1. Contour plot for Cu adhesion layer thickness as EDX-measured across the Cu-Au film on (a) Mo substrate and (b) sapphire substrate.

Cu film thickness was measured by EDX on a $12 \times 12 \text{ mm}^2$ area grid with 1 mm spacing, centered on the $14 \times 14 \text{ mm}^2 \text{ Al}_2\text{O}_3$ substrate as shown in Figure 6.1 (b). The maximum thickness of the Cu wedge reaches 23 ± 1 nm, and linearly decreases with position to zero. The uniform thickness of Au was determined to be 49 ± 2 nm. The reported thickness at each EDX-measued points includes with an measurement uncertainty of $\pm 2\%$ of the nominal values.

6.3.2 XPS depth profile by varying temperature and heating time

The surface composition measured by XPS can be influenced by the different Ar^+ sputtering rates for the individual alloy components during depth profiling. ²³⁻²⁷ The incident Ar^+ ion colliding with the sample surface leads to the sputtering removal of atoms, which results in a surface composition different from bulk. ²⁷⁻²⁹ In the Cu-Au binary system, the real composition can be corrected from XPS measured surface composition by Equation 1. ³⁰⁻³²

$$\frac{C_{Cu}}{C_{Au}} = \frac{C_{Cu}^{S}}{C_{Au}^{S}} \times \frac{r_{Cu}}{r_{Au}} \tag{1}$$

where C_i and C_i^S are the real composition and the surface composition for component *i*, respectively, and r_i is the sputtering rate for component i. Here r_i is constant and independent of composition. The Ar⁺ sputtering rate for each component was calibrated on pure Cu and Au thin film with known thicknesses, and were calculated to be 1.05 nm/s (Cu) and 1.75 nm/s (Au) at the same experimental conditions as described in Section 6.2.3. These calibrated Ar⁺ sputtering rate for Cu and Au are comparable with literature values for pure metals.³³ The total sputtering depth (r_{total}) can also be calculated by knowing the Ar⁺ sputtering rate and XPS surface composition for individual components using Equation 2.^{30, 34, 35}

$$r_{total} = r_{Cu} C_{Cu}^S + r_{Au} C_{Au}^S \tag{2}$$

The XPS depth profiles were performed at four EDX characterized Cu thicknesses (25, 18, 8, and 0 nm) on Mo substrate to quantify the amount of interdiffusion between Cu and Au as a function of temperature. The interdiffusion was examined for the as-deposited film and after heating at temperatures of 320, 360, 440 and 520 K. To better understand the characteristic of



Figure 6. 2. Overlayed XPS depth profiles measured at the 8nm Cu wedge position with 39 nm of Au deposited on top. Atomic percent Au reported, where the similar slopes at the interfaces at ~39nm indicate that the as deposited sharp interface is maintained at annealing temperatures up to 520K.

measured XPS depth profiles, one example of XPS depth profiles measured at Cu thickness 8 nm and Au thickness 39 nm has been shown in Figure 6.2, where Cu, Au, and Mo through-plane compositions have been measured as a function of Ar⁺ sputtering depth on the film for both asdeposited and after annealing at 320, 360, 440 and 520 K for 30 mins. For the "as deposited" film, the diffusion of Cu into Au is negligible at room temperature. ^{36, 37} The resolution of the XPS depth profiling measured at the Au-Cu interface is ~15 nm, which may result from the following scenarios: (1) the momentum transfer induced by Ar⁺ ion sputtering in the collision cascade region can result in atomic mixing of surface atoms; (2) residuals metal atoms are left from unevenly distributed Ar⁺ beam rastering across the 1 mm² sputtering area. Similar XPS profiles were obtained after heating at temperature of 320 and 360 K for 30 minutes, but no interdiffusion was observed. However, after annealing at 440 K, Cu rapidly crossed the interface and uniformly distributes itself in the Au layer to form a Cu-Au alloy with 8 atomic percent of Cu. Subsequent annealing at 520K for 30 minutes, resulted in Cu and Au being completely interdiffused, forming a homogenous alloy. Inspection of the XPS depth profiles shown in Figure 6.2 reveal that the slope of the concentration profiles at the interface is unchanging with annealing temperature. Since the "as deposited" film has a sharp interface between Cu and Au, similar slopes for the other temperatures indicate that the interface at those temperatures can also be considered sharp. This observation is consistent with Erdelyi's simulated diffusion of Cu-Ni, using the assumption that the diffusion coefficient depends on the local composition.^{38, 39} They found that the concentration profile across the interface would remain sharp if one component diffuses much faster than the other component after annealing at elevated temperatures.^{38, 39} For instance, this has been experimentally observed from bilayer systems such as Ni-Cu, Si-Ge, Ag-Al and Al-Zn.^{38, 40, 41} Their deterministic model and Monte Carlo simulation also demonstrated that intermixing between Cu and Ni layers with an initially wide interface, produces a sharp interface.^{39, 42, 43}

