High-throughput surface science and catalysis across ternary alloy composition space

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Abstract

Transition metals alloys have been widely used in catalysis for over a hundred years. Their advantages of having high activity, stability, and allowing flexibility in catalyst design, etc., also bring challenges to researchers due to the vast parameter space to explore and optimize. High-throughput experimentations developed in recent decades have greatly accelerated the exploration and screening of materials, and their potential have been demonstrated in numerous cases. Among these, Composition Spread Alloy Films (CSAFs) and Surface Structure Spread Single Crystals (S⁴Cs) are two types of high-throughput libraries suitable for the exploration of the alloy composition space and the surface structural space. Coupling these techniques with high-throughput surface characterization tools, such as spatially resolved Energy Dispersive X-ray Spectroscopy (EDX), X-ray Photoelectron Spectroscopy (XPS), Low Energy Ion Scattering Spectroscopy (LEIS), Ultraviolet Photoelectron Spectroscopy (UPS), and Mass Spectroscopy (MS), we can perform a comprehensive analysis of an alloy system or a surface structural space.

The equilibrium surface segregation property was first studied on three alloy systems, including CuAuPd, NiPdAu, and CuAgAu. The mapping of LEISderived surface compositions with high compositional resolution showed the effects of temperature, crystalline structure, long-range ordering, and adsorbates on surface segregation. A segregation model was derived to describe the segregation in ternary alloys. Rich datasets were generated, which could be used for benchmarking computational works. Inspired by the interesting behaviors that we observed during the equilibrium segregation studies, the kinetics of surface segregation under UHV and oxygen environment was then examined in detail on CuAu alloys and a CuAgAu alloy using LEIS and Near Ambient Pressure XPS (NAP-XPS). A series of experiments were designed to properly account for the damage of ion scattering caused to the surfaces, and the time scale of segregation kinetics was measured across the binary alloy composition space and a temperature range of 300-500 K.

The structural dependence of initial-stage oxygen adsorption on Cu surfaces has been investigated. High-throughput characterization of oxygen adsorption on a Cu(111)-14° S⁴C at 500 K was performed by XPS. The kinetic behavior of oxygen adsorption was examined using several kinetic models, including 1st order, LH 2nd order, and precursor-state 2nd order adsorption models. At least three types of sites were identified on surfaces vicinal to Cu(111) during oxygen adsorption and oxygen-induced surface reconstruction, and the distribution of these sites was compared to the structure of ideal clean surfaces.

Next, the performance of alloys in isopropyl alcohol (IPA) partial oxidation reaction was studied using CSAFs and a high-throughput catalytic microreactor array. Mo showed high activity in converting IPA to propene at above 500 K, and Mo oxide was identified to be the active species. While other metals such as Cu, Ag, Pd, and Pt all showed activity in IPA oxidation, either to propene or to acetone, their activities were too low to be studied using the high-throughput microreactor setup limited by the small contact area and short contact time. Furthermore, the potential of Angle-resolved XPS (AR-XPS) being used in quantifying the top-surface alloy compositions was explored on a CuAgAu CSAF. With the parallel data acquisition mode in ThetaProbe, the concentration information at various depths was collected by measuring XPS at four different emission angles with respect to the surface normal. Three lines with different binding energies were chosen for each element to collect information at different effective depths below the surface. The segregation in 20 CuAu alloys, 20 CuAg alloys, and 20 AgAu alloys was measured and compared to the compositions determined by EDX and LEIS.

All in all, in this study, we have explored the applications of several highthroughput experimental methodologies in surface science and catalysis, including topics such as surface segregation, oxygen adsorption, and catalytic evaluation.

Table of contents

Acknow	iii iii
Abstract	·
List of f	iguresxi
Chapter	1 Introduction 1
1.1 search	High throughput experimental methods and their application in material
1.2	Surface segregation in alloy systems1
1.3	Oxygen adsorption on single crystal Cu surfaces
1.4	Catalysis using alloys
1.5	Scope of this research
1.6	References
Chapter	2 Experimental methodology
2.1	E-beam thin film deposition and rotatable shadow mask
2.1.	1 Composition Spread Alloy Films (CSAFs)
2.1.	2 Rotatable shadow masks
2.2	Composition mapping across physical space
2.2.	1 Energy dispersive x-ray spectroscopy16
2.2.	2 X-ray photoelectron spectroscopy
2.2.	3 Low energy ion scattering
2.2.	4 Ultraviolet photoelectron spectroscopy
2.3	Curved single crystal
2.4	High throughput catalytic micro-reactor array
2.5	References
Chapter	3 Equilibrium segregation in ternary alloy systems: CuAuPd, NiAuPd,
CuAgAu	۱
3.1	Introduction
Seg	regation studies and conventional methodologies
3.2	Experimental methods
3.3	Segregation modeling

3.4	Re	sults and discussion	
3	.4.1	CuAuPd alloy system	35
3	.4.2	NiPdAu alloy system	52
3	.4.3	CuAgAu alloy system	56
3	.4.4	Segregation under oxygen environment	77
3.5	Co	nclusion	86
3.6	Re	ferences	88
Chap	oter 4 S	Segregation kinetics	99
4.1	Int	roduction	99
4.2	Ex	perimental procedures	102
4.3	Re	sults and discussion	102
4	.3.1	Sputtering, heating, reconstruction, and segregation	102
4	.3.2	Kinetics of segregation in CuAgAu alloys	104
4.4	Co	nclusion	128
4.5	Re	ferences	129
Chap	oter 5 (Dxygen adsorption across structural space	
5.1	Int	roduction	
5.2	Ex	perimental procedures	134
5.3	Re	sults	137
5.4	Ide	eal surface structures	
5.5	Ki	netic modeling of oxygen adsorption	144
5	5.5.1	First-order adsorption	145
5	5.5.2	Second-order adsorption	146
5	5.5.3	Single-site precursor-state model	147
5	5.5.4	Multi-site first-order adsorption	148
5	5.5.5	Multi-independent-site second-order adsorption	152
5	5.5.6	Multi-site precursor-state model	154
5 a	5.5.7 bove	Summary of complexity and performance of all model 155	lels discussed
5	5.5.8	Interpretation of kinetic model fitting results	158
5.6	Co	nclusion	

5.7	References	. 162
Chapter	6 Catalytic oxidation reaction evaluation across composition space	. 166
6.1	Introduction	. 166
6.2	Experimental procedures	. 167
6.2	.1 Catalysts preparation	167
6.2	.2 Catalytic activity tests	167
6.3	Results and discussion	. 170
6.2	.3 Activity on pure metal wires	170
6.2	.4 Mo catalyzed IPA dehydration	173
6.2	.5 Mo-Pd catalyzed IPA dehydration/oxidation	174
6.3	Conclusion	. 177
6.4	References	. 178
Chapte	r 7 Discussion on Angle-resolved XPS (AR-XPS)	. 179
7.1	Motivation	. 179
7.2	Experiment design	. 180
7.3	Results and discussion	. 182
7.4	Conclusion	. 189
7.5	References	. 191
Append	lix	. 192
8.1	Section 1 Alloy phase diagrams	. 192
8.2	Section 2 Images of CSAF surfaces	. 197
8.3	Section 3 EBSD on CSAFs	. 204
8.4	Section 4 Segregation kinetics	. 207
8.5	Section 5 Derivation of equations	. 214
8.6	Section 6 Oxygen adsorption on Cu(111) S ⁴ C	. 217
Chapte	r 9 General conclusions	. 223

List of figures

Figure 2.1 Schematic of Composition Spread Alloy Film using the example of Cu _x Ag _y Au _{1-x-y} . All ternary and binary alloy compositions and pure components can be found on a single sample
Figure 2.2 The use of rotatable shadow masks during e-beam thin film deposition. Substrate faces downwards, and shadow masks orient 120 degrees from each other
Figure 2.3 Photo of Cu(111) S ⁴ C, taken from literature ¹⁰ 24
Figure 2.4 Schematic of microreactor array system consists of mass flow controllers (MFC), glass microreactor array body, CSAF, heater, sampling system, Mass Spec, and capillary tubes as connections
Figure 2.5 Side-view of microreactor system: A) Flow-splitter distributes reactant gas into 102 capillaries. B) Reaction zone consists of a glass reactor body, gasket, CSAF, and heater. C) 102 capillaries connected to individual channels. D) Sampling system consists of capillary tubes, a flex hose, and a motor that allows sequential measuring of gases from individual channels. E) Mass spectrometer chamber consists of a turbo-molecular pump, ion gauge, and mass spectrometer
Figure 3.1 EDX map of CuAuPd CSAF used in segregation study. Binary CuAu, CuPd and AuPd alloy regions (concentration of the third element <1 at%) are labeled in blue, red and green, respectively. Sampling sequences in LEIS measurements are labeled at each of 164 points colored in yellow
Figure 3.2 Ternary composition diagram indicating the bulk compositions determined by EDX (grey \blacksquare). LEIS spectra were collected at selected bulk compositions (black \blacksquare). Surface compositions examined in published LEIS studies by various authors are labeled in color: blue Swartzfager ⁶⁰ (blue, \blacktriangle), Yi ⁵⁹ (blue, \blacklozenge) and Boes ²² (blue \bullet) measurements on PdAu. In green, Priyadarshini ⁷ (green, \triangleright) measurements on CuPd. In purple, Beikler ⁶⁹ and Taglauer ^{69,70} (purple, \blacktriangleleft) measurements on CuAu. In red, Miller ¹⁰ (red, \blacktriangledown)
measurements on CuAuPd
Figure 3.3 He ⁺ LEIS spectra at 164 bulk $Cu_xAu_yPd_{1-x-y}$ alloy compositions obtained at 500 K (left) and 600 K (right); (He ⁺ E ₀ =1 keV; scattering angle = 103°; scan time = 50 sec/pt; He ⁺ beam diameter = 500 µm). The Cu, Au, and Pd peaks are well-resolved and their peak energies, E/E ₀ , match the predictions of the binary collision model
Figure 3.4 Ternary diagrams showing the fractional excess surface atom density, $f \rho x$, y , defined by eq. 7. Data was obtained at 500 K (left) and 600 K (right). The blue region centered at Cu _{0.5} Pd _{0.5} shows notably lower (~50%) surface atom density than expected, indicating the presence of the B2 structure

Figure 3.5 Ternary diagrams showing excess surface concentrations of Pd, Cu, Au defined by eqs. 2 a,b,c. Data was obtained at 500 K (first row) and 600 K (second row). The blue regions on the Cu and Pd maps indicate lower surface coverage of Cu, Pd than in the bulk, and the red regions on the Au maps indicate the Au-enriched top surface; Cu is enriched on the surface only at low Au compositions.	43
Figure 3.6 Ternary diagrams showing pair-wise segregation Gibbs free energies defined by eq. 13. Data was obtained at 500 K (first row) and 600 K (second row), figures from left to right are $\Delta GPdCu$, $\Delta GAuPd$, $\Delta GCuAu$ in a unit of kJ/mol. Pair-wise segregation free energies <10 kJ/mol are observed in these experiments.	45
Figure 3.7 Comparison of PdCu segregation profile at 500 K with similar data in the literature ⁷ . Obvious deviations occur over the <i>xCu</i> range of 40%-60%, which reveals suppression of the Au segregation relative to alloys outside this range Compositions boundaries of FCC, B2, and transition regions from the literature are labeled with dotted lines. An offset of ~4 at% in the B2 phase region is observed between current work and literature.	46
Figure 3.8 PdAu segregation profiles at 500 K and 600 K (open symbols) compared with data from Swartzfager, ⁶² Yi, ⁶¹ and Boes. ¹⁷ Au segregation are enhanced at higher temperatures. The segregation profiles all show deviation from convex to concave curvature at a bulk Au fraction of $xAu = 0.5$.	48
Figure 3.9 Segregation of Au in Au _x Cu _{1-x} at 500 K and 600 K. Segregation does not show temperature dependence over the measured range. The excess surface coverage of Au is higher over the Au rich composition range than over the Cu rich range. The top surface composition is ~100% Au when the bulk Au concentration is >70 at%	48
Figure 3.10 A) one set of 164 UPS spectra collected on CuAuPd CSAF. B- D) UPS spectra on binary alloys. E) background-subtracted UPS using 8 eV cut-off. F) band-center of background-subtracted UPS spectra. G) d-band energy	51
Figure 3.11 (A) 176 points were selected on NiPdAu CSAF based on SEM- EDX measured compositions for segregation studies. (B) Ternary NiPdAu composition diagram showing the compositions at which EDX and LEIS spectra were obtained from the CSAF	53
Figure 3.12 XPS depth profiles of a PdAu binary alloy, a uniform Ni film, and a NiAu binary alloy on the same NiAuPd CSAF. Peak areas of Ni 2p _{3/2} , Au 4f _{7/2} , Pd 3d _{5/2} and Mo 3d _{5/2} are plotted versus Ar etch time. An increase in substrate Mo signal indicates a thin film-substrate interface. Uniform alloy composition across depth can be found on PdAu alloy, but NiAu alloy shows a non-uniform depth profile, probably due to phase separation.	55

Figure 3.13 Surface segregation profiles of NiAuPd alloy system	n. Au
enrichment and Ni depletion were found on all alloy compositions, when	hile Pd
richment was only found on alloys with low Au content	56
Figure 3.14 Thickness-composition-position maps of 3 CuAgAu CSAF	⁷ s used
n this work. The size of each circle represents the local film thickn	ess, as
ndicated by the black scale bar on the right-hand side of each figure;	circles
are colored by their atomic composition determined using EDX with	R-G-B
nixing (corresponding to Cu-Ag-Au, as shown in subtitles of figures)	59
Figure 3.15 Ternary CuAgAu composition diagram showin	g the
compositions (open squares) at which EDX and LEIS spectra were of	otained
from the CSAF. These demonstrate complete coverage of the comp	osition
pace by the CSAF. Also shown are the compositions at which s	surface
regregation on AuAg and CuAu alloys has been studied in other work	c using
LEIS (filled squares). The filled triangles denote binary and ternary	y alloy
compositions studied using Auger Electron Spectroscopy	
Figure 3.16 Representative SEM images of the CSAF at three	alloy
compositions after segregation measurements. a) Cu _{0.98} Ag _{0.02}	forms
nanoparticles as a result of thin-film dewetting. b) Cu _{0.06} Ag _{0.94} forms a	porous
2D network structure, intermediate between the intact film and nanopa	rticles.
c) Ag _{0.4} Au _{0.6} has large pinholes. d) Cu _{0.4} Au _{0.6} does not dewet and remain	ains an
tact film.	61
Figure 3.17 Contrast-enhanced images of CuAgAu CSAF after vextents of annealing under UHV; (Right) Mo 3d _{5/2} XPS map composition space after annealing, indicating the extent of the dewetting (exposure of Mo substrate)	various across in-film 63
Figure 3.18 As-deposited CuAgAu CSAF and dewetted CuAgAu CSA hermal annealing up to 800 K	F after 64
Figure 3.19 Mo substrate exposure as a result of dewetting after annea	ling at
300 K calculated with SEM imaging and Mo 3d XPS. Substrate expo	sure is
nainly concentrated in Cu-rich and Ag-rich regions, with maximum su	bstrate
exposure being 50% of the total surface at Cu _{92.8} Au _{0.7} Ag _{6.5} composition	n. The
evolution of substrate exposure as a function of annealing temperatu-	are and
ime can be found in Supporting Information (Figure S4 – S6)	65
Figure 3.20 SEM-EDX mapping of Cu _{0.5} Ag _{0.5} composition region	on. A)
Electron image, particles \sim 1 um in diameter. B) Over layered electron	image
and EDX maps of Cu Ka1 and Ag La1 lines. Although constrained by	spatial
resolution, phase segregation of CuAg alloy into Cu-rich and Ag-rich	phases
can be seen.	
Figure 3.21 Core-level XPS peak positions (binding energies in eV)	of Cu,
Ag and Au in CuAgAu alloys relative to their pure metals	68
Figure 3.22 First row: top-surface composition θCu , θAg , θAu at neasured by LEIS (in at%); Second row and below: the difference be op-surface composition at 500 to 750 K and the top surface composition	800 K etween tion at

800 K. It is clear that segregation of Ag is weaker when $T > 700$ K, while the surface concentration of Au is only weakly dependent on temperature	70
Figure 3.23 Top panel) Segregation profile of AuAg binary alloys. (Orange filled region) measured at 500 - 800 K in this work; (solid triangles) LEIS measurements; (empty triangles) AES measurements. Segregation of Ag is observed at all bulk alloy compositions in this work, showing a smooth segregation profile across composition space. Bottom panel) Excess Ag concentrations, defined by $\Delta Ag = \theta Ag - xAg$, are displayed in a heat map across the same temperature and composition range. Segregation is weakly dependent on temperature.	71
Figure 3.24 Linear fit of segregation free energy over temperature on selected AgAu alloy compositions, while intercept and negative slope are taken as segregation enthalpy and segregation entropy. Segregation enthalpy and entropy as a function of AgAu alloy composition	72
Figure 3.25 Segregation profile of CuAu alloys. A) (shaded region) 500-800 K measured in this work; (empty squares and circles) data from the literature. 8B) Map of excess surface concentration of Au across 500-800 K range. Au surface enrichment is shown in all alloy compositions, with stronger segregation on the Au-rich side; weaker Au enrichment is found at higher temperatures as a result of the entropy effect.	74
Figure 3.26 Segregation profile of CuAg alloys. 9A: (black squares) measured at 600 K before film dewetting in this work. (Inset graph) comparison with available literature: (solid squares) AES measurements by Romeo; (empty triangles) AES measurements by van Wyk. Strong segregation of Ag is observed at all bulk alloy compositions in this work, with lower Ag concentration than literature at Ag<1 at%, which may indicate surface equilibrium was not achieved at 600 K. 9B: segregation measured at 500-800 K after CSAF annealing at 800 K, showing weaker Ag segregation with increasing temperatures when Ag<20 at% in the bulk, while alloy surfaces are fully covered by Ag when Ag>20 at%.	76
Figure 3.27 Bulk and surface compositions of the 13 points measured in this work before and after near-ambient-pressure oxygen treatment and hydrogenation treatment.	80
Figure 3.28 Metallic near-surface composition and oxygen signal of 13 points on the CuAgAu CSAF after exposure to various oxygen pressures at ~620 K. The non-zero initial oxygen level at some positions was due to thin-film dewetting and the corresponding oxidation of the Mo substrate. The 'half- pressure' of a transition is defined by the pressure at which surface composition is in the middle of the initial and the final (or maximum Cu) states, as illustrated by the figure in the lower-left corner. The 'half-pressure' as a function of alloy composition is shown in the figure in the lower-right corner.	83

] (]	Figure 3.29 Metallic near-surface composition of 13 points on the CuAgAu CSAF on ternary diagram after exposure to various oxygen pressures at ~620 K
1 0 1 0 1 1 1 1 1 1	Figure 3.30 Cu spectra at the end of the experiment after oxidation at 1 Torr oxygen environment. Indices labeled in the figures are the same as those abeled on the lower-right corners in Figure 3.28. Two groups of Cu spectra can be observed based on their oxidation state, while high-Cu alloys (Cu >25 at% in the bulk, or >37% in the near-surface before oxidation) in the left figure show only two characteristic peaks of Cu(0)/Cu(I), low-Cu alloys in he right figure show satellite peaks and shoulder peaks at ~934 eV that ndicate the further oxidation of Cu(I) to Cu(II)
l V t	Figure 4.1 He ⁺ LEIS signal of Cu and Au collected during one experiment in which 13 CuAu alloy surfaces were iteratively measured during a kinetic ransition. Data points are colored by their iterations (time)
1	Figure 4.2 Kinetics of segregation on 3 CuAu alloys studied using He ⁺ LEIS. Three temperatures and three He pressures were used to explore the interplay between sputtering/reconstruction/segregation
1 (1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	Figure 4.3 Monte Carlo simulation of collision between 0.75keV He ⁺ and Cu _{0.5} Au _{0.5} alloy surface. The upper left figure shows the trajectory of He ⁺ nside the Cu _{0.5} Au _{0.5} lattice; the upper right figure summarizes the distribution of He ⁺ appearance in all 10000 trajectories as function of depth; ower left figure shows the distribution of vacancies in Cu _{0.5} Au _{0.5} created upon collision, while Cu vacancy concentration is higher than that of Au due to its lower formation energy and more efficient momentum transfer during collision; lower right figure shows the sputtering yields of Cu and Au as well as total vacancy yield as functions of CuAu composition
ן t נ (Figure 4.4 (Part 1) Temperature-ramp experiment on 7 CuAu alloys. A emperature range of 400-700 K was covered by linearly changing sample emperature while iteratively measuring the surface composition of 7 alloys using He ⁺ LEIS. Equilibrium surface compositions at 500 K (orange), 600 K (blue), and 700 K (magenta) for each alloy are indicated by dotted lines 115
ן t נ נ	Figure 4.5 (Part 2) Temperature-ramp experiment on 7 CuAu alloys. A emperature range of 400-700 K was covered by linearly changing sample emperature while iteratively measuring the surface composition of 7 alloys using He ⁺ LEIS. Equilibrium surface compositions at 500 K (orange), 600 K (blue), and 700 K (magenta) for each alloy are indicated by dotted lines 117
l s f	Figure 4.6 An example of segregation kinetics on a ternary CuAgAu alloy studied using He ⁺ LEIS. Cu and Au responded immediately upon heating from 400 K, while Ag started to diffuse out at a slightly higher temperature 119
]	Figure 4.7 Temperature-jump experiment on seven CuAu alloys
l s t	Figure 4.8 Sputter-jump experiment on five CuAu alloys. Surfaces were sputtered with 3 kV Ar^+ at room temperature, then heated to target temperature within 1 min

Figure 4.9 Half-times of 'sputter-jump' kinetics on five CuAu alloys	. 124
Figure 4.10 Summary comparison plot between equilibrium segregation, steady-state 'thermostatic He ⁺ sputtering', and steady-state 'sputter-jump' experiments.	. 125
Figure 4.11 Evolution of Cu, Ag, and Au XPS signal during oxidation and reduction under near-ambient pressures. Cu peaks showed the emergence of Cu(I) upon oxidation and its disappearance upon reduction.	. 126
Figure 5.1 Oxygen dosing geometry in UHV chamber. Oxygen can be introduced into the chamber through two leak valves integrated with a flood gun and ion gun, respectively. The Oxygen uniformity test showed that while both dosing directions are angled (not from top-down of the sample), the doser from the ion gun leak valve is further away from the sample and thus gave relatively uniform oxygen coverage	. 136
Figure 5.2 Oxygen coverage across Cu(111) S4C surface after various exposures (0-1200 Langmuir) at 500 K. 3-fold symmetry in oxygen uptake can be observed due to symmetry in FCC (111) surface structure	. 138
Figure 5.3 Map of linear step density as a function of the ideal surface structure covered in this study using (111)-centered curved single crystal; [1 0 0] and [1 0 0] directions are labeled along dotted lines. $s1/(1 1 0)$ and $s0/(1 0 0)$ types of steps as well as kinks composed of $s1$ and $s0$ steps are labeled on corresponding ideal structures. Angular kink density distribution is shown as a colored arc, in which blue represents zero kink density and red represents maximum density.	. 139
Figure 5.4 Surface oxygen uptake at various oxygen exposures at 500 K. [1 0 0] direction is indicated by dashed lines; oxygen exposures in the unit of Langmuir (1 $L=10^{-6}$ Torr·sec) calculated with calibrated Mass Spectrometer are labeled next to each map. Saturation coverages are defined by oxygen uptakes at 1000 L exposure, while the difference in oxygen uptake between 500 L and 1000 L is within experimental error.	. 141
Figure 5.5 Oxygen uptake along (100) and (110) directions at various exposures. (100) steps show higher activity in dissociating oxygen than (110) steps, while both are higher than that on terrace sites	. 142
Figure 5.6 Surface oxygen uptake on 63 surfaces studied in this work at various oxygen exposures from 0.76-1000 L. Step edge density is used to color data points without distinguishing the type of step. Surfaces with low step density showed slower adsorption kinetics.	. 142
Figure 5.7 Ideal structure of surfaces vicinal to Cu(111). Two types of step sites are shown by rectangles and labeled as (110) and (100) steps. A kink site is composed of one (110) step and one (100) step.	. 143
Figure 5.8 Calculation of areal surface site coverage. αc is the angle between the (111) plane and (110) or (100) planes, e.g., $\alpha c(100) = 54.7^{\circ}$, $\alpha c(110) =$	

35.3°. α is the angle between the (hkl) plane and the (111) plane ($0 \le \alpha \le 12^{\circ}$ in this work)
Figure 5.9 Relative concentration of sites calculated for the ideal surfaces along the edge of the S^4C sample studied in this work. Depending on the definition of sites, one can either see a kink site being one pair of (110)-step and (100)-step sites, or a kink site as an independent site
Figure 5.10 Fittings of oxygen adsorption on Cu (111), (322), and (332) surfaces using the 'one-site' assumption. Precursor-state model, 1 st order model, and 2 nd order model are compared
Figure 5.11 3-site 1 st order fitting results on (322) and (332) surfaces. Three common sites are assumed to be dominant sites on all 63 surfaces, while their relative abundance is allowed to vary on each surface. Adsorption follows 1 st order behavior on each site with a rate constant k. The 'type-1' site is absent from 322) surface and the 'type-2' site is absent from (332) surface. k_1 =0.0069, k_2 =0.020, k_3 =1.36; corresponding to sticking probability of ~0.34%, 0.95% and 68%
Figure 5.12 Parity plots of 1 st order fittings by assuming 1-4 common sites are shared among 63 surfaces
Figure 5.13 Fitted site distribution and corresponding uncertainties. 3 types of common independent sites are assumed, all sites have 1 st order kinetic behavior. Color bars corresponding to the site distributions and uncertainties are shown in the bottom row
Figure 5.14 Parity plots of 2 nd order fittings by assuming there are 1-4 common sites shared among 63 surfaces
Figure 5.15 3-site precursor-state fitting results on (322) and (332) surfaces. 3 common sites are assumed to be dominant sites on all 63 surfaces, while their relative abundance is allowed to vary on each surface. Adsorption follows precursor-state behavior on each site with initial sticking coefficient S ₀ and desorption/diffusion terms K ₁ , K ₂ . 'type-1' site is absent from (322) surface and 'type-2' site is absent from (332) surface. Initial sticking probabilities on 3 sites are ~0.26%, ~1.3%, and ~100%. The chance of precursor desorption from empty sites of 'type-1' and 'type-3' without another available site nearby is high, whereas it is low on 'type-2' sites
Figure 5.16 Site distributions along high symmetry directions. A) Terrace site, (100)-step and (110)-step sites on the ideal surface structures. B) Sites 1-3 on reconstructed surfaces predicted by the precursor-state model
Figure 5.17 Summary of model performance 156
Figure 6.1 Schematics of microreactor system consists of mass flow controllers, microreactor array, reaction zone, sampling system, and mass spectrometer

Figure 6.2 Microchannel glass block with 100 inlet channels and 100 outlet channels. Each pair of channels together with one rectangle region of the gasket consist a reaction zone that is isolated from neighboring zones and acts as an independent reactor when combined with a CSAF.	169
Figure 6.3 IPA oxidation catalyzed by a 2-inch Pt wire. 5 ml/min Ar/IPA, 1 ml/min O_2 , 300-530 K. Reactivity (IPA consumption) started at ~ 415 K and approached maximum at ~ 530 K, leading to the formation of acetone and CO_2 , while the selectivity towards CO_2 increased significantly at above 500 K.	172
Figure 6.4 SEM/EDX images of Mo surface after used as catalyst in IPA oxidation reaction. A) Array of channels spaced at 1 mm. B) Zoom-in on one channel. C) Pieces of MoO ₃ formed inside channel region. D) Surface under glass gasket where no MoO ₃ crystals formed. E) MoO ₃ nanocubes. F) EDX-SEM overlapped image of MoO ₃ nanocubes, red-Oxygen, green-Mo	174
Figure 6.5 IPA oxidation conversion on Pd-Mo catalysts	176
Figure 6.6 SEM images of Pd-Mo surfaces after used as catalyst in IPA oxidation reaction.	176
Figure 7.1 XPS survey scan on pure Cu, Ag and Au surfaces. Peaks of high intensity and different binding energies were selected to represent signal from different information depth in order to probe the near-surface composition with AR-XPS.	183
Figure 7.2 Relative sensitivity factor (RSF) determination using AR-XPS signal collected on binary CuAg, AgAu alloys at 4 different collection angles. ~20 alloy compositions were used along each binary composition line at 700 K. Ag MN refers to Ag M4N45N45 Auger emission line	184
Figure 7.3 Relative sensitivity factor (RSF) determination using AR-XPS signal collected on binary CuAu alloys at 4 different collection angles. ~ 20 alloy compositions were used along each binary composition line at 700 K. Cu LM refers to Cu L ₃ M ₄₅ M ₄₅ Auger emission line	185
Figure 7.4 Comparison of segregation profiles of CuAu alloys determined by LEIS versus Angle-resolved XPS using different emission lines. 'Angle-4' refers to the most surface-sensitive angle; Cu 2p _{3/2} has the highest binding energy and thus being the most surface-sensitive among the 3 Cu emission lines selected.	187
Figure 7.5 Comparison of segregation profiles of CuAg alloys determined by LEIS versus Angle-resolved XPS using different emission lines. 'Angle-4' refers to the most surface-sensitive angle; Cu LM2 and Ag 3p3/2 lines suffered from peak-overlapping issue and thus not presented here	188
Figure 8.1 Phase diagram of Mo-Ag alloy	192
Figure 8.2 Phase diagram of Mo-Au alloy	193
Figure 8.3 Phase diagram of Mo-Cu alloy	193

Figure 8.4 Phase diagram of Mo-Ni alloy 194
Figure 8.5 Phase diagram of Mo-Pd alloy 194
Figure 8.6 Phase diagram of Mo-Pt alloy 195
Figure 8.7 Phase diagram of Cu-Pd alloy 195
Figure 8.8 Phase diagram of Cu-Pd-Au alloy
Figure 8.9 Phase diagram of Ni-Pd-Au alloy
Figure 8.10 Phase diagram of Cu-Ag-Au alloy
Figure 8.11 SEM images of AgAu alloys after vacuum thermal annealing. The field of view in each image is 68x51 um ²
Figure 8.12 SEM images of CuAu alloys after vacuum thermal annealing. The field of view in each image is 68x51 um ²
Figure 8.13 SEM images of CuAg alloys after vacuum thermal annealing. The field of view in each image is 68x51 um ²
Figure 8.14 25×25 SEM images across Cu-Ag-Au composition space
Figure 8.15 (1-13) SEM images of CuAgAu CSAF after oxidation; index matches that labeled in Figure 3.27. (lower-right) Photo of sample surface and the analyzer cone taken by a side-camera used for sample position alignment. Scale bar: 20 um
Figure 8.16 Microscopic images of annealed CuAgAu CSAF surface before contrast enhancement. Annealing conditions: 1) 700 K, 3 hour. 2) 750 K, 3 hour. 3) 800 K, 3 hour. 4) 800 K, 5 hour
Figure 8.17 Pole figures of EBSD indexing on selected alloy compositions from pure Cu to pure Au. At each point, a region of ~63x40 um was mapped out using a step size of 2 um and spot size of 320 nm; EBSD patterns were matched to the Cu lattice to determine surface orientations, which gave almost identical results as that given by matching to the Au lattice due to their similarity in lattice constants and both being FCC lattice; on average ~50% of all EBSD patterns were successfully indexed, while the rest were either blurry or contained overlapping patterns from different grains. All alloy compositions on CuAu CSAF show FCC (111) being the dominant surface orientation
Figure 8.18 EBSD indexing of annealed CuAu CSAF 205
Figure 8.19 EBSD indexing of annealed CuAu CSAF
Figure 8.20 0.75 keV He ⁺ LEIS signal evolution on 3 CuAu alloys at 300 K, 400 K and 500 K using 200 nA sample current with 1 mm circular spot
Figure 8.21 0.75 keV He ⁺ LEIS signal evolution on 3 CuAu alloys at 300 K, 400 K and 500 K using 40 nA sample current with 1 mm circular spot 209

Figure 8.22 Raw LEIS Cu and Au signal evolution during the temperature- ramp experiment, corresponding to data shown in Figure $4.3.2.2 - 4.3.2.3$. ~40 nA	. 210
Figure 8.23 Raw LEIS Cu and Au signal evolution during the temperature- ramp experiment, corresponding to data shown in Figure $4.3.2.2 - 4.3.2.3$. ~40 nA	. 211
Figure 8.24 LEIS signal of Cu and Au corresponding to surface composition data shown in Figure. The last plot shows the total LEIS signal, defined by the summation of Cu and Au multiplied by its sensitivity factor (1.8 in this case); data before first reaching 700 K had lower ion yield, which was likely due to initial surface contaminant at 500 K and eventually sputtered away by 1 kV He^+ . ~40 nA	. 212
Figure 8.25 NAP-XPS spectra of Cu 2p _{3/2} , Ag 3d _{5/2} and Au 4f during oxidation and reduction periods.	. 213
Figure 8.26 O ₂ P-T traces during exposure experiments measured by a calibrated mass spectrometer. Title in each subplot indicates the date of experiment as well as the initial exposure target, while cumulative exposures calculated by the integral under curve are labelled on the bottom of each subplot. The mass spec data in one of the experiments (labelled as '32 L' in Figure 5.3.7) was missing, and 32 Langmuir was the target exposure, while the actual exposure was likely to be slightly higher than the target.	. 217
Figure 8.27 A) bulk compositions of 146 points across the CuAgAu CSAF on ternary diagram. B) deviations in bulk compositions if the probing beam position is off by 100 um. C) the effect of position offset in x-direction. D) the effect of position offset in y-direction. E) 2-D colorbar indicating the offset value and direction.	. 218
Figure 8.28 Fitted site distribution and corresponding uncertainties. 3 types of common independent site are assumed, all sites have 2 nd order kinetic behavior. Color bars corresponding to the site distributions and uncertainties are shown in the bottom row	. 219
Figure 8.29 Fitted site distribution and corresponding uncertainties. 4 types of common independent site are assumed, all sites have 1 st order kinetic behavior. Color bars corresponding to the site distributions and uncertainties are shown in the bottom row	. 220
Figure 8.30 Fitted site distribution and corresponding uncertainties. 4 types of common independent site are assumed, all sites have 2 nd order kinetic behavior. Color bars corresponding to the site distributions and uncertainties are shown in the bottom row.	. 221
Figure 8.31 (left) first order, (right) second order; color-bars: (left) site distributions, (right) uncertainties	. 222

Chapter 1 Introduction

1.1 High throughput experimental methods and their application in material search

Traditional methodologies for exploring material properties in a multicomponent system involve preparation of one or more samples with discrete compositions and their characterization by various methods, such as measurement of their surface tension, catalytic activity, electronic structure or surface composition, etc. This level of effort per sample incurs costs that have been limiting factors to the comprehensive study of properties spanning composition space. High-throughput experimentation with automated sample preparation and characterization enables materials studies that have been hitherto intractable ^{1–4}. High throughput methods are ideally suited to scientific problems which require comprehensive sampling of alloy composition space, e.g., analysis of surface segregation in alloys with all possible alloy compositions. High throughput methods require the preparation, characterization, and study of libraries - these are physical samples containing many different materials that span the desired space of sample characteristics.