Interestingly, the XPS data of Figure 6.2 shows a buildup of Cu at the surface of the film after diffusing through the Au layer after heating at 440 K for 30 mins, but this observation is contradictory to previous studies that Au prefers to segregate on the top layer in the Au and Cu alloy thin film.⁴⁴ The accumulation of Cu at the surface may be the result of surface Cu oxidation while the film is exposed to ambient air during sample transfer from the deposition chamber to EDX and XPS measurements.³⁷ The sample was then annealed at 520 K for 30 minutes, where Cu and Au completely interdiffused and a relatively homogeneous alloy was formed.

Last but not least, interdiffusion between Cu and Au was observed at a temperature of 440 K. The heating time effect on the extent of interdiffusion was examined at a fixed temperature 460 K. The XPS depth profiles were performed at five EDX characterized Cu thicknesses which are 28, 25, 20, 12, 0 nm. Figure 6.3 shows an example of XPS depth profiles measured at Cu thickness 20 nm and Au thickness 46 nm, where Cu, Au, and Mo through-plane composition have

been measured as a function of Ar^+ sputtering depth on the film for as-deposited and after annealing at 460 K for 20, 60, 240 mins.



Figure 6. 3. XPS depth profiles measured at Cu thickness 20 nm and Au thickness 46 nm, where Cu, Au, and Mo through-plane composition measured as a function of Ar+ sputtering depth (nm) on the film for as-deposited, after annealing at 460 K for 20 mins, 1 h, and 4h, and finally at 520 K for 20 mins.

6.3.3 Quantification for molar areal concentration of Cu and Au measured by XPS depth profiling

In the "as deposited" Cu-Au bilayer film, the initial molar areal concentration $(M_i^{initial})$ for each Cu and Au layer can be quantified by EDX. However, as an example shown in Figure 6.2, the resolution of XPS depth profiling measured at the Cu-Au interface is about 15 nm that could not represent the real sharpness of the Cu-Au interface. Based on previous discussion, the diffusion of Cu into Au is negligible at room temperature, and the interface of Cu-Au remains sharp along diffusion. Thus, we define the interface locates at which Cu raises to 10% from its

uniform concentration distributed within the Au layer. Given EDX-measured $M_{Cu}^{initial}$, the molar areal concentration (M_{areal}) of Cu at left side of interface can be quantified by Equation 3.

$$M_{Cu} = M_{Cu}^{initial} \times \frac{Area_{Cu}}{Area_{total}}$$
(3)

where $Area_{total}$ is the total area under Cu XPS depth profile curve, and $Area_{Cu}$ is the area on the left side of interface of Cu XPS depth profile curve. The Au molar areal concentration can be also calculated from the XPS depth profile using the same methodology.

6.3.4 Conductance measurements

Using the laser pump/probe technique of Frequency Domain Thermoreflectance (FDTR), we measured *G* as a function of adhesion layer thickness and annealing temperature, for annealing temperatures of 30 minutes. Measurements of the as-deposited film are shown as blue diamonds in Figure 5 and the values agree within the uncertainty of the values of Jeong *et al.*² The uncertainties in our measurements result from uncertainty in the input parameters for the fitting analysis of *G.*²¹



Figure 6. 4. Measurements of G vs Cu wedge thickness for the films as-deposited, 360 K, 440 K, 460 K, 480 K, and 520 K. Data at 360 K are similar to values for as-deposited. Measurements of 440, 460, and 480 K produce similar values. Data at 520 K match literature values for fully interdiffused films.