1.2 Surface segregation in alloy systems

In multicomponent materials such as alloys, surface segregation is ubiquitous, resulting in the material's surface having a composition different from that of the bulk. Segregation minimizes the surface free energy and arises from differences between the component surface energies, strain energy caused by lattice mismatch of bulk components, and interactions of surface components with adsorbates. Under equilibrium conditions, the relationship between the bulk and the surface compositions is described by the Langmuir-McLean model parameterized by the Gibbs free energy of segregation. Detailed segregation models try to relate the enthalpy and entropy contributions to the free energy to bulk composition, adsorbate type, and ambient pressure.⁵ As adsorption, desorption, catalytic reactions, and many other surface phenomena occur on the outer-most surface, all are influenced by surface segregation. The surface composition of a multicomponent material dictates adsorption site distributions and influences surface reactions;⁶ thus, understanding alloy surface segregation is critical to understanding alloy surface chemistry.

Numerous methods for determining the surface composition of a multicomponent material have been applied in studies of surface segregation. These methods can be categorized into those sensitive to the top-layer composition and those that measure near-surface composition. Among the top-layer composition measurement methods, scanning transmission electron microscopy (STEM) and high-resolution TEM (HRTEM)⁷ give both atom type and position with high spatial resolution. Fourier-transform infrared spectroscopy (FTIR) combined with CO adsorption provides vibrational spectra that can be used to quantify the coverage of those surface atom types to which CO adsorbs.^{8,9} It should be noted, however, that CO adsorption can be invasive because of the different binding energies of CO to the various components of the surface and, therefore, CO may influence the surface composition. Xe adsorption is less invasive and,

combined with UV photoemission, can be used to identify and quantify the surface atoms to which Xe adsorbs.¹⁰ Perhaps the most common method for the study of surface segregation is low energy He⁺ ion scattering (LEIS) which quantifies the topmost surface composition.¹¹

Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and angle-resolved XPS have been used widely to determine near-surface composition. In these analysis methods, the depth resolution is dictated by the mean free paths of the photo-emitted electrons, usually ~1 nm. Ion sputtered depth profiling combined with LEIS or XPS is a destructive method for studying depth-dependent composition. Secondary ion mass spectrometry with time-of-flight detection (ToF-SIMS) can be operated in a static mode with low detection limits.¹² Among the many techniques mentioned, LEIS developed by Brongersma has proven to be the most effective and sensitive way of measuring top-surface compositions and thus has been widely used in surface segregation studies.¹³

To completely understand the key factors governing segregation, a comprehensive study across alloy composition space is needed; however, such studies are rare and most studies only focus on the single alloy composition. The complicated interactions within a ternary system make it essential for studies to span the entire composition space rather than just using a few discrete compositions.^{14–19} Although thermodynamic models^{20–25} and computational methods^{26–29} for binary alloy segregation have been developed based on numerous experimental studies under vacuum¹¹ and in the presence of adsorbates,^{7,17,30–35} they

cannot be easily extended and validated to describe segregation in ternary alloys due to a lack of experimental data.³⁶

1.3 Oxygen adsorption on single crystal Cu surfaces

Many properties of materials are sensitive to their surface structure at an atomistic level, e.g., catalytic activity, structural stability, adsorption, corrosion, etc. Thus, understanding the influence of surface micro-structure on these properties has always been a topic that attracts researchers' attentions. The adsorption of oxygen on Cu has been used as a model system and repeatedly studied over the last century, yet there are still mysteries that might be unveiled using of high-throughput experimentations.

Oxygen adsorption on low Miller index Cu surfaces have been extensively studied by LEED^{37–43}, AES^{37,40,42}, XPS^{44–47}, STM^{41,43,45,46,48,49}, UPS^{38,39,44}, EELS^{38,39,50}, ellipsometry³⁷, inverse photoemission⁵¹, ion scattering⁴² and secondharmonic generation⁴⁷, in which a broad temperature range (4~773 K) and pressure range (10⁻⁸~1⁻⁴ Torr) have been covered. Some consensus has been achieved in these literature regarding the structure of saturated surfaces, and the kinetics of initial stage oxidation: at room temperature and relatively low oxygen exposures (< 10⁴ L), oxygen dissociative adsorb on all low index surfaces, forming (2 × 1), and $(\sqrt{2} × 2\sqrt{2})$ R45° superstructures on Cu(110) and Cu(100) surfaces at 'saturation' coverage, respectively^{37,40,45,51}. Under the same conditions, a disordered oxide addlayer is formed on Cu(111) surface, which turns into the so-called '44' – $(\sqrt{73}$ R5.8° × $\sqrt{21}$ R – 10.9°) and '29' – $(\sqrt{13}$ R46.1° × 7R21.8°) structures^{38,41,49,50} by further annealing to 473 K and 673 K. Adsorption on Cu(111) surface at low coverages (< half of the corresponding saturation coverage) can be described by the precursor-state kinetic model⁵² (one of the second-order kinetics⁵³). Oxidation studies on stepped surfaces are comparably scarce, with only a few works presented to the best of the author's knowledge^{43,46,54}, while the oxidation kinetic study on stepped surfaces is still absent.

Since Cu catalysts are often used in the form of nanoparticles⁵⁵, which possess a collection of surface orientations and contain high density of surface defects such as steps and kinks, the study of oxidation kinetics and surface reconstruction on stepped Cu surfaces will have practical value in the guidance of catalyst design.

1.4 Catalysis using alloys

Alloys provide researchers with another dimension in designing heterogeneous catalysts: the combination of elements and their ratios. By mixing two or more metals, the material can benefit from the creation of surface sites that do not exist on any of the pure metals. The electronic and geometric effects resulting from the interaction between species allow more flexibility in the catalyst design but at the same time, bring challenges to catalyst optimization due to the vast parameter space involved. Nowadays, controllable properties in an alloy catalyst include its composition, support, size and shape of the nanoparticle^{56–58}, layered structure (e.g., core-shell structure), and sometimes the dispersion of atoms in the material⁵⁹ (e.g., single-atom-alloy). Among these parameters, alloy composition is an essential factor determining the economics of its usage and affects the stability of many other parameters.

1.5 Scope of this research

The main goal of this thesis is to explore the use of high-throughput experimental tools in surface science and catalysis and provide successful examples of their applications. Specifically, the goals include 1) demonstrating the ability of high-throughput methodologies being used in surface chemistry studies; 2) understanding the scientific details behind the big dataset generated during highthroughput experimentations.

Several topics in surface science will be addressed in this thesis using highthroughput experimental methodologies: Chapter 3 focuses on the equilibrium characteristics of surface segregation on polycrystalline alloys; Chapter 4 discusses the kinetic behavior of segregation; Chapter 5 focuses on the oxygen adsorption kinetics and the possible surface reconstructions on Cu surfaces; Chapter 6 explores the IPA oxidation reaction using alloy catalysts.

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Chapter 2 Experimental methodology

2.1 E-beam thin film deposition and rotatable shadow mask

2.1.1 Composition Spread Alloy Films (CSAFs)

High-throughput experimentation has greatly accelerated material exploration over the past decade.¹⁻⁵ High-throughput experimentation allows parallel production and characterization of numerous materials with different compositions or structures. Composition spread alloy films (CSAFs) are high throughput libraries first developed in the 1950s to determine alloy phase diagrams.⁶ Since then, they have been successfully applied to study the phase diagrams, electronic structures⁷, and many other properties of multicomponent alloy systems. A CSAF is typically a multicomponent thin film deposited onto a substrate using physical vapor depositions methods, including e-beam evaporation, effusion cell evaporation, sputtering and reactive sputtering; it contains more than one ratio of component mixing on different physical locations on the substrate. There are several ways of creating composition gradients: 1) positioning the evaporation source near one side of the substrate to generate a flux gradient based on the distance between the source and different locations on the substrate. The atomic utility can be higher than other methods, but samples made this way usually only span a portion of binary, ternary or quaternary composition space, and a complete mapping across composition space requires several samples 2) by masking part of the substrate and adjusting mask positions during evaporation, flux is piece-wise uniform as a function of time, and such sample prepared this way requires more intense thermal annealing to achieve uniform mixing between layers;

3) by using a shadow mask. Flux gradients determined this way is based on the geometry of source opening, source-substrate distance, and mask position. The atomic utility is usually low, but a complete binary or ternary composition space can be mapped using only one sample.

So far, CSAFs have been successfully applied to study surface composition, surface electronic structure (d-band energy and core-level shift) as well as catalytic properties in our group.

2.1.2 Rotatable shadow masks



Figure 2.1 Schematic of Composition Spread Alloy Film using the example of $Cu_xAg_yAu_{1-x-y}$. All ternary and binary alloy compositions and pure components can be found on a single sample.

Figure 2.1 is a schematic of a ternary CSAF prepared by combining shadow mask and e-beam deposition of three alloy components with composition gradients oriented at 120°.⁸ Such CSAFs span the entirety of ternary composition space and, when analyzed using spatially resolved methods, provide much more data in one experiment than traditional methods. Figure 2.2 shows the geometry of the source-mask-substrate setup; a shadow mask can entirely block flux towards one end of the substrate. A flux gradient can be created inside the region where the flux is

partially blocked, and a wedge-shaped thickness profile will form over time. By co-evaporating several metal sources and independently controlling their shadow mask orientations, flux gradients can be added at different angles and create a thin film sample that covers entire ternary composition space, as depicted in Figure 2.2.



Figure 2.2 The use of rotatable shadow masks during e-beam thin film deposition. Substrate faces downwards, and shadow masks orient 120 degrees from each other.

E-beam sources are heated by electrons emitted from filaments colliding with high-voltage crucibles, reaching a temperature close to the melting point of the source material. A step-motor can control the orientation of individual masks with angular accuracy better than 1°. Before deposition onto substrates, all masks are rotated until opening directions are the same. A Quartz Crystal Microbalance (QCM) above sample position is lowered to sample height, and ~ 1 cm towards mask opening direction measures the maximum flux region of the 'wedge'. Another 3-way rotatable mask is used to block other sources during the flux calibration of a source. This mask can also be set to an 'open' position that allows materials from all sources to deposit onto the substrate. Once calibration is done, the step-motor on each shadow mask controls its orientation; QCM is lifted, and the substrate is positioned facing downwards for thin film deposition.

2.2 Composition mapping across physical space

High-throughput experimentation is usually a combination of high throughput sample fabrication/preparation and efficient/automated characterization of property of interest across physical space. The following section will introduce several automated surface property characterization tools regularly used in this work, including their fundamental working principle and specific setups in our lab.

2.2.1 Energy dispersive x-ray spectroscopy

Energy-dispersive X-ray spectroscopy (EDX/EDS) is usually combined with SEM or TEM for elemental identification and quantification of a small area on the sample. A high voltage accelerated electron beam ejects core-level electrons of an element, and the energy of X-ray generated during higher-level to core-level electron transfer can be used to uniquely identify the element and quantify its abundance within information depth, which is usually on the order of 1 um depending on incident electron energy and material mass density. One EDX spectrum collected on a CuAuAg CSAF deposited onto Mo substrate is shown in Figure 2.2.1. Incident electron energy of 20 keV is typically used for this study as peaks are generally crowded at 1-3 keV energy range composed of contributions from carbon and oxygen contaminants, Mo K-alpha line, Au K-alpha line, etc. Deconvolution of overlapping peaks brings uncertainty in composition analysis. Thus lines at higher X-ray energy, e.g., Au L line and Cu L line, will help with more accurate quantification. Electron energies higher than 20 keV will increase the information depth, being less surface sensitive and thus less precise for thin-
film analysis since the typical CSAF thickness used in this study is between 50-200 nm.

In an EDX composition screening, CSAF will be moved following a predefined grid, usually within a range of 12-13 cm and grid point spacing of 0.5-1 mm; upon each sample movement, an EDX spectrum is collected by rastering the electron beam over a 50-400 um square region around the grid point center. A smaller rastering region gives information averaged over a narrower composition range, thus being more accurate as a location function. A larger region may better align with the region on which other surface characterization tools will operate and thus be more meaningful for a direct comparison, which will be discussed in XPS and LEIS sections (sections 2.2.2 and 2.2.3).

Beam intensity is regularly calibrated during screening using a Ni single crystal in the SEM chamber to account for signal drifts. Signal drift is usually downward over time, especially when it is close to the end of filament lifetime, and an up to 50% decrease can be observed during a 4-10 hour screening. Without constant calibration or other post-acquisition numerical treatment, which will be mentioned in Chapter 7, the thickness and composition estimation of the thin film can be very far off. Quantification of EDX spectrums is performed using *ThinFilm ID* commercial software. A layer-by-layer thin film – substrate structure can be set with known elements in each layer, and unknown layer compositions can be fit using the signal intensities of selected excitation lines. In the fitting algorithm, k-ratios, defined as the ratio between the intensity of one line in the sample and that in a pure metal, are used in a physical model which accounts for many parameters,

including the mass density of materials, mean free path of electrons, layer thickness, etc.; a least-square criterion using absolute k-ratio values is usually applied in optimization to get think film thickness and composition. When there is a drift in the signal caused by unstable filament emission, peak intensities of all elements probed decrease proportionally; however, due to the least-square algorithm, the optimum solution will favor high concentration species and sacrifice low-intensity signals, causing an inaccurate composition determination. Careful inspection of fitting errors is highly recommended in high throughput screening processes, especially when a long operation time is needed. Again, examples with and without post-acquisition numerical correction will be shown in Chapter 7 to illustrate its importance.

2.2.2 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a conventional tool for determining the surface composition and chemical state. It is very surface sensitive due to the short mean free path of core-level electrons inside materials. Its information depth is usually estimated to be 1-10 nm depending on excitation photon energy, material property, binding energy, and emission/detection angle. Most XPS data presented in this work was collected using a Thermo Fisher ThetaProbe, in which a base pressure of ~10⁻⁹ Torr can be reached without liquid nitrogen cooling. An automated stage with a programmable list of points enables efficient XPS mapping across composition space.

For CSAF surface composition screening, an effective spot size much smaller than the sample size is needed to achieve high compositional resolution. A 400 um oval spot (~300 um and 500 um along minor and major axes) was typically used in this work, which gives enough signal level for metal signal quantification using an average spectrum acquisition time of 1 min/peak; angle-resolved XPS and detailed peak deconvolution requires longer acquisition time. Pass energy is another vital factor influencing energy resolution and signal gain (and thus signalto-noise level). Higher values of pass energy can give a much higher signal and thus reach the same signal to noise level with a shorter acquisition time, or equivalently, have a higher signal to noise level using the same acquisition time. Lower pass energies can give higher energy resolution – peaks will be narrower and better separated, allowing more accurate peak deconvolutions. Depending on the element and peak of interest, pass energies used in this study vary from 50 eV to 300 eV, typically 50 eV to 100 eV for metallic peaks and higher energies for carbon and oxygen peaks due to their intrinsic sensitivity difference.

2.2.3 Low energy ion scattering

The ion scattering technique was developed in the 1950s for surface composition analysis. Noble gas ions, including He⁺, Ne⁺, and Ar⁺ are typically used due to their high neutralization probability and thus high surface sensitivity; other alkali metal ions have also been used to reach a specific mass resolution. Ions accelerated to a certain voltage are projected to the surface of the sample and collide with surface atoms. While the majority of ions are neutralized during a collision, especially those that penetrate into deep layers, a small fraction of the ions keep charged and can be analyzed using a conventional hemisphere analyzer designed for XPS and AES. Neutralized ions can also be detected using time-of-flight

detectors in more advanced instruments, which is beyond the scope of this short introduction. Based on the incident ion energy, ion scattering can be classified into low energy, medium energy, and high energy ion scattering, while different levels of information depth can be achieved.

Low energy ion scattering (LEIS) was used in this work in a ThetaProbe, sharing the same hemisphere analyzer as XPS, enabling convenient switching between two surface sensitive techniques and good sample position consistency, which is critical for CSAF characterizations. 0.75-1.0 kV He⁺ was used in this study for surface composition determination due to its excellent surface sensitivity. According to literature, more than 99% of backscattered ions went through only a single collision with top atomic layer atoms, while He⁺ colliding with deeper layers are mostly neutralized and not detected in this analyzer setup.

The selection of beam size, He pressure, filament emission as well as pass energy, and spectrum acquisition time should be considered as a whole to minimize surface damage, as LEIS is a destructive way for surface composition determination; it becomes more critical when continuous LEIS sampling is needed in the case of segregation kinetic studies. The principle of parameter selection is calculating the average ion dose per atom during each spectrum collection: net sample current caused by He⁺ flux, usually computed using the difference between measured sample current with and without ion beam on, should be divided by the beam size to get the number of ions per unit area per unit time and compare to the product of atom density on the sample surface and acquisition time of a single spectrum. Ideally, less than 5% of all surface atoms should be bombarded by He⁺ during each measurement. However, that number also depends on the property of interest: for equilibrium segregation experiments, since usually only one spectrum is collected on each physical point after sputter-anneal cycles, even if one component within all 5% of the atoms hit by incident ions is completely sputtered off from surface while other species stay, it will not significantly alter the conclusion in segregation profiles. However, tens or even hundreds of spectrums are usually collected on the same physical point in one experiment for kinetic studies. Minimizing ion dose is critical to observing other processes (e.g., surface reconstruction, segregation).