The effect of diffusion, as a function of Cu adhesion layer thickness, on *G* for the annealing temperatures of 360, 440, 460, 480, and 520 K are depicted in Figure 6.4. At 360 K, the thermal interface conductance is essentially equivalent to "as deposited" values, which is consistent with the XPS data: undetectable amounts of interdiffusion have occurred between the films as deposited and at 360 K. At 440, 460, and 480 K, values of *G* are notably lower than at 360 K. Examining the XPS data at 460 K, it is clear that some diffusion has occurred and Au has diffused to the interface between Cu and Al₂O₃, which is responsible for the lower *G*. This hypothesis is founded on the work of Freedman *et al.* which showed that as the Au content is increased in a Au-Cu homogeneous alloy, *G* at the metal-sapphire interface is reduced.⁴⁵ Further comparison to Freedman's work can be made since XPS shows our films are fully intermixed at 520 K. Using the as-deposited Au and Cu film thicknesses, the atomic percentage of Au was calculated and

compared to the thermal interface conductances of Freedman's work to generate the hexagrams in Figure 6.4. As shown, the two sets of data show good agreement, further corroborating that total interdiffusion has occurred at 520 K.

6.4 Modelling

6.4.1 Diffusion modelling



Figure 6. 5. Depiction of diffusion in the Au-Cu, thin film system. The green line denotes the fixed position of the interface. Cu diffuses to the right and Au to the left, changing the thickness of each side with respect to time. The rate at which each species is dependent on the permeability of the interface to that species. Once a species crosses the interface, it uniformly redistributes itself on that side of the barrier.

Analysis of the XPS profiling data reveals that once the Au and Cu atoms have crossed the interface between the two films, their respective distributions are relatively uniform. Therefore, it can be concluded that the major resistance to interdiffusion between Au and Cu thin films, is at the interface between the two. Hence, to simplify the analysis, we now derive a mass diffusion model where spatial gradients in composition are ignored in analogy to the lumped capacitance model for heat transfer as depicted in Figure 6.5.³⁶

The change of flux of each species across the interface can be described as follow.⁴⁶

$$\frac{d(n_{CuL}(t))}{dt} * \frac{1}{A} = -P_{Cu} \left(\frac{n_{CuL}(t)}{L_L(t)} - \frac{n_{CuR}(t)}{L_R(t)} \right) * \frac{1}{A}$$
(4)

$$\frac{d(n_{AuL}(t))}{dt} * \frac{1}{A} = P_{Au} \left(\frac{n_{AuR}(t)}{L_R(t)} - \frac{n_{AuL}(t)}{L_L(t)} \right) * \frac{1}{A}$$
(5)

where P_{Au} and P_{Cu} are the permeability of the interface to Au and Cu, n_{Au} and n_{Cu} are the number of moles of Au and Cu, L_{side} is thickness and A is a unit area in the plane of the interface, and the subscripts L and R designate the side of the interface. The system can be thought of as having two containers of different gases separated by an infinitesimally thin membrane, where the membrane has a different permeability to each species. Once a species crosses the interface it will uniformly distribute itself in the new container. The sizes of the containers can vary with time to capture the effect of the solid films getting thinner/thicker as the net flux of atoms moves from one side to the other.

In these two equations there are six unknowns. Two more equations relate the thicknesses to the number of moles of each species.

$$L_L(t) = \frac{N_A a^3}{4A} * (n_{AuL}(t) + n_{CuL}(t))$$
(6)

$$L_R(t) = \frac{N_A a^3}{4A} * (n_{AuR}(t) + n_{CuR}(t))$$
(7)

where N_A is Avogadro's number and *a* is the average lattice constant of the cubic unit cell for a face center cubic crystal structure (valid if the two species have similar lattice constants). Plugging these equations into Equations 4-5 yields

$$\dot{n}_{CuL}(t) = -\frac{4P_{Cu}A}{N_A a^3} \left(\frac{n_{CuL}(t)}{n_{AuL}(t) + n_{CuL}(t)} - \frac{n_{CuR}(t)}{n_{AuR}(t) + n_{CuR}(t)} \right)$$
(8)

$$\dot{n}_{AuL}(t) = \frac{4P_{Au}A}{N_A a^3} \left(\frac{n_{AuR}(t)}{n_{AuR}(t) + n_{CuR}(t)} - \frac{n_{AuL}(t)}{n_{AuL}(t) + n_{CuL}(t)} \right)$$
(9)