A recommended set of parameters for the data collection on alloy samples in ThetaProbe is given for reference: 750 eV He⁺ incident energy with optimized condenser and objective voltages (should adjust after each filament replacement), 500 um - 1000 um beam size, 1 mA filament emission current (mainly for the sake of filament lifetime), 0.5-1.0 E-9 mbar He pressure above base pressure, 0.5 eV energy step size, 600-750 eV kinetic energy window for spectrum collection (for elements heavier than Ni), four angle-channels (angle-resolved LEIS), 100 ms dwell time with 1 scan, 500 eV pass energy (since LEIS peaks are in general wide and lower pass energy does not help with peak deconvolution, while high pass energies can compensate the signal loss due to low ion dose). While there are many parameters to adjust, and some may give a similar effect on signal-to-noise level, it is highly recommended that only 1-2 parameters are changed (e.g., dwell time or number of scans). In contrast, others are kept constant over a long period (e.g., a few years) since comparison across different experiments would be easier and more meaningful.

In principle lower energy He⁺ beam causes minor damage to the sample surface. Still, the much higher neutralization probability of low energy He⁺ will result in a lower signal level in LEIS spectra and a much lower S/N level. In contrast, a longer acquisition time per spectrum or a higher ion dose is needed to compensate. In practice, 500 - 750 eV He⁺ can be used in the ThetaProbe setup with a reasonable signal level that allows collecting a spectrum covering metal components (0.8-1.0 incident energy range) within 1 min.

2.2.4 Ultraviolet photoelectron spectroscopy

Ultraviolet photoelectron spectroscopy (UPS) has been widely used as a surface-sensitive tool to measure a material's electronic structure since its commercialization in 1967. Work function and electron density of valence orbitals can be determined using UPS. It has similar working principles as XPS but uses a much lower energy excitation source (ultraviolet photons instead of X-rays). Thus, it only probes a depth < 10 nm and provides higher energy resolution. A helium discharge lamp is usually used as a photon source, which gives a photon energy of 21.2 eV (corresponding to 1 α line); other source gases or emission lines can provide source energies between 10 eV to 50 eV.

2.3 Curved single crystal

Most UHV surface science studies have been performed on single crystal surfaces due to their well-defined surface terminations, making it simple to compare with computational efforts and identify the role of primary surface sites such as terrace, step, kink, and other surface defects in a surface reaction. A wellstudied model system usually has data available on several low index surfaces, e.g. (100), (110), and (111) for FCC structure, and a few high index surfaces; however, this is far from enough for a comprehensive understanding of a system, while preparing more high index single crystalline surfaces is very costly and timeconsuming.

Structural Spread Spherical Single Crystal (S⁴C) is a library that spans surface structural space. The idea of polishing a single crystal into curved shapes to expose continuously changing surface facets was first implemented by Linder⁹ in 1927. Due to the limitation of experimental equipment, S⁴C was not widely used as an efficient tool to accelerate screening across surface structural space until spatially resolved surface analysis techniques advanced in the late 90s. Two types of curved single crystals have been adopted in the research. One is a partial cylindrical shape on which surface orientation changes along only one axis; another is a partially spherical or a dome-shaped crystal on which surface orientation changes along both x- and y-axes. Due to the limitations of the sample manipulating systems, a set of S⁴Cs is usually required to cover the entire structural space.

A Cu(111) S⁴C – a cylindrical Cu single crystal nano-machined into a spherical dome-shape with (111) surface orientation at the center, 10 mm in diameter and 20 mm in curvature was used in this work. The surface orientation of the S⁴C was determined with EBSD. A PBN button heater underneath S⁴C was used for heating, and a K-type thermal couple was spot-welded to the side of the

sample for temperature monitoring; sample temperature can be controlled within 0.02 K with respect to target temperature at steady-state using a PID controller.



Figure 2.3 Photo of Cu(111) S⁴C, taken from literature¹⁰.

Figure 2.3 shows a photo of Cu(111) S⁴C, which is not the crystal used in this work but illustrated the same idea. Details of data acquisition on S4C can be found in Chapter 5.

2.4 High throughput catalytic micro-reactor array

Lab-scale fixed-bed flow reactors made of quartz or stainless steel tubes are probably the most common type of reactor used in catalytic reaction studies, in which quartz wool is usually used to hold catalyst powder in place. In such a setup, the fresh catalyst will be loaded into the reactor, and catalytic activity will be monitored over time after specific pretreatment steps until the catalyst is deactivated or long-term stability is confirmed. As bimetallic and even trimetallic catalysts are widely studied, a series of catalysts with various compositions need to be prepared and tested under the same condition to identify the role of each element in catalytic performance. There are several drawbacks of such a method, 1) many catalysts have to be prepared separately and thus making it time-consuming; 2) many conditions such as temperature, flow rate, size of catalyst powder, etc., have to be carefully monitored and controlled to make different trials comparable.



Figure 2.4 Schematic of microreactor array system consists of mass flow controllers (MFC), glass microreactor array body, CSAF, heater, sampling system, Mass Spec, and capillary tubes as connections.

To overcome such limitations and accelerate catalyst composition screening for an alloy system, a micro-reactor array was designed for use with CSAF libraries (section 2.1). As shown in Figure 2.4, a glass gasket isolates the CSAF surface into 100 independent regions, and a glass block formed by a stack of 21 glass sheets each having 10 inlet channels or 10 outlet channels (i.e. 100 inlets and 100 outlets in totals) is contacting the gasket. Together with flow controllers, capillary tubes, and mass spectrometer, they consist of a micro-reactor array system with 100 reaction volumes, each in principle has alloy catalyst with a specific composition, which is controlled by the CSAF fabrication step. In this setup, the reaction temperature is controlled by a heating unit on the back of CSAF, and all 100 channels share the same reactant gas flow and have the same temperature at all times; a sampling capillary and a programmable moving stage can collect the gaseous products from each channel just by inserting the capillary into each stainless steel outlet tube since the vacuum is applied on the end of the sampling capillary, sending products into a mass spectrometer.



Figure 2.5 Side-view of microreactor system: A) Flow-splitter distributes reactant gas into 102 capillaries. B) Reaction zone consists of a glass reactor body, gasket, CSAF, and heater. C) 102 capillaries connected to individual channels. D) Sampling system consists of capillary tubes, a flex hose, and a motor that allows sequential measuring of gases from individual channels. E) Mass spectrometer chamber consists of a turbo-molecular pump, ion gauge, and mass spectrometer.

Besides its advantages of being able to screen catalytic activity across alloy composition space and ensuring reaction condition uniformity across all channels, there are also a few limitations one should bear in mind when using this microreactor: 1) since the body of the reactor is made of glass, elevated temperature (>600 K) should be avoided. 2) Sampling across 100 channels usually requires 20-40 min; thus, comparison across channels depends on the assumption that a steadystate reaction is reached, which should be verified since activation/deactivation over time may pose systematic errors and might be misinterpreted as compositiondependent properties. 3) Due to the small contacting area in each channel, only reactions with high activity can be accurately studied using this system, and 'clean' reactions that don't permanently deactivate catalysts are highly preferred.

2.5 References

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Chapter 3 Equilibrium segregation in ternary alloy systems: CuAuPd, NiAuPd, CuAgAu

3.1 Introduction

Segregation studies and conventional methodologies

In multicomponent materials such as alloys, surface segregation is ubiquitous, resulting in the material's surface having a composition different from that of the bulk. Segregation minimizes the surface free energy and arises from differences between the component surface energies, strain energy caused by lattice mismatch of bulk components, and interactions of surface components with adsorbates. Under equilibrium conditions, the relationship between the bulk and the surface compositions is described by the Langmuir-McLean model parameterized by the Gibbs free energy of segregation. Detailed segregation models try to relate the enthalpy and entropy contributions to the free energy to bulk composition, adsorbate type, and ambient pressure¹. As adsorption, desorption, catalytic reactions, and many other surface phenomena occur on a material's outer-most surface; all are influenced by surface segregation. The surface composition of a multicomponent material dictates adsorption site distributions and influences surface reactions;² thus, understanding alloy surface segregation is critical to understanding alloy surface chemistry.

Numerous methods for determining the surface composition of a multicomponent material have been applied in studies of surface segregation. These methods can be categorized into those sensitive to the top-layer composition and those that measure near-surface composition. Among the top-layer composition measurement methods, scanning transmission electron microscopy (STEM) and high-resolution TEM (HRTEM)³ give both atom type and position with high spatial resolution. Fourier-transform infrared spectroscopy (FTIR) combined with CO adsorption provides vibrational spectra that can be used to quantify the coverage of those surface atom types to which CO adsorbs.^{4,5} It should be noted that CO adsorption can be invasive because of the different binding energies of CO to the various components of the surface and, therefore, CO may influence the surface composition. Xe adsorption is less invasive and, combined with UV photoemission can be used to identify and quantify the surface atoms to which Xe adsorbs.⁶ Perhaps the most common method for the study of surface segregation is low energy He⁺ ion scattering (LEIS) which quantifies the topmost surface composition.⁷

Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and angle-resolved XPS have been used widely to determine the nearsurface compositions. In these analysis methods, the depth resolution is dictated by the mean free paths of the photo-emitted electron, usually ~1 nm. Ion sputtered depth profiling combined with LEIS or XPS is a destructive method for studying depth-dependent composition. Secondary ion mass spectrometry with time-offlight detection (ToF-SIMS) can be operated in a static mode with low detection limits.⁸ Among the many techniques mentioned, LEIS developed by Brongersma has proven to be the most effective and sensitive way of measuring top-surface compositions and thus has been widely used in surface segregation studies.⁹

3.2 Experimental methods

All CSAF depositions were performed in two identical UHV deposition chambers, with base pressure $<1\times10^{-8}$ Torr before deposition and $<2\times10^{-8}$ Torr during deposition. Molybdenum substrates with $14 \times 14 \times 3$ mm³ were used, while sample temperature was monitored using K-type thermocouples and heat supplied using a BN heater underneath the Mo substrate. Three e-beam sources (MANTIS) were used in each deposition containing metals corresponding to each alloy system studied (CuAuPd, NiAuPd and CuAgAu). The deposition rate of each source is measured by a quartz crystal microbalance (QCM) which is lowered to substrate position during calibration, and each e-beam source power is independently controlled to give a deposition rate of 1-2 Å/min. Target average film thickness was set to 100 nm, which is enough to give material properties similar to that of corresponding bulk alloys, and the concentration in deeper layers will not be affected by surface segregation. A typical deposition usually lasts for 8-12 hours, and the deposition rate is calibrated and adjusted every 2-3 hours to account for the deposition rate decay caused by evaporation of source material over time. Postdeposition annealing was performed on the CuAuPd CSAF at 800 K for 1 hour, while annealing was performed more carefully with a gradual increase in temperature on NiAuPd and CuAgAu CSAFs after samples were transferred to the XPS/LEIS chamber under monitor due to the concern of thin-film dewetting.

After e-beam deposition, samples were transferred into an SEM chamber for EDX mapping across composition space. 20 keV electron energy was used for both microstructure observation and EDX spectra collection. A grid of 13×13 mm² with a grid spacing of 0.5-1.0 mm was used for mapping, and the signal intensity was periodically calibrated using a Ni single crystal next to the CSAF sample. On average, each spectrum was collected over 1-2 min using INCA software; film thickness and composition were analyzed using *ThinFilm ID* software.

Samples were then loaded into ThetaProbe for surface composition quantification. The sample position can be aligned using a digital camera directly above the sample with accuracy within 50 um. Base pressure of $\sim 1E-9$ Torr can be reached after proper sample degassing (up to 600 K). A few cycles of Ar⁺ sputtering (3 kV, ~1 uA sample current) and annealing (600-800 K depending on alloy system) were performed on each sample to remove surface carbon and oxygen contaminants. XPS (300×500 um² oval beam) of all metal components and the substrate Mo $3d_{5/2}$ were then collected on selected locations for near-surface composition mapping. LEIS (500-1000 um circular beam) was used for top-surface composition mapping at several temperatures. According to literature, equilibrium surface composition can only be reached at elevated temperatures, while prolonged time is needed for lower temperatures. Under such considerations, samples were annealed at 800 K for surface equilibrium, cooled slowly to target temperatures and kept for 1 hour before LEIS mapping. Although longer stabilization time before equilibrium measurements is preferred, it is infeasible as some of the elements (such as Cu, Ni and Pd) can be easily contaminated by water, oxygen, and carbon oxide from the UHV chamber. Since each cycle of LEIS mapping across a set of \sim 160 points takes 2-3 hours, arranging compositions prone to contamination at the top of the list have proved to be a good practice.

3.3 Segregation modeling

The Langmuir-McLean equation has been widely used to describe equilibrium surface segregation in binary alloys.³² The Langmuir-McLean model describes a system in which different metal atoms can swap their positions between the bulk and the surface, and the alloy maintains a constant number of available surface sites during segregation.⁸³ For a two-component equilibrium describing segregation in AuPd

Equation 3.1
$$\frac{\theta_{Au}}{\theta_{Pd}} = K_{AuPd} \frac{x_{Au}}{x_{Pd}} = \frac{x_{Au}}{x_{Pd}} \cdot exp\left(\frac{-\Delta G_{AuPd}}{RT}\right)$$

where θ_i represents the fractional surface composition of component *i* and x_i represents its fractional contribution to the bulk composition. This is equivalent to

Equation 3.2
$$\theta_{Au} = \frac{K_{AuPd} x_{Au}}{x_{Pd} + K_{AuPd} x_{Au}}$$

Equation 3.3
$$\theta_{Pd} = \frac{x_{Pd}}{x_{Pd} + K_{AuPd} x_{Au}}$$

where K_{AuPd} is the equilibrium constant describing the following atom-exchange reaction:

Equation 3.4
$$Au^{bulk} + Pd^{surf} \rightleftharpoons Au^{surf} + Pd^{bulk}$$

A negative value of the segregation free energy, ΔG_{AuPd} , implies excess Au at the surface; i.e. $\theta_{Au} > x_{Au}$.

Segregation in the Cu_xAu_yPd_{1-x-y} ternary system can be described using three two-atom exchange reactions and their corresponding equilibrium constants:

Equation 3.5
$$Au^{bulk} + Pd^{surf} \rightleftharpoons Au^{surf} + Pd^{bulk}$$
 $K_{AuPd} = \frac{\theta_{Au}x_{Pd}}{x_{Au}\theta_{Pd}}$
Equation 3.6 $Pd^{bulk} + Cu^{surf} \rightleftharpoons Pd^{surf} + Cu^{bulk}$ $K_{PdCu} = \frac{\theta_{Pd}x_{Cu}}{x_{Pd}\theta_{Cu}}$

Equation 3.7
$$Cu^{bulk} + Au^{surf} \rightleftharpoons Cu^{surf} + Au^{bulk}$$
 $K_{CuAu} = \frac{\theta_{Cu}x_{Au}}{x_{Cu}\theta_{Au}}$

These represent only two independent systems in equilibrium because $K_{AuPd}K_{PdCu}K_{CuAu} = 1$, or equivalently, $\Delta G_{AuPd} + \Delta G_{PdCu} + \Delta G_{CuAu} = 0$. Note that these definitions imply that in the case $K_{CuAu} > 1$ (or $\Delta G_{CuAu} < 0$), the first component, Cu segregates preferentially over the second, Au

The surface compositions can be expressed as functions of bulk composition and the equilibrium constants:

Equation 3.8
$$\theta_{Pd} = \frac{x_{Pd}}{x_{Pd} + K_{PdCu}^{-1} x_{Cu} + K_{AuPd} x_{Au}}$$

Equation 3.9
$$\theta_{Cu} = \frac{K_{PdCu}^{-1} x_{Cu}}{x_{Pd} + K_{PdCu}^{-1} x_{Cu} + K_{AuPd} x_{Au}}$$

Equation 3.10 $\theta_{Au} = \frac{K_{AuPd}x_{Au}}{x_{Pd} + K_{PdCu}^{-1}x_{Cu} + K_{AuPd}x_{Au}}$

Equation 3.11 $\Delta G_{AB} = -RT \cdot lnK_{AB}$

Alternatively, other than writing segregation as three pair-wise (A-B, A-C, B-C) atomic exchanges, one can also re-write the equations to be A-M, B-M, and C-M exchanges in which M does not represent any specific element but rather a representation of all other species when we are only interested in the relative enrichment/depletion of an element on the surface compared to itself. In such a

case, only one equation is needed to describe a species, as shown in Equation 3.12 below. It is equivalent to the combination of Equation 3.13 and Equation 3.14

Equation 3.12
$$Ag^{bulk} + M^{surf} \rightleftharpoons Ag^{surf} + M^{bulk}$$

Equation 3.13
$$Ag^{bulk} + Au^{surf} \rightleftharpoons Ag^{surf} + Au^{bulk}$$

Equation 3.14
$$Ag^{bulk} + Cu^{surf} \rightleftharpoons Ag^{surf} + Cu^{bulk}$$

Equation 3.12 can also be written as the following:

$$1Ag^{bulk} + aCu^{surf} + (1-a)Au^{surf} \rightleftharpoons 1Ag^{surf} + aCu^{bulk} + (1-a)Au^{bulk}$$

• Equation 3.12 = a * Equation 3.13 + (1 - a) * Equation 3.14

$$K_{AgM} = \frac{\theta_{Ag} x_M}{x_{Ag} \theta_M}, K_{AgAu} = \frac{\theta_{Ag} x_{Au}}{x_{Ag} \theta_{Au}}, K_{AgCu} = \frac{\theta_{Ag} x_{Cu}}{x_{Ag} \theta_{Cu}}$$

The relation between K_{AgM} , K_{AgAu} and K_{AgCu} can be derived:

Equation 3.15
$$a = \log_{K_{CUAU}} \frac{K_{CUAU} + \frac{\theta_{CU}}{\theta_{AU}}}{1 + \frac{\theta_{CU}}{\theta_{AU}}}$$

Equation 3.16
$$-\frac{E_{AgM}}{RT} = a\left(-\frac{E_{AgAu}}{RT}\right) + (1-a)\left(-\frac{E_{AgCu}}{RT}\right)$$

This provides another way of defining segregation free energy.

3.4 Results and discussion

3.4.1 CuAuPd alloy system

Pd alloys catalyze many hydrogenation^{10,11} and oxidization^{5,12} reactions and can be used as hydrogen purification membranes^{13–24}. Segregation in PdAu ^{1,24–31}, PdCu^{7,32–35} and CuAu^{36,37} binary alloys has been described frequently in the literature, and CuAuPd segregation has also been reported at a few discrete compositions^{13,38}. It is known that under vacuum conditions Au and Cu alloys are surface enriched elements. Their segregation minimizes system energy by reducing the strain energy of the bulk lattice and by covering the surface with low surface energy alloy components. The phase diagram of CuAuPd has also been studied^{15,39–} ⁴². While all three pure components have face-centered cubic bulk structures, the Cu_xPd_{1-x} binary alloy exhibits a B2 phase over the composition range $x = 0.45 \rightarrow$ 0.65. The B2 phase has a CsCl structure with an ordered body-centered cubic (BCC) lattice. In the ternary Cu_xAu_yPd_{1-x-y} alloy, this B2 phase extends to a Au composition of y=0.20. This ordered B2 phase is stable at low temperature and shows superior H₂ permeability and considerable tolerance to impurities such as H₂S in H₂ containing gas streams^{43,44}. Due to its industrial relevance and ease of characterization, CuAuPd is an ideal system for ternary alloy segregation study.

In this work, surface segregation in CuAuPd under UHV conditions was measured at 500 K and 600 K at 164 different bulk compositions on a Cu_xAu_yPd_{1x-y} CSAF spanning ternary composition space, $x = 0 \rightarrow 1$ and $y = 0 \rightarrow 1$ -x. The existence of the B2 phase was observed by the LEIS signal intensity, and the influence of the B2 phase on surface segregation has been demonstrated experimentally. Segregation along the three binary alloy compositions matches that reported in earlier studies. Measurements of surface segregation have also been made spanning the ternary composition space and the free energies of segregation were estimated using a Langmuir-McLean model extended for application to ternary systems⁴⁵. 3.4.1.1 EDX mapping

A grid of 26×27 (702 in total) points spaced 0.5 mm was mapped using EDX, and a list of 164 points was finally selected for the subsequent segregation studies, as shown by the labeled yellow circles in Figure 3.1. As shown in Figure 3.2, the compositions of 702 points are indicated by grey squares, and that of 164 points are plotted in black squares. Colored shapes indicate compositions on which segregation studies are available in the literature. Selected 164 points fully cover ternary composition space with an emphasis on a known B2 phase region near Cu₅₀Pd₅₀.



Figure 3.1 EDX map of CuAuPd CSAF used in segregation study. Binary CuAu, CuPd and AuPd alloy regions (concentration of the third element <1 at%) are labeled in blue, red and green, respectively. Sampling sequences in LEIS measurements are labeled at each of 164 points colored in yellow.



Figure 3.2 Ternary composition diagram indicating the bulk compositions determined by EDX (grey ■). LEIS spectra were collected at selected bulk compositions (black ■). Surface compositions examined in published LEIS studies by various authors are labeled in color: blue Swartzfager⁶⁰ (blue, ▲), Yi⁵⁹ (blue, ◆) and Boes²² (blue ●) measurements on PdAu. In green, Priyadarshini⁷ (green, ►) measurements on CuPd. In purple, Beikler⁶⁹ and Taglauer^{69,70} (purple, ♥) measurements on CuAu. In red, Miller¹⁰ (red, ♥) measurements on CuAuPd.

3.4.1.2 XPS mapping

XPS of Cu $2p_{3/2}$, Au $4f_{7/2}$ and Pd $3d_{5/2}$ on 164 points were collected after annealing at 800 K, and corresponding details can be found in an earlier work published by Xiaoxiao. The core-level shift in Cu $2p_{3/2}$ clearly showed the existence of the B2 phase region, in which the ordered BCC structure changed the coordination number of Cu inside the lattice.

Angle-resolved XPS was also collected at 16 different detection angles.

3.4.1.3 LEIS mapping

Several sets of 164 LEIS spectrums were collected by Chunrong Yin on a CuAuPd CSAF after proper surface treatment. Due to the long time needed to reach equilibrium composition at low temperatures and surface contamination during this period, datasets collected at 300 K and 400 K surface temperatures could not represent equilibrium conditions as LEIS ion yield in these datasets was much lower than a normal level, which indicates the presence of surface carbon and oxygen adsorbates; 1 hour of stabilization before data collection was also far from the time needed to reach equilibrium. Thus, only two datasets collected at 500 K and 600 K surface temperature are shown in the following analysis.



Figure 3.3 He^+ LEIS spectra at 164 bulk $Cu_xAu_yPd_{1-x-y}$ alloy compositions obtained at 500 K (left) and 600 K (right); ($He^+ E_0=1$ keV; scattering angle = 103°; scan time = 50 sec/pt; He^+ beam diameter = 500 µm). The Cu, Au, and Pd peaks are well-resolved and their peak energies, E/E_0 , match the predictions of the binary collision model.

Figure 3.3 shows a set of 164 LEIS spectrums collected at 600 K using a collection angle of 27.5 degrees from the sample surface normal, and Cu-Pd-Au components can be resolved following an increased kinetic energy order, as predicted by the binary collision model. The standard way of quantifying a LEIS spectrum requires knowledge of relative sensitivity factors (RSFs) between

different components, which is a combined effect of scattering cross-section, neutralization probability, and surface packing density. Such RSFs can be determined by taking LEIS spectrums on well-defined single crystal surfaces of each pure metal so that the surface atom density is known and the product of scattering cross-section and neutralization probability can be calculated using the ion yield and sample current. This method usually leads to the discussion of many details due to anisotropy since the angle between incident ions and crystalline orientation can strongly affect the ion yield, and more experiments need to be conducted. A polycrystalline surface contains a collection of grains with various surface orientations, so a calibration using polycrystalline pure metals would be more appropriate. However, such calibration is not necessary when the full composition space of an alloy system is mapped in a single batch of high throughput experiments, since there are regions with pure components on the sample that can be readily used as a calibration.

By plotting the signal intensity of one metal, usually using the peak area of that component, against that of another metal using data along binary composition lines, one should get a straight line if the matrix effect is absent and surfaces are smooth and clean. The slope of that line is the RSF between two components without considering surface atom density differences. More assumptions behind this statement include that all alloys have the same crystal structure or different structures with the same surface atom density, and the number of grains inside the ion beam region is large enough to be statistical, so that it is safe to assume anisotropy can be averaged out. Slopes between CuPd, CuAu and PdAu are 2.0, 2.0, and 1.0, which are later used for surface composition quantification.



Figure 3.4 Ternary diagrams showing the fractional excess surface atom density, $f_{\rho}(x, y)$, defined by eq. 7. Data was obtained at 500 K (left) and 600 K (right). The blue region centered at Cu_{0.5}Pd_{0.5} shows notably lower (~50%) surface atom density than expected, indicating the presence of the B2 structure.

How LEIS should be quantified, how RSF is used, and how normalized LEIS intensity is defined will be illustrated in the following section using a set of equations:

Ignoring matrix effects, the LEIS intensity (peak area) from each component should be proportional to its areal surface atom density, ρ_i ,

Equation 3.17 $I_{Pd}(x, y) = I_{Pd}^{\circ} \frac{\rho_{Pd}(x, y)}{\rho_{Pd}^{\circ}}$

where I_{Pd}° and ρ_{Pd}° are the LEIS intensity and surface atom density of a clean, pure Pd surface, respectively. The surface atomic fraction can be expressed as

Equation 3.18 $\theta_{Pd}^{top}(x, y) = \frac{\rho_{Pd}(x, y)}{\rho_{tot}(x, y)} = \frac{\rho_{Pd}(x, y)}{\rho_{Cu}(x, y) + \rho_{Au}(x, y) + \rho_{Pd}(x, y)}$

Substituting Equation 3.17 into Equation 3.18 gives

Equation 3.19 $\theta_{Pd}^{top}(x,y) = \frac{\rho_{Pd}^{\circ} \frac{I_{Pd}(x,y)}{I_{Pd}^{\circ}}}{\rho_{Cu}^{\circ} \frac{I_{Cu}(x,y)}{I_{Cu}^{\circ}} + \rho_{Au}^{\circ} \frac{I_{Au}(x,y)}{I_{Au}^{\circ}} + \rho_{Pd}^{\circ} \frac{I_{Pd}(x,y)}{I_{Pd}^{\circ}}}$

Equation 3.20
$$\theta_{Pd}^{top}(x, y) = \frac{\frac{I_{Pd}(x, y)}{I_{Pd}^{\circ}}}{\left[\frac{I_{Pd}(x, y)}{I_{Pd}^{\circ}}\right] + \frac{\rho_{Cu}^{\circ}}{\rho_{Pd}^{\circ}} \left[\frac{I_{Cu}(x, y)}{I_{Cu}^{\circ}}\right] + \frac{\rho_{Au}^{\circ}}{\rho_{Pd}^{\circ}} \left[\frac{I_{Au}(x, y)}{I_{Au}^{\circ}}\right]}$$

The value of $\rho_{tot}(x, y) = \rho_{Cu}(x, y) + \rho_{Au}(x, y) + \rho_{Pd}(x, y)$ used in Equation 3.18 can be estimated using Vegard's law and the lattice constants of the three pure components. The surface atom density at any given bulk composition, (x, y) can be estimated from the measured LEIS signals.

Equation 3.21
$$\rho_{tot}(x,y) = \frac{\rho_{Cu}^{\circ}}{I_{Cu}^{\circ}} \cdot I_{Cu}(x,y) + \frac{\rho_{Au}^{\circ}}{I_{Au}^{\circ}} \cdot I_{Au}(x,y) + \frac{\rho_{Pd}^{\circ}}{I_{Pd}^{\circ}} \cdot I_{Pd}(x,y)$$

This can be compared with the expected value of the surface atom density based on the primitive lattice constant, *a*, predicted from Vegard's law, $\rho_V = a^{-2/3}$, at each alloy composition. The fractional surface atom density observed relative to that expected from the FCC bulk structure of the three pure components is now defined as

Equation 3.22
$$f_{\rho}(x, y) = \frac{\rho_{tot}(x, y)}{\rho_V(x, y)}$$

Following the idea of getting RSFs, we can back-calculate and check whether all surfaces satisfy our assumptions. A normalized LEIS intensity is defined in Equation 3.22, equivalent to the sum of all metal signals divided by their corresponding signal on a pure component point. When such normalized LEIS intensity is plotted as shown in Figure 3.4, we can see values close to identity on most compositions but with two exceptions: one low-signal region with up to 50% signal decrease overlaps with known B2 phase region, and another one with 20-30% signal decrease close to equimolar PdAu composition. The low LEIS signal in the B2 (ordered BCC structure) phase region is not surprising since pure FCC structure no longer exists, while BCC does not possess a close-packed surface termination, and the low surface atom density results in a drop in LEIS signal. Signal drop in the PdAu region is consistent with the segregation profile along the PdAu binary composition line, in which a convex curvature can be found in the same composition region, indicating at least a relative decrease of Au on the surface. Such curvature was also found in literature, and yet its origin is still unclear; according to the author's experience and observations in other experiments, this is correlated with slight surface contamination in this specific alloy composition region, while this tendency of being covered by adsorbates faster than neighboring compositions again indicates a unique chemical or structural property.



Figure 3.5 Ternary diagrams showing excess surface concentrations of Pd, Cu, Au defined by eqs. 2 a,b,c. Data was obtained at 500 K (first row) and 600 K (second row). The blue regions on the Cu and Pd maps indicate lower surface coverage of Cu, Pd than in the bulk, and the red regions on the Au maps indicate the Auenriched top surface; Cu is enriched on the surface only at low Au compositions.

The surface atomic fraction of each component was calculated using Equation 3.20, and for the sake of easier comparison, excess surface concentrations - defined as the difference between surface and bulk concentrations of a component, were plotted in ternary diagrams as shown in Figure 3.5. Au segregation/enrichment occurred on all Au-containing compositions, which is consistent with two main driving forces of surface segregation: surface energy and lattice strain. Au has the lowest surface energy among the three elements in the CuAuPd alloy system, and it also has the largest atom diameter; segregating to the top surface can reduce the surface energy and also release lattice strain. Cu segregation was found in all CuPd alloys, as shown in Figure 3.7, mainly driven by its lower surface energy compared to Pd. In the B2 phase region, segregation is weak due to the short-range ordering tendency, which reflects the strong interaction between Cu and Pd. The CuPd binary segregation profile can be well-explained by segmenting it into FCC, B2, and transition regions. CuAu and PdAu segregation profiles (Figure 3.8, Figure 3.9) both show enrichment of Au, and are compared to available results from the literature.

By extending the Langmuir-McLean equation to the ternary system, segregation in a ternary alloy can be viewed as three pair-wise atom exchange processes. Using top-surface compositions determined by LEIS and bulk alloy compositions determined by EDX, equilibrium constants of 3 pair-wise exchange 'reactions' can be calculated using equation set 3.4.1.3.3, which can be further converted to segregation free energy. With free energies at several different temperatures, one can in principle separate enthalpy and entropy contributions, but

it is not possible here due to the narrow temperature window and the slight difference between 500 K and 600 K data. Pair-wise segregation energies are shown in Figure 3.6, with values ranging from 5 to 20 kJ/mol. Since equilibrium constant is defined by ratio, determination of segregation free energy is not accurate when any term in the denominator is close to zero; thus, each free energy plot only covered a portion of the ternary diagram.



Figure 3.6 Ternary diagrams showing pair-wise segregation Gibbs free energies defined by eq. 13. Data was obtained at 500 K (first row) and 600 K (second row), figures from left to right are ΔG_{PdCu} , ΔG_{AuPd} , ΔG_{CuAu} in a unit of kJ/mol. Pair-wise segregation free energies <10 kJ/mol are observed in these experiments.



Figure 3.7 Comparison of PdCu segregation profile at 500 K with similar data in the literature⁷. Obvious deviations occur over the \bar{x}_{Cu} range of 40%-60%, which reveals suppression of the Au segregation relative to alloys outside this range. Compositions boundaries of FCC, B2, and transition regions from the literature are labeled with dotted lines. An offset of ~4 at% in the B2 phase region is observed between current work and literature.

Many surface segregation studies on PdCu have been published;^{7,32–35,84–87} most on discrete composition samples,^{33,84,86,87} in presence of adsorbates^{32,33} or studied by surface analysis methods that are not as accurate as LEIS.⁸⁵ Only Priyadarshini's work,⁷ whose measurements were also done on a CSAF with a continuous composition spread and under UHV conditions, will be compared with data from the current work. Points on the CSAF with bulk *Au* atomic concentrations < 2% (within EDX uncertainty) have been normalized to describe only their *Pd-Cu* binary compositions, and the corresponding segregation profiles at 500 K and 600 K are shown in Figure 8 and compared to that of Priyadarshini *et al.*⁷ Compositions outside the B2 region agree fairly well with earlier results, while an obvious deviation can be seen within the B2 region, where *Cu* shows little tendency to segregate.

Several differences between the experimental setup and treatment of the CSAFs in Priyadarshini's work and this experiment may have contributed to the fact that the effect of the B2 phase was not observed earlier. A single crystal Mo(110) substrate was used in Priyadarshini's work, which may lead to preferential ordering of grain orientations, while a polycrystalline Mo substrate was used in this study. The previous work also took only two measurements across the composition region of the B2 phase. Perhaps the most critical difference between the two experiments is the fact that in Priyadarshini's experiments, the sample was cooled actively using liquid nitrogen, allowing much more rapid cooling from the annealing temperature to the measurement temperature. Prior work has shown that rapid cooling can freeze the CuPd alloy into the high-temperature FCC phase at all compositions^{86,88}. This would be sufficient for the B2 phase to have been missed in the earlier segregation study.