Mass conservation relations of the following two equations:

$$n_{AuR}(t) = n_{Au} - n_{AuL}(t) \tag{10}$$

$$n_{CuR}(t) = n_{Cu} - n_{CuL}(t) \tag{11}$$

Are substituted into Equation 8 and 9 to yield the two coupled rate equations, with two unknowns:

$$\frac{N_A a^3}{4P_{Cu}A} \dot{n}_{CuL}(t) = \left(-\frac{n_{CuL}(t)}{n_{AuL}(t) + n_{CuL}(t)} + \frac{n_{Cu} - n_{CuL}(t)}{n_{Au} - n_{AuL}(t) + n_{Cu} - n_{CuL}(t)}\right)$$
(12)

$$\frac{N_A a^3}{4P_{AuA}} \dot{n}_{AuL}(t) = \left(\frac{n_{Au} - n_{AuL}(t)}{n_{Au} - n_{AuL}(t) + n_{Cu} - n_{CuL}(t)} - \frac{n_{AuL}(t)}{n_{AuL}(t) + n_{CuL}(t)}\right)$$
(13)

Adding these two equations together produces

$$\frac{\dot{n}_{CuL}(t)}{P_{Cu}} + \frac{\dot{n}_{AuL}(t)}{P_{Au}} = 0$$
(14)

which demonstrates that the rate at which Cu and Au cross the interface is proportional to the ratio of their respective permeabilities. Integrating both sides of this equation and plugging in initial conditions $(n_{AuL}(0) = 0, \text{ and } n_{CuL}(0) = n_{Cu})$ produces

$$n_{AuL}(t) = \frac{P_{Au}}{P_{Cu}} * (n_{Cu} - n_{CuL}(t))$$
(15)

Substituting Equation 15 into Equations 12-13 yields the following two uncoupled first order nonlinear homogenous differential equations:

$$\dot{n}_{CuL}(t) = \frac{4P_{Cu}}{N_A a^3} \left(-\frac{n_{CuL}(t)}{\frac{P_{Au}}{P_{Cu}} * (n_{Cu} - n_{CuL}(t)) + n_{CuL}(t)} + \frac{n_{Cu} - n_{CuL}(t)}{n_{Au} - \frac{P_{Au}}{P_{Cu}} * (n_{Cu} - n_{CuL}(t)) + n_{Cu} - n_{CuL}(t)} \right)$$
(16)

$$\dot{n}_{AuL}(t) = \frac{4P_{Au}}{N_A a^3} \left(\frac{n_{Au} - n_{AuL}(t)}{n_{Au} - n_{AuL}(t) + n_{Cu} - \frac{P_{Cu}}{P_{Au}} * n_{AuL}(t) - n_{Cu}} - \frac{n_{AuL}(t)}{n_{AuL}(t) - \frac{P_{Cu}}{P_{Au}} * n_{AuL}(t) + n_{Cu}} \right)$$
(17)

These equations can be solved simultaneously using a computational differential equation solver to determine P_{Cu} and P_{Au} , by fitting experimental data of molar concentration of Cu and Au on left side of interface. The molar areal concentration of Cu and Au on each side of the interface were quantified from XPS depth profiles. Specifically, to determine the permeability of Cu and Au at 460 K, the molar concentration of Cu and Au were calculated at four XPS depth profiles with increasing annealing time at 0, 20, 60, and 240 mins at each Cu wedge thickness. Calculation details are described in Section 6.3.3. The best-fit permeability values for Cu and Au were optimized by minimizing the sum of squared error between model-predicted molar areal concentration values and XPS-derived ones.

6.4.2 Conductance modelling

The Diffuse Mismatch Model (DMM) is a common method for predicting G at non low temperature. To model the Au-Cu alloy interface with Al₂O₃, the DMM was employed, Freedman et al. used a Born Von Karman dispersion continuously varied based on alloy composition defined by Vegard's law and the average atomic mass paired with an experimental dispersion for Al₂O₃.⁴⁵ This work has been accomplished by Malen's group. In order to make comparative predictions with experimental data, the analytical diffusion model is utilized to calculate the alloy composition of the two metal layers as a function of time and temperature, where permeability is the temperature dependent parameter, for the "as deposited" Cu thicknesses and Au thickness of interest. The alloy compositions of each layer are then input into the DMM model. DMM predicted values for the "as deposited" film, 460K, and fully intermixed 520K are shown in Figure 6.6, with experimental data for comparison.

For the 460 K DMM, the best-fit permeabilities used were 1.00e-12 m/s for P_{Cu} , and 5.11e-13 m/s for P_{Au} and the model uses a diffusion time of 60 minutes. One hour was used because prior to being annealed at 460 K for 30 minutes, the sample was annealed first at 360K for 30 minutes, and then 440 K for 30 minutes. Since the XPS data shows that little diffusion at 360 K,



Figure 6. 6. DMM predictions of G compared with experimental values. Reasonable agreement is seen between DMM and experimental data, which indicates that the DMM can be used as a predictive tool to determine how diffusion will affect G based on initial film thickness, temperature, and permeability.

and assuming the same permeability at 440 K as 460 K, a total annealing time of one hour at 460K is used. The shaded regions of the DMM demarcate 10% variation in both the P_{Cu} and P_{Au} permeabilities. Although the DMM does not consider the quality of the interface, and so is a very rudimentary model that does not predict *G* with the highest accuracy, the results shown in Figure 6.5 indicate that it can be useful to estimate interface conductance for different diffusion conditions.^{6, 47}

6.5 Conclusions

Through the use of experimental XPS depth profiling measurements we have derived an analytical model to describe the unique diffusion behavior in the thin film Au-Cu system. Utilizing

this model for DMM calculations, we have created a predictive tool for electronic/thermal engineers to simulate diffusion in Au-Cu films, and predict thermal interface conductance with a dielectric substrate, according to the thermal conditions of their devices and initial film thicknesses. Comparing DMM calculated values to our experimental thermal interface conductance data indicates that this predictive tool should allow device designers to roughly determine the time evolution behavior of Cu-Au thin films in their devices, and improve their designs to extend device lifetimes.

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Chapter 7 Thesis impacts

The research will contribute the high-throughput study of catalytic and thermal properties of multicomponent alloy materials including different combination of Pd, Cu, Au and Ag through material libraries that span parameter spaces such as composition, size, and morphology. We have successfully developed the fabrication and characterization methodologies to advance the design and development of complex materials. Our results in mapping of CLSs across Pd_zCu_{1-z} CSAF shows FCC phase can be dimensionally stabilized under a certain film thickness over the composition range where B2 phase exists in the bulk. This promising results can potentially advance the development of Pd_zCu_{1-z} NP catalysts in H₂ separation. Furthermore, XPS was used to characterize the composition and electronic structure across the CSAFs. We observed *v*-band center shifts to the Fermi level with increasing Pd atomic fractions. The mapping of the electronic structure of Pd_xAg_{1-x} and Pd_xCu_yAu_{1-x-y} CSAFs across the composition space can be correlated with kinetic parameters of H₂-D₂ exchange reaction. Herein, we have successfully shown a high throughput methodology in preparation, characterization and measurement of the functionality in catalysis studies.

In the second part of my thesis, we focus on the study of thermal property of the alloys and of alloy-substrate interfaces. First, we have successfully demonstrated the first measurements to study the alloy composition effect on G across a metal-dielectric interface on Au_xCu_{1-x} and Au_xPd_{1-x} CASFs. Moreover, we also determine how the interdiffusion of Cu adhesion layer impacts on G across the Au-dielectric interface using XPS depth profiles technique. These studies provide insights in understanding and control of G across metal alloy-dielectric interfaces and adhesion layer-dielectric interface, which is extremely valuable to Nano electronic and optoelectronic applications.