We observe a decrease in the *Cu* segregation over the composition range of the B2 phase existence (Figure 3.7) to the point that there is no excess surface Cu at bulk Cu compositions in the range $0.45 < x_{Cu} < 0.52$. The origin of the apparent discontinuity in the Cu segregation profile over the composition range associated with the B2 phase may be the fact that the B2 phase is an ordered alloy (*CsCl* structure on a BCC lattice) while the FCC phase is disordered. The ordered bulk structure implies that enthalpy has dominated over the configurational entropy of the disorder FCC structure. Presumably, this also inhibits the exchange of Cu atoms from the bulk B2 structure with surface *Pd* atoms. Verifying this would require computational simulation of segregation in the CuPd system.³⁵



Figure 3.8 PdAu segregation profiles at 500 K and 600 K (open symbols) compared with data from Swartzfager,⁶² Yi,⁶¹ and Boes.¹⁷ Au segregation are enhanced at higher temperatures. The segregation profiles all show deviation from convex to concave curvature at a bulk Au fraction of $\bar{x}_{Au} = 0.5$.



Figure 3.9 Segregation of Au in Au_xCu_{1-x} at 500 K and 600 K. Segregation does not show temperature dependence over the measured range. The excess surface coverage of Au is higher over the Au rich composition range than over the Cu rich range. The top surface composition is ~100% Au when the bulk Au concentration is >70 at%.

At T>700 K, Cu_xAu_{1-x} alloys at all compositions form random solid solutions on an FCC lattice (see Figure S3).⁸⁹ Cooling to T<500 K results in the formation of three ordered phases with nominal stoichiometries Cu₃Au, CuAu and

CuAu₃. At 600 K, one has order phases over the range $0.2 < x_{Au} < 0.65$. Special attention has been paid to Cu₃Au because of its surface ordering properties.⁹⁰ As a result of strong ordering tendency, Cu₃Au (100) exhibits almost ideal termination at T<663 K³⁷ (order-disorder transition temperature) with a top layer *Au* composition of $\theta_{Au} = 0.5$ and a second layer *Au* composition of $\theta_{Au}^{2nd} = 0$. On Cu₃Au (100) some intermixing was observed⁹¹ between the first and second atomic layers, and $\theta_{Au} \approx 0.4$ at around 500-600 K. A LEED study⁹² shows no segregation of Au on the Cu₃Au (111) surface. On CuAu (100) a topmost layer Au composition of $\theta_{Au} = 0.93$ was measured by LEIS at 400-700 K.^{81,93}

Figure 3.9 shows segregation profiles obtained in this work at 500 K and 600 K, revealing excess Au at all surface compositions and low-temperature dependence. However, it is quite clear that the degree of surface segregation over the bulk Au composition range $0.2 < x_{Au} < 0.5$ is relatively low. In contrast, for bulk Au compositions over 50 at%, $x_{Au} > 0.5$, the degree of surface segregation increases dramatically to the point that for $x_{Au} > 0.7$ the topmost surface has $\theta_{Au} \approx 1$. This is consistent with observations from the literature,⁹² in which stronger Au segregation was observed at $x_{Au} = 0.75$ than that at $x_{Au} = 0.25$ by AES.

3.4.1.4 UPS mapping

UPS spectrums were collected on the same 164 CuAuPd alloy compositions at sample temperatures ranging from 400 to 600 K. One set of spectrums is shown in Figure 3.10 A, in which the color of each line indicates the bulk composition of the alloy. Several characteristic features can be observed: Au has an excitation peak at ~6 eV in binding energy, Pd has a strong peak near the Fermi level, and Cu has a peak near 2 eV. The high binding energy end of the spectrums is attributed to secondary electrons and does not contain much detailed information. Figure 3.10 B-D compare UPS spectrums along each binary alloy composition line, and the line colors in each plot represent concentration gradients. A smooth transition from one spectrum shape to another when composition changes can be seen in all plots.

Work function can be calculated by subtracting bandwidth from excitation source energy. Figure 3.10 G shows work functions across composition space. It is clear that Pd has the highest work function among the three elements, which extends to a large region in high-Pd compositions, although segregation results indicate Au-enriched surfaces. Based on the peak positions in UPS spectrums collected, the cut-off binding energy of 8 eV was chosen for background subtraction: for binding energies higher than the cut-off value, measured spectrums only consist of the background from inelastic scattering; for binding energies lower than the cutoff value, 'total backgrounds' were subtracted following an iterative procedure described in the literature⁹⁴, which assumes each electron generates an energyindependent distribution of secondary electrons at lower kinetic energies. One set of 164 background-subtracted UPS spectrums was shown in Figure 3.10 E.



Figure 3.10 A) one set of 164 UPS spectra collected on CuAuPd CSAF. B-D) UPS spectra on binary alloys. E) background-subtracted UPS using 8 eV cut-off. F) band-center of background-subtracted UPS spectra. G) d-band energy.

Band centers were also calculated by finding binding energy that evenly splits the area under curve of the background-subtracted spectrums, and are shown in the ternary diagram in Figure 3.10 F.

UPS spectra collected in this work are consistent with existing works on CuAu binary alloys⁹⁵, demonstrating the capability of using CSAF as a high-throughput platform for UPS mapping across alloy composition space. The detailed analysis of UPS is beyond the scope of this work.

3.4.2 NiPdAu alloy system

Similar to other Pd-containing alloys, NiAuPd alloys found their application in the hydrogen separation process as membrane material⁴⁶: the addition of Au increases its tolerance to sulfur poisoning, and the addition of Ni can lower material cost while maintaining similar H₂ permeability or even enhance permeability at a proper Ni concentration. NiAuPd was also proved to be an efficient Pt-free catalyst for direct ethanol fuel cell application^{47–49}, showing higher power density than that of pure Pd or commercial Pd/C and Pt/C catalysts. Other applications of NiAuPd include low-resistance ohmic contact⁵⁰ in semiconductors and electrocatalyst for ORR/OER⁵¹.

The phase diagram of the NiAuPd alloy system is well known from databases, and it is included in the Appendix (section 1) for reference. An immiscibility gap exists along NiAu binary compositions and extends to ~15 at% Pd. Surface segregation in NiAu^{52,53}, AuPd^{1,5,27} and NiPd^{54–58} binary alloys are also studied in several works. NiAu is also a prominent example of 'rational catalyst
design⁵⁹, in which the surface composition can be accurately tuned by controlling the temperature and gas environment.

3.4.2.1 EDX mapping

Two NiPdAu CSAFs were prepared and studied in this work. Figure 3.11 shows the selection of 176 points on one CSAF that spans ternary composition space. These points were selected to have a minimum spatial separation of 500 um so that there is no substantial overlap between points during XPS and LEIS measurements; a 5 at% compositional resolution was also targeted, and the 176 points were chosen to best satisfy these requirements. The sampling sequence was decided such that high Ni content compositions were sampled first, since surface contamination (adsorption from the ambient environment) is always a problem on high Ni-content surfaces even under UHV conditions, while Au-rich surfaces can stay clean much longer.



Figure 3.11 (A) 176 points were selected on NiPdAu CSAF based on SEM-EDX measured compositions for segregation studies. (B) Ternary NiPdAu composition diagram showing the compositions at which EDX and LEIS spectra were obtained from the CSAF.

3.4.2.2 XPS mapping

XPS of Ni 2p_{3/2}, Pd 3d_{5/2} and Au 4f_{7/2} were collected to determine nearsurface compositions, and CLS can also be determined by comparing the peak position of each element in alloys and that in pure components. Due to overlaps between Pd 3d_{5/2} and Au 4s, accurate deconvolution and peak position determination are challenging and not discussed here.

XPS depth profiles on selected positions of the CSAF were also collected to examine the uniformity of alloy composition throughout the film, as shown in Figure 3.12. XPS of Pd 3d_{5/2}, Ni2p_{3/2}, Au 4f_{7/2} and Mo 3d_{5/2} were taken after every 10-20 sec of 3kV Ar⁺ sputtering until the signal from the CSAF component disappeared. The initial signal increase in Pd, Ni and Au was due to the removal of surface contaminants. While uniform depth profiles were observed on PdAu binary alloy, there was a continuous change in composition in NiAu alloy film, which might be caused by immiscibility between Ni and Au, resulting in the formation of Au-rich near-surface region and Ni-rich underlayer. Thus, careful examination is needed when similar alloys are studied using similar thin-film methodologies; otherwise, there could be a big mismatch between average bulk composition and actual near-surface composition, which will also bring difficulties to data reproducibility.



Figure 3.12 XPS depth profiles of a PdAu binary alloy, a uniform Ni film, and a NiAu binary alloy on the same NiAuPd CSAF. Peak areas of Ni $2p_{3/2}$, Au $4f_{7/2}$, Pd $3d_{5/2}$ and Mo $3d_{5/2}$ are plotted versus Ar etch time. An increase in substrate Mo signal indicates a thin film-substrate interface. Uniform alloy composition across depth can be found on PdAu alloy, but NiAu alloy shows a non-uniform depth profile, probably due to phase separation.

3.4.2.3 LEIS mapping

Figure 3.13 shows segregation profiles with surface compositions determined by He⁺ LEIS. Figure 3.13A and Figure 3.13B show the Ni-concentration-dependent segregation of Au and Pd: with the same Au concentration in the bulk, Au enrichment became the strongest as Ni content increased; the same applied to Pd, while Pd depletion from the surface was observed when there was no Ni, Pd enrichment was found at high Ni contents. Figure 3.13C provides another way of visualizing pair-wise interactions, in which 'normalized' bulk and surface compositions are defined as shown in the axes labels.



Figure 3.13 Surface segregation profiles of NiAuPd alloy system. Au enrichment and Ni depletion were found on all alloy compositions, while Pd enrichment was only found on alloys with low Au content.

3.4.3 CuAgAu alloy system

Coinage metals (Cu, Ag and Au) have been used as catalysts for many oxidation and reduction reactions, including CO oxidation^{60–62}, CO₂ reduction⁶³, alkene partial oxidation^{64–66}, alcohol partial oxidation^{67,68}, etc. Besides its widespread application, the CuAgAu system was chosen in this study for the following reasons: 1) Cu, Ag and Au have very different masses ($m_{Cu} = 63.5, m_{Ag}$ = 107.9, $m_{Au} = 197.0$), which allows resolution of the peaks in He⁺ LEIS spectra and thus easy quantification of surface composition; 2) all three elements stay relatively clean under UHV conditions, especially Ag and Au, which minimizes surface contamination during experiments, as a clean surface is needed in LEIS measurements; 3) surface segregation in all three binary alloys ($CuAg^{69-71}$, $CuAu^{72,73}$ and $AuAg^{15-18}$) has been described in the literature providing some benchmarks for our study of the ternary system; 4) Cu, Ag and Au have fcc structures in their pure metals as well as alloys, and the binary as well as ternary phase diagrams [Appendix section 1] are known and reveal a big immiscibility gap originating from CuAg binary compositions extending to ~60 at% Au. Thus, segregation behavior inside the immiscibility gap can be studied comprehensively for the first time.

Existing segregation studies of the CuAgAu system are mostly limited to binary alloy compositions (see Section 4.2 for details). The only measurement of surface segregation in a true ternary CuAgAu alloy was made by Hoffmann and Wynblatt⁷⁸ on three Cu-rich compositions (Cu₉₂₋₉₇Ag_{0.3-1}Au₂₋₇) using AES. Due to the high surface energy of Cu relative to Ag and Au ($\gamma_{Cu} = 1.409$, $\gamma_{Ag} = 1.091$ and $\gamma_{Au} = 0.886$ J/m² on the fcc (111) surfaces⁷⁹) and the large lattice mismatches ($a_{Cu} = 3.615$, $a_{Ag} = 4.085$ and $a_{Au} = 4.078$ Å), depletion of Cu was observed in CuAg^{69–71} and CuAu^{36,72,80,81} alloys. Ag enrichment up to 20 at% in the top-surface was observed in AuAg alloys^{15–18}; Au enrichment up to 20 at% was observed in CuAu alloys, and surface coverage of $\theta_{Ag} \cong 1$ was observed in CuAg alloys even at bulk Ag concentrations as low as $x_{Ag} = 1$ at% ^{69–71}. It should be noted that Cu and Ag are immiscible in the bulk CuAg alloy, and two fcc_A1 phases⁸² [Appendix section 1] co-exist at T < 1050 K. Due to the strong segregation of Ag in CuAg alloys and the broad immiscibility gap (spanning from 1 at% < x_{Ag} < 99 at% at 600 K), the surfaces of CuAg alloys having compositions within immiscibility gap are expected to be almost fully covered by Ag. However, this has not been explicitly reported in the literature, to the best of our knowledge. Surface segregation in several Cu-rich compositions of CuAgAu was measured by Hoffman and Wynblatt⁷⁸ and showed strong Ag segregation at 800 K. Au segregation only occurred when little or no Ag was present in bulk.

3.4.3.1 SEM/EDX mapping

Three CuAgAu CSAFs were prepared for segregation studies, dewetting characterizations as well as near-ambient-pressure (NAP) XPS studies. Composition-position maps were shown in Figure 3.14, color of each circle represents its bulk composition using an R-G-B mixing, corresponding to the atomic fractional concentration of Cu, Au and Ag, respectively. The size of each circle represents the thickness of the as-deposited thin film at the corresponding location, while less than 10% of total thickness loss was observed in CSAF #1 and #2 which were used in equilibrium and kinetic studies under UHV conditions, and there was no significant bulk composition change due to material loss in surface sputtering and evaporation. CSAF #3 went through cycles of annealing under oxygen as well as hydrogen environments during NAP-XPS, while a significant amount of material loss was found after the experiment, and the composition change in the bulk composition of thin-film will be discussed in corresponding sections.



Figure 3.14 Thickness-composition-position maps of 3 CuAgAu CSAFs used in this work. The size of each circle represents the local film thickness, as indicated by the black scale bar on the right-hand side of each figure; circles are colored by their atomic composition determined using EDX with R-G-B mixing (corresponding to Cu-Ag-Au, as shown in subtitles of figures).

Figure 3.15 is an overview of the composition space and compositional resolution mapped out in this work, as well as compositions on which segregation was studied in the literature. A fine grid with ~5 at% resolution was achieved, and the reproducibility of segregation under the UHV conditions was confirmed using two separate CSAFs.



Figure 3.15 Ternary CuAgAu composition diagram showing the compositions (open squares) at which EDX and LEIS spectra were obtained from the CSAF. These demonstrate complete coverage of the composition space by the CSAF. Also shown are the compositions at which surface segregation on AuAg and CuAu alloys has been studied in other work using LEIS (filled squares). The filled triangles denote binary and ternary alloy compositions studied using Auger Electron Spectroscopy.

High-resolution SEM images were taken on the as-deposited as well as postexperiment CSAFs to characterize microstructure change upon annealing. Besides ex-situ SEM imaging, in-situ imaging with a digital camera was also applied to keep track of sample morphology changes during annealing. On both CSAF #1 and CSAF #2 that went through annealing under UHV up to 800 K, dewetting was found to be composition dependent, as illustrated in Figure 3.16: 4 SEM images representing surfaces of different alloy compositions were compared. All compositions along Cu-Au binary line maintained intact and smooth surfaces, while a large portion of ternary alloys with low to medium Au content dewetted into nanoparticles or formed pin-holes, and almost all Cu-Ag binary alloys also dewetted. Such dewetting pattern is consistent with the immiscibility gap in CuAu-Ag ternary phase diagram, in which phase segregation occurred during annealing, and the formation of the Cu-rich phase and Ag-rich phase destabilized the thin film. More SEM images showing the surface morphology transition along binary compositions can be found in Appendix section 2.



Figure 3.16 Representative SEM images of the CSAF at three alloy compositions after segregation measurements. a) $Cu_{0.98}Ag_{0.02}$ forms nanoparticles as a result of thin-film dewetting. b) $Cu_{0.06}Ag_{0.94}$ forms a porous 2D network structure, intermediate between the intact film and nanoparticles. c) $Ag_{0.4}Au_{0.6}$ has large pinholes. d) $Cu_{0.4}Au_{0.6}$ does not dewet and remains an intact film.

The evolution of dewetting as a function of annealing temperature and time can also be seen from images taken by a digital camera/microscope. Due to the field-of-view limit, a collection of 196 images were taken in each round on a 14×14 mm² grid, and the center 1×1 mm² square region of individual images was combined to give a full view of the sample surface. Images can be found in Appendix section 2. The original images were dark due to insufficient lightening

inside the UHV chamber, but images after brightness and contrast enhancement showed a clear location-dependent surface structure: consistent with the dewetting map, stronger photon yields/brighter images were found in the Cu-rich region as well as Ag-rich region, which matched the boundary of immiscibility gap. The bright feature in the Cu-rich region was first observed upon annealing at 700 K under UHV for 15 min, and it grew brighter and larger after prolonged annealing. It is known that coinage metals (Cu, Ag and Au) have unique light-scattering properties, and the formation of nanoparticles enhanced the scattering of visible light, thus the microscopic images showed the same pattern as that of electron microscopic images. A series of images taken by the digital camera in the XPS chamber was shown in Figure 3.17, with annealing conditions labeled aside each image; photos of CSAF before and after annealing were shown in Figure 3.18, and Mo 3d_{5/2} XPS maps alongside Figure 3.18 for reference. The quantitative substrate exposure was estimated by comparing SEM images with Mo XPS at the end of the experiment, in which the largest substrate exposure area was ~50% and linked to the strongest Mo XPS signal. Results of substrate exposure estimation are shown in Figure 3.19.



Figure 3.17 Contrast-enhanced images of CuAgAu CSAF after various extents of annealing under UHV; (Right) Mo $3d_{5/2}$ XPS map across composition space after annealing, indicating the extent of thin-film dewetting (exposure of Mo substrate)



Figure 3.18 As-deposited CuAgAu CSAF and dewetted CuAgAu CSAF after thermal annealing up to 800 K

Dewetting phenomenon itself is an interesting topic in thin-film studies, but the main reason why it was examined with great care in this work is its potential influence on surface segregation quantification. In LEIS measurements, quantification of surface composition relies on the mass separation between major components. In the case of dewetting, however, since the mass of Mo is similar to that of Ag (and also similar to Pd in the case of CuAuPd and NiAuPd ternary systems; Mo = 96.0, Ag = 107.9, Pd = 106.4), exposure of substrate upon the formation of pinholes or nanoparticles will bring difficulties to LEIS spectra deconvolution and increase its uncertainty. It was found that in NiAuPd alloys, dewetting of thin-film exposed Mo substrate underneath, and the Mo signal can be resolved in LEIS spectrums due to its mass difference from Pd. In CuAgAu alloys, ~50% of the substrate surface was not covered by thin-film or nanoparticle/nanonetwork in the most dewetted region determined by XPS, as shown in Figure 3.19. However, such Mo was absent from LEIS spectrums even in regions where dewetting was confirmed by XPS, digital camera imaging as well as SEM imaging. It can be explained by the nature of surface segregation – segregation is driven by the tendency to minimize surface energy, while Ag has much lower surface energy

than Mo such that a monolayer coverage of Ag on Mo surfaces can significantly stabilize the system. Thus, only more Ag could be found on dewetted zones of CuAgAu alloys rather than Mo in LEIS. Due to the already strong Ag enrichment on the top surface, extra Ag signal covering on the exposed substrate did not significantly alter the absolute values of the atomic fraction.



Figure 3.19 Mo substrate exposure as a result of dewetting after annealing at 800 K calculated with SEM imaging and Mo 3d XPS. Substrate exposure is mainly concentrated in Cu-rich and Ag-rich regions, with maximum substrate exposure being 50% of the total surface at Cu_{92.8}Au_{0.7}Ag_{6.5} composition. The evolution of substrate exposure as a function of annealing temperature and time can be found in Supporting Information (Figure S4 – S6)



Figure 3.20 SEM-EDX mapping of $Cu_{0.5}Ag_{0.5}$ composition region. A) Electron image, particles ~ 1 um in diameter. B) Over layered electron image and EDX maps of Cu Ka1 and Ag La1 lines. Although constrained by spatial resolution, phase segregation of CuAg alloy into Cu-rich and Ag-rich phases can be seen.

The evolution of dewetting during thermal treatment was tracked in-situ inside the UHV chamber during segregation studies by microscopic imaging and XPS, and SEM/EDX information was also collected before and after all studies performed in the UHV chamber. A microscope right above the CSAF surface with a field of view of $\sim 2 \times 1.5$ mm was used to record images at a grid of points, then the centers of images were combined to give the full picture of the sample surface, as is shown in Appendix section 2. Due to insufficient lighting in the UHV chamber, the original images were dark, while contrast enhancement of images makes the dewetting pattern more obvious. Such combined images were taken after various thermal annealing at 700 K, 750 K, and 800 K, and the bright band starting from the Cu-rich corner (lower-left in images) as well as the moisty region in AgAu binary compositions indicate the start and evolution of dewetting.

3.4.3.2 XPS

XPS spectrums of Cu 2p_{3/2}, Ag 3d_{5/2} and Au 4f_{7/2} were collected across composition space on the clean CSAF surface. Core-level shift (CLS) can be calculated by comparing binding energies in alloys with that of pure metals, and is shown in Figure 3.20. Although pass energy used in XPS was 100 eV accurate quantitative composition determination, which resulted in broad peaks (FWHM \sim 2 eV), it is still clear that CLS is a smooth function of composition. Cu and Ag both shift to lower binding energies by less than 0.2 eV when alloyed, expect a minor increase in binding energy within the immiscibility gap; Au peak shifts to higher binding energies with a maximum of \sim 0.5 eV in Cu-rich alloys, while \sim 0.2 eV shift is observed in Ag-rich alloys.



67



Figure 3.21 Core-level XPS peak positions (binding energies in eV) of Cu, Ag and Au in CuAgAu alloys relative to their pure metals

3.4.3.3 LEIS

Low energy ion scattering spectrums on 143 different bulk compositions (including pure components) were collected at 500 - 800 K. Figure 3.21 is a summary of equilibrium surface compositions. Surface segregation can be illustrated by mapping the coverage of each alloy component in the topmost layer, θ_i , across ternary alloy composition space or by mapping the surface excess of each component relative to the bulk alloy composition of that component, $\theta_i - x_i$. Figure 3.21 shows the measured surface compositions at 800 K in the form of surface concentration maps, as well as maps of the differences between surface concentrations and 800 K and those at temperatures in the range of 500 to 750 K. As shown in the top row of Figure 3.21, Cu is absent from the topmost surface at most bulk compositions across the 500 to 800 K range, resulting in AgAu binary alloy surfaces. Depletion of Cu and enrichment of Ag on the surface at all alloy compositions are consistent with their surface energies (~1.8, ~1.25 and ~1.5 J/m² for Cu, Ag and Au, respectively on fcc (111) surfaces⁹⁶), with the components having lower surface energies being enriched on the surface. Au segregation was

observed only near the CuAu binary composition line in the ternary diagram; i.e. when there was little Ag present. Along the CuAu binary line, Au segregates preferentially as a result of its having lower surface energy than Cu. In addition, Au segregation also releases strain in the bulk lattice arising from its diameter being greater than that of Cu. Au enrichment rapidly turns into depletion when Ag is present in the alloy. Temperature dependency is most prominent in a Cu-rich region, which coincides with thin-film dewetting; this clear temperature dependency is not surprising since Ag segregation is very strong and all bulk alloys with Ag content >20 at% are basically free of Cu on the surface, so the temperature dependency of entropy-driven segregation can only be observed in Cu-rich region.

A comparison of data collected in this work with existing literature along 3 binary composition lines is shown in Figure 3.22, Figure 3.24 and Figure 3.25.



Figure 3.22 First row: top-surface composition θ_{Cu} , θ_{Ag} , θ_{Au} at 800 K measured by LEIS (in at%); Second row and below: the difference between top-surface composition at 500 to 750 K and the top surface composition at 800 K. It is clear that segregation of Ag is weaker when T > 700 K, while the surface concentration of Au is only weakly dependent on temperature.

3.4.3.3.1 Segregation of AgAu alloys

AgAu alloys have been tested as catalysts in several reactions including CO oxidation^{61,62} and 4-nitrophenol reduction^{97–99}. Au and Ag have FCC structures in their solid forms, and due to their negative formation energy, AgAu alloys are miscible at all ratios, forming FCC alloys. AgAu segregation has also been studied in several prior studies using LEIS^{76,77} and AES^{74,75}. The surface-bulk concentration relationship measured over the temperature range of 500 - 800 K in this work is shown in Figure 8A, along with experimental results from Nelson⁷⁷, Kelly⁷⁶, Yabumoto⁷⁵ and King⁷⁴. The comparison of segregation at temperatures spanning the range 500 - 800 K is shown in Figure 3.22. Results in this work have been repeated on two CSAFs with high reproducibility and are consistent with earlier work using LEIS, further verifying the ability to study surface segregation using CSAFs. Due to the lower surface sensitivity of Auger Electron Spectroscopy (AES) compared to LEIS, surface enrichment of Ag measured using AES on polycrystalline AgAu alloys (red empty triangles in Figure 3.22.) is underestimated. Segregation enthalpy and entropy shown in Figure 3.23 suggest



Figure 3.23 Top panel) Segregation profile of AuAg binary alloys. (Orange filled region) measured at 500 - 800 K in this work; (solid triangles) LEIS measurements; (empty triangles) AES measurements. Segregation of Ag is observed at all bulk alloy compositions in this work, showing a smooth segregation profile across

composition space. Bottom panel) Excess Ag concentrations, defined by $\Delta_{Ag} = \theta_{Ag} - x_{Ag}$, are displayed in a heat map across the same temperature and composition range. Segregation is weakly dependent on temperature.

that swapping bulk Ag with surface Au atoms is energetically favorable, but due to the loss in entropy, segregation is weaker at elevated temperatures.



Figure 3.24 Linear fit of segregation free energy over temperature on selected AgAu alloy compositions, while intercept and negative slope are taken as segregation enthalpy and segregation entropy. Segregation enthalpy and entropy as a function of AgAu alloy composition

Examples of linear fitting of segregation free energy ΔG_{AgAu} on selected Ag_yAu_{1-y} alloys as a function of temperature are shown in Figure 3.23A, while segregation enthalpy ΔH_{AgAu} and segregation entropy ΔS_{AgAu} were taken from the intercept and negative slope of each fitting, respectively. ΔH_{AgAu} and ΔS_{AgAu} along the binary AgAu composition line are shown in Figure 3.23B. It has been generally assumed that segregation is mainly driven by the surface energy difference between components, and the enrichment of component with lower surface energy stabilize the surface. At the same time, the deviation from random solid solution as a result of preferential enrichment decreases system entropy. Thus, both segregation enthalpy and segregation entropy should be negative. However, fitting of segregation free energy over temperature gave positive numbers for both

energies in AgAu segregation. One possible explanation is that within the temperature range studied in this work (500 - 800 K), true equilibrium surface structures were not reached, while measured surface compositions are mainly affected by vacancies formation. As described in a recent study on Cu_{0.75}Au_{0.25}(111) single crystal¹⁰⁰ using near-ambient-pressure XPS and STM, higher temperature results in a higher concentration of thermal vacancies in the lattice; due to the lower formation energy of a Cu vacancy than that of an Au vacancy as well as its lower migration barrier, there will be much more Cu vacancies in the bulk at elevated temperatures, resulting in the formation of Cu-rich clusters on top of the planar surface. Thus, the measured surface compositions are affected by the existence of these clusters. When a surface is cooled down from elevated temperatures, nanoclusters tend to incorporate back into the lattice but can be kinetically limited. Following a similar analysis, Ag has even lower evaporation energy than Cu (300.3, 250.6 and 334.4 kJ/mol for Cu, Ag and Au, respectively), thus the equilibrium concentration of Ag vacancies in the bulk lattice should also be higher than Au vacancies, and this difference will become larger at elevated temperatures, providing sources for the formation of Ag-rich clusters on the surface. It should be mentioned that although the fittings of segregation free energy over temperature gave relatively good linear trends, the maximum differences in surface compositions between highest and lowest temperatures are quite small (on average 5 at%); that means the conclusion might be heavily affected by other systematic factors such as the stage expansion during heating/cooling, in which a slight 100 um position drift can cause 1.5 at% change in bulk composition. The main

takeaway from this work is that temperature and composition-dependent steadystate properties of alloys can be mapped out in a single batch of experiments using our high-throughput setups.

3.4.3.3.2 Segregation of CuAu alloys

CuAu alloys have been used as catalysts in CO₂ reduction⁶³ and HMF oxidation¹⁰¹ reactions. Both metals have FCC structure, and several ordered phases are known to exist at compositions Cu₃Au, CuAu and CuAu₃ below their transition temperatures (390°C, 410°C, and 199°C, respectively⁸¹). Segregation studies have mostly focused on these discrete compositions^{36,81,102–104}, while (100) surface is the most extensively studied surface orientation; the dependence of segregation on crystalline facets has been identified. The only known segregation study on continuous CuAu compositions using LEIS is a previous study done in our group on segregation in CuAuPd alloys, and their comparisons are shown in Figure 8; results from two more AES studies on CuAu surfaces by McDavid⁷³ and Reniers¹⁰⁴ are also shown for comparison. Surface enrichment of Au at all compositions is observed in both works, with stronger segregation on the Au-rich side.



Figure 3.25 Segregation profile of CuAu alloys. A) (shaded region) 500-800 K measured in this work; (empty squares and circles) data from the literature. 8B) Map of excess surface concentration of Au across 500-800 K range. Au surface

enrichment is shown in all alloy compositions, with stronger segregation on the Aurich side; weaker Au enrichment is found at higher temperatures as a result of the entropy effect.

However, data collected in this work shows stronger segregation on the Cu-rich side than in our previous study, which is likely due to the different thermal history of samples before LEIS measurements. Excess surface Au concentrations across composition and temperature range are shown in Figure 3.24, in which an overall trend of weaker Au segregation at higher temperatures can be observed, although linear fittings of segregation free energy over temperature are poor on individual compositions, and thus segregation enthalpy, as well as entropy, are not able to be determined accurately.

3.4.3.3.3 Segregation of CuAg alloys

CuAg system has a big immiscibility gap in its phase diagram [Appendix section 1], starting from < 1 at% Ag to > 99.5 at% Ag at 600 K. Most available segregation studies have focused on Cu-rich compositions using AES, in which strong Ag segregation was observed. Figure 3.3.3.12 A shows the segregation profile of CuAg consisting of 18 normalized compositions (Au content lower than 1 at% in the bulk), where normalized compositions are defined as follows:

$$x_{Cu}^{norm} = \frac{x_{Cu}}{x_{Cu} + x_{Ag}}$$
$$\theta_{Cu}^{norm} = \frac{\theta_{Cu}}{\theta_{Cu} + \theta_{Ag}}$$

The inset graph in Figure 3.25A shows segregation data in several existing literature^{70,105} on single crystals, and weaker Ag surface enrichment can be

observed in this work compared to literature. It should be pointed out that due to the extremely low concentration of Ag, uncertainties in bulk compositions are relatively high in all works, and thus the offset does not necessarily mean disagreement with previous works. Figure 3.25 shows the surface composition of Cu_{0.94}Ag_{0.06} alloy at 500-800 K. Temperature dependence in segregation can be observed, in which segregation is weaker at elevated temperatures as a result of the entropy effect. Due to the almost full surface coverages of Ag in alloys with bulk Ag content higher than 20 at%, temperature dependence cannot be accurately measured on these compositions.



Figure 3.26 Segregation profile of CuAg alloys. 9A: (black squares) measured at 600 K before film dewetting in this work. (Inset graph) comparison with available literature: (solid squares) AES measurements by Romeo; (empty triangles) AES measurements by van Wyk. Strong segregation of Ag is observed at all bulk alloy compositions in this work, with lower Ag concentration than literature at Ag<1 at%, which may indicate surface equilibrium was not achieved at 600 K. 9B: segregation measured at 500-800 K after CSAF annealing at 800 K, showing weaker Ag segregation with increasing temperatures when Ag<20 at% in the bulk, while alloy surfaces are fully covered by Ag when Ag>20 at%.

It is worth noticing that the surface diffusion of Ag across the lateral direction of the CSAF may affect the segregation results quantitatively: it was observed in our experiment that regions that were initially Ag-free had Ag signal in both LEIS and XPS after keeping at 600 K for more than two days, which in principle can due to surface diffusion or bulk diffusion and subsequent surface segregation. But since the surface diffusion coefficient is usually several orders of magnitude higher than that of lattice diffusion, and the grain sizes in the CSAF shouldn't exceed 10 um, the combination of high grain boundary diffusion area and high diffusion coefficient should make surface/grain-boundary diffusion the dominant factor resulting in the occurrence of Ag.

3.4.4 Segregation under oxygen environment

In previous sections, surface segregation and the effect of structure and temperature on segregation were discussed. Among the most important factors influencing segregation, the catalytic environment is at the top of the list. Adsorbate-induced segregation has been shown in numerous prior publications^{106–} ¹¹², with most studies conducted in such a way that samples were treated in a gas environment and then the surface compositions were measured after the evacuation of the gases. Due to the limitations of UHV equipment and methods, most surfacesensitive tools cannot operate under a pressure above 10⁻⁶ Torr, especially when oxidative/corrosive gases are involved. Surface characterization tools that operate at high pressures are either not surface-sensitive enough or not quantitative ¹¹³. Thanks to the recent advances in equipment design and manufacturing, more surface characterization tools can now operate at pressures closer to atmospheric levels, including a series of X-ray-based instruments such as near-ambient-pressure XPS (NAP-XPS). The use of an X-ray transparent window and a series of turbomolecular pumps makes it possible to allow the exposure of samples to pressures

up to ~ 10 Torr while maintaining the X-ray generation source and the detector under UHV conditions. Representative works that studied surface segregation using NAP-XPS include the study of CuNi nanoparticle phase segregation during CO_2 hydrogenation ¹¹⁴ and CuAg nanoparticle surface segregation during ethylene epoxidation ¹¹⁵.

In this work, the surface evolution of CuAgAu alloys under an oxygen and hydrogen environment was studied using a CSAF and the NAP-XPS instrument at the Center for Functional Nanomaterials (CFN) in Brookhaven National Laboratory.

3.4.4.1 Experimental section

A CuAgAu CSAF was deposited onto a Mo substrate of $14 \times 13 \times 3$ mm in dimension, as described in sections 3.1 and 3.4.1. The CSAF was first annealed and characterized with XPS under UHV. At CFN, the sample was loaded into the NAP-XPS chamber, in which proper position alignments were first conducted; XPS parameters, including the binding energy window for each element of interest, pass energy, and spectrum acquisition time, were estimated and optimized to allow efficient screening of 13 different locations on the CSAF within 2 hours. Heating control was achieved by using a laser focused on the bottom of the CSAF and a thermocouple spot-welded into the side of the substrate. The pressure over the range <10⁻⁴ Torr was controlled using a leak valve; while in order to reach higher pressures, the gate valve between the main turbopump and the chamber was closed, and the gas was pumped out through the tiny opening on the analyzer cone and evacuated by a series of turbopumps before reaching the detector.

The XPS spectra of Cu 2p3/2, Ag 3*d*, Au 4*f*, and O 1*s* core levels were taken on the clean CSAF surface and on the surface after exposures at various pressures and at ~620 K. The oxygen pressure was raised from UHV to 1 Torr in a step-wise manner. NAP-XPS spectra were taken after 30 min of exposure at each oxygen pressure, which was shown to be sufficient to reach a steady-state extent of oxidation (details in Chapter 4). Upon initial exposure to oxygen, oxidation occurred and a thin layer of oxide was formed. When the oxygen pressure increased, the chemical potential of oxygen in the gas phase drove the further segregation of Cu to the surface, and a thicker layer of oxide was developed. The surface compositions determined using NAP-XPS at each oxygen pressure will be presented and discussed in the following section.

3.4.4.2 Results and discussions

The initial EDX measurements of composition at the 13 points studied in this work are shown in Figure 3.26 by black symbols. Due to material evaporation (especially Ag) during heating under oxidative and reductive environments, the thin-film compositions have shifted and the corresponding EDX-determined compositions after measurements were made are shown by blue symbols. XPS compositions on the clean surface right before oxygen exposure and data collection are shown by red symbols. The above-mentioned compositions on individual points are circled together. The offsets between the EDX- versus XPS-determined compositions might also be attributed to the sample position misalignment in NAP-XPS chamber, as only a camera $\sim 30^{\circ}$ w.r.t. the sample plane was used for visual sample alignment and this is prone to uncertainties.



Figure 3.27 Bulk and surface compositions of the 13 points measured in this work before and after near-ambient-pressure oxygen treatment and hydrogenation treatment.

The atomic compositions of metallic components after oxygen exposures in the range 10^{-6} to 10^{0} Torr are shown in Figure 3.27. Therein the oxygen XPS signal was not taken into account in composition quantification since it has two sources: one from the oxidized CSAF surface, and the other from the oxidized Mo substrate exposed due to thin-film dewetting. The labeled number on the upper-left corner in each subplot indicated the sequence in actual data acquisition, while the data presented in Figure 3.27 was sorted in such a way that alloys with similar compositions and profiles are next to each other. On the CuAu binary alloy surfaces, the increase in the oxygen pressure caused the segregation of Cu to the surface, reaching a surface completely covered by Cu oxide at a pressure of 1 Torr. On the AgAu binary alloy surfaces, a slight increase of Ag as a function of oxygen pressure was observed, with a level of ~5 at% increase at 1 Torr compared to their initial surface compositions. CuAg binary alloys are missing from this dataset due to constraints on the sample motion control system, and the fact that the CuAg binary compositions lay near one edge of the sample. Moving to those positions runs the

risk of doing damage to the detector by the heating laser. The oxygen signal level at 1 Torr was much lower on AgAu binary alloy surfaces than that on Cu-containing alloys. Most points measured in this work have ternary alloy compositions, while the Cu-rich compositions showed monotonic Cu increase as a function of the oxygen pressure, which approached ~90 at% or above in Cu content, the low-Cu composition (point #6, Cu ~ 10 at%) showed a peak in Cu concentration at 0.01 Torr, which was due to the formation of CuO and insufficient compensation in XPS quantification.

To describe the pressure range in which oxygen-induced segregation occurred, a 'half-pressure' was defined as illustrated in the bottom subplot in Figure 3.27. Since the segregation was characterized by an enrichment of Cu, the initial and final (or maximum) Cu contents (at %) were used to calculate the Cu content that described the middle of the transition, and corresponding oxygen pressures were estimated and presented in the last subplot of Figure 3.27 in a ternary diagram. It is clear that the transition started (reached 'half-transition') at lower oxygen pressures on low-Cu alloys, while the high-Cu alloys required as much as 0.1 Torr to achieve the same 'half-transition' state.

The above-mentioned evolution in surface composition are also shown in Figure 3.28 on ternary diagrams.





Figure 3.28 Metallic near-surface composition and oxygen signal of 13 points on the CuAgAu CSAF after exposure to various oxygen pressures at ~620 K. The nonzero initial oxygen level at some positions was due to thin-film dewetting and the corresponding oxidation of the Mo substrate. The 'half-pressure' of a transition is defined by the pressure at which surface composition is in the middle of the initial and the final (or maximum Cu) states, as illustrated by the figure in the lower-left corner. The 'half-pressure' as a function of alloy composition is shown in the figure in the lower-right corner.



Figure 3.29 Metallic near-surface composition of 13 points on the CuAgAu CSAF on ternary diagram after exposure to various oxygen pressures at ~620 K.

Most of the Cu AP-XP spectra taken in the section above- used a narrow binding energy window of 930-935 eV in order to maximize efficiency. To verify the oxidation state of Cu after being exposed to 1 Torr of oxygen at ~620 K, one set of Cu spectra with wider energy range were taken at the end of the experiment, as shown in Figure 3.29. Based on the peak shapes, the Cu spectra were sorted into two groups: high Cu content alloys only showed two peaks at 932.4 eV and 952 eV, corresponding to Cu(I) $2p_{3/2}$ and Cu(I) $2p_{1/2}$, respectively; low Cu content alloys also had satellite peaks at 940-945 eV and 960-965 eV, while the appearance of Cu(II) $2p_{3/2}$ and Cu(II) $2p_{1/2}$ at ~934 eV and ~954 eV, respectively, confirms the formation of CuO upon oxidation at 1 Torr.

The finding that low-Cu alloys are oxidized at lower pressures and form Cu(II) contradicts the observations in the literature, in which alloying of Cu with metals such as Ag and Au improved their resistivity to oxidation^{95,116,117}, although experiments were conducted at either lower temperature or lower oxygen pressures in these papers. The accumulative oxygen exposure at the end of this experiment

was estimated to be $\sim 10^{10}$ L, and a bulk Cu₂O structure is expected to form on pure Cu surface under the same oxidation condition¹¹⁸. It should be noted that at Cu₂O and CuO can also decompose at above 600 K^{119–121}, and the relative stability between Cu, Cu₂O, and CuO depends on the oxygen pressure and temperature. Thus, it is possible that Cu(II) was not stable at 623 K below 1 Torr of oxygen on high Cu content alloys.



Figure 3.30 Cu spectra at the end of the experiment after oxidation at 1 Torr oxygen environment. Indices labeled in the figures are the same as those labeled on the lower-right corners in Figure 3.28. Two groups of Cu spectra can be observed based on their oxidation state, while high-Cu alloys (Cu >25 at% in the bulk, or >37% in the near-surface before oxidation) in the left figure show only two characteristic peaks of Cu(0)/Cu(I), low-Cu alloys in the right figure show satellite peaks and shoulder peaks at ~934 eV that indicate the further oxidation of Cu(I) to Cu(II).

The oxidized CSAF was treated in an H₂ environment, and a reduction time of 40 min with 0.1 mbar H₂ pressure at \sim 700 K was shown to be sufficient to recover the metallic surfaces determined by NAP-XPS. The reduction of the oxidized surface was also studied in the preparation chamber of ThetaProbe, and 3 hours of treatment under 10⁻⁵ mbar H₂ at 700 K also removed the surface oxide on CuAgAu surfaces.

3.5 Conclusion

In this work, $Cu_xAu_yPd_{1-x-y}$, $Ni_xAu_yPd_{1-x-y}$, and $Cu_xAg_yAu_{1-x-y}$ composition spread alloy films (CSAFs) have been shown to serve as valuable material libraries for high throughput study of surface properties of alloys using EDX, XPS, UPS, EBSD, He⁺ LEIS, and NAP-XPS across composition space. Temperature, crystalline structure, and gas environment were shown to have impacts on surface segregation, and a segregation model was developed to describe segregation in ternary systems. The main findings of this work include:

- The segregation tendency under UHV follows the order of Ag>Au>Cu>Pd>Ni, which is consistent with their calculated solid-vapor surface energies (1.1, 1.3, 1.6, 1.7, 2.1 J/m², respectively).
- 2) On the surfaces of disordered alloys, a weaker segregation can be expected at higher temperatures; while for ordered alloys (such as Cu-Au in this work), maximum segregation occurs at their order-disorder transition temperatures.
- Crystalline structure can affect segregation in CuPd alloys, in which the ordered B2 structure suppresses Cu enrichment.
- 4) While a >300 K difference in temperature causes <10 at% change in surface composition under UHV, adsorbate that strongly interact with alloy components (such as O-Cu interaction) can significantly alter the surface composition by >80 at%, especially at high pressures, while adsorbate that does not preferentially interact with any alloy component (such as H-CuAgAu) makes little difference.

It is important to note that while the CSAFs has the virtue of allowing the study of all alloy compositions in the ternary space in one experiment, they are not single crystals with well-defined surface orientations. Rather they are representatives of polycrystalline alloy materials and are closer to catalysts in industrial applications.

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Chapter 4 Segregation kinetics

4.1 Introduction

Kinetics of surface segregation in alloys is a diffusion problem, and depending on the mechanism, it is mainly classified into lattice diffusion and grain boundary diffusion. Diffusion through ordered lattice usually involves the generation and migration of lattice vacancies (other diffusion mechanisms have higher energy barriers), and temperature plays an important role in determining the concentration of thermal-induced vacancies. Whereas in grain boundary diffusion, the type and concentration of grain boundaries are the determining factors. In polycrystalline materials, apparent material diffusion is a combination of the two processes mentioned above. Diffusion coefficient through lattice is usually several orders of magnitude lower than that along grain boundaries¹², where the energy barrier of atomic motion is much lower and is comparable to that on a free surface; as a result, grain boundary diffusion contributes the most to apparent diffusion measurements³⁻⁵, especially at low temperatures <600 K, whereas lattice diffusion becomes more important at high temperatures and in case of crystals with large grains. Following Harrison's definition in 1961⁶, segregation kinetics can be classified into three regimes: so-called A-type kinetics refers to lattice-dominant diffusion where grain boundary diffusion is negligible, which usually requires large grain size and elevated temperatures; B-type kinetics has a comparable contribution from the two factors and C-type kinetics is mainly a result of grain boundary diffusion.

To measure diffusion coefficients of lattice and grain boundary diffusions, several experimental methods have been developed: Radio-tracer experiment^{7–9} was first applied in several works in the 1960s, in which a radioactive isotope is added to the surface of a crystal and underwent intensive thermal annealing over several hours; depth profile of radiotracer is then measured by anodization-etching and liquid scintillation radio-assay. Each depth profile gives an apparent diffusion coefficient corresponding to its annealing condition, and several such measurements using various annealing temperatures can provide an estimation of activation energy. The radiotracer method is suitable for A-type regime studies as the minimum amount of materials in each etching step limits its application in quantifying shallow profiles. The temperature used in radiotracer experiments is usually above $0.6 \times T_m$ (melting temperature), and the profile depth can be as deep as 100 um.

Non-radioactive isotope combined with Secondary Ion Mass Spectroscopy (SIMS) is a more experimentally friendly approach for diffusion studies⁸. Ions sputtered off the material surface are detected using a mass spectrometer, which gives the depth profile of non-radioactive isotope. Typically⁸, measurement depth is below 15-20 um and annealing temperature below 0.6-0.8 T_m .

High energy ion scattering was also applied in the grain boundary diffusion study of the CuAu system³. Like the SIMS method, it suffers from the preferential sputtering issue, but that does not limit its application in diffusion studies. Compared to the other two methods, HEIS is not suitable for self-diffusion studies due to its poor mass resolution and inability to distinguish between isotopes. In the B-type diffusion regime, a so-called triple-product¹⁰, the product of grain boundary diffusion coefficient, boundary layer thickness, and segregation factor, can be determined from the tail of the depth profile^{11–13}. By combining B-type and C-type experiments, one can separately assess the contributions of lattice diffusion coefficient and grain boundary diffusion coefficient.

As far as catalysis application is concerned, one would like to know changes in surface compositions (segregation) near equilibrium conditions: alloys are usually well-mixed initially, while surface composition evolves in a catalytic environment driven by annealing and adsorbate-induced segregation, which is generally limited to near-surface regions within a few nanometers or a few atomic layers in depth. In such cases, there may exist other diffusion mechanisms¹⁴ that differ from lattice diffusion and grain boundary diffusion in the following ways: 1) due to the existence of a free surface on one side, the material interdiffusion between the top two atomic layers is different from that between adjacent layers deeper in the bulk lattice, since the presence of atoms in the free surface allows its interchange with a subsurface atom in a concerted pathway. 2) The direction of the driving force in near-surface segregation, either determined by temperature or chemical environment, is perpendicular to the free surface plane, which is different from that in grain boundary diffusion, where atomic migration occurs along the boundary; although lateral diffusion along a grain boundary has a lower diffusion barrier than lattice diffusion, grain boundary diffusion still has higher energy barrier than that on a free surface and cannot fully represent the latter. Thus, the add-layer diffusion experiments are not completely appropriate for studying near-surface segregation, and a more surface-sensitive tool is needed.

In sections 4.3.2.1 - 4.3.2.4, surface segregation kinetics of CuAu alloys under UHV will be discussed; and in section 4.3.2.5, segregation kinetics of a CuAgAu alloy under oxygen and hydrogen environment will be discussed.

4.2 Experimental procedures

Three CSAF samples were used in segregation kinetic studies, including two CuAgAu ternary CSAFs (CSAF #2, #3 described in Chapter 3) and a CuAu binary CSAF, all fabricated using the procedures described in Chapter 2. The sample temperature control and surface cleaning protocols used in this work are similar to those used in the equilibrium segregation work in Chapter 3, which was described in Chapter 2.

Depending on the type of experiment, detailed experimental parameters, including the shape of the temperature profile and the ion dose during He⁺ LEIS, may vary, which will be discussed in the following section.

4.3 Results and discussion

4.3.1 Sputtering, heating, reconstruction, and segregation

LEIS is probably the most surface-sensitive tool for surface composition quantification and is, thus, applied in this work for segregation kinetic measurements. However, due to the semi-destructive nature of ion sputtering, several aspects must be carefully dealt with to interpret the data correctly. All considerations discussed below deal with the same issue: how can we ensure a sufficiently high signal-to-noise level while minimizing surface damage.

Incident ion energy and ion dose are the first factors to consider in assessing S/N versus surface damage: lower ion energies are always preferred to minimize surface damage as the sputter yield is a function of ion energy, but at the same time, reionization probability is also negatively correlated to incident energy, and thus a balance must be considered. 750 eV He⁺ is the best choice according to assessment, while 1 keV He⁺ also gives reasonably good results. Ion dose is usually calculated using sample current and beam size, and ideally, less than 5% of all surface atoms would undergo collision with He⁺ during the collection of a spectrum; such number can be reduced to less than 1% in more advanced instruments that are specially designed for conducting LEIS measurements^{15–17}.

It is known that surface roughness can affect ion yield in LEIS¹⁸, and a decrease of 40% in the signal can be observed on a rough surface relative to a smooth surface^{16,19,20}. On samples that have experienced numerous sputter-anneal cycles, such surface roughness can still arise from sputter-induced surface defects during continuous LEIS measurements or diffusion processes.

Other experimental design parameters in LEIS-studied segregation kinetic include initial surface structure, sample temperature, and sampling frequency. In order to interpret kinetics data, the sample must start from a well-defined initial state and end up in another well-defined state. Such a statement may seem meaningless but actually is the key to all issues: temperature dependent differences in surface compositions between equilibrium states are usually minor under UHV, especially on polycrystalline samples; e.g., the maximum difference in surface composition of an AgAu alloy between 400 K and 800 K is only around 5 at%, and if such equilibrium states are set to be initial and final states of a kinetic process, then one will need both high-quality LEIS spectrums and high enough sampling frequency to capture the small change over time; these are usually competing each other when considering S/N. Sample temperature during kinetic measurement usually determines the time for the transition from the initial state into the final state; lower temperature and thus longer time will allow more data points to be collected during the transition, but it also allows more surface contamination caused by adsorption from ambient UHV. More data points also mean more surface damage caused by sputtering. Such dilemma exists in almost all experiment designs, so careful estimation of surface damage, the difference in surface composition between initial and final states, the time scale of the transition, the relationship between spectrum acquisition time and S/N level, etc., must be performed before making measurements.

4.3.2 Kinetics of segregation in CuAgAu alloys

It has been shown by literature that equilibrium between surface and bulk compositions can only be reached at elevated temperatures²¹, usually above 600 K, while segregation at lower temperatures is kinetically limited. Plenty of catalysts work under temperatures below 600 K, and how the surface composition evolves during catalytic reactions on these catalyst surfaces is an interesting topic. Although both lattice diffusion and grain boundary diffusion coefficients can be determined using the methodologies introduced in the previous section (4.1), surface segregation is not a simple combination of the two. As shown in many experimental and theoretical works, surface segregation is usually limited to the top few atomic layers of material, with the most significant difference between the top 2 layers. Unlike diffusion deep inside a lattice, atom swap or exchange can happen with a much lower energy barrier near-surface since the top-layer atoms are less constrained in position. Such atom exchange between top layer and sublayer atoms has a slightly higher energy barrier than the lateral diffusion along free surface or grain boundaries. Still, it is much faster than vacancy-mediated diffusion in a wellordered lattice considering the low concentration of vacancies at moderate temperatures. Segregation at the surface of a well-mixed alloy is not driven by the concentration gradient (because there is none), which is another big difference compared to classic diffusion studies.

To study segregation kinetics and provide guidance in studying real catalyst surface evolution, experiments were conducted using CuAu as a model alloy system. CuAu alloys were chosen for many reasons: 1) diffusion properties in Cu, Au, and CuAu alloys are already well-studied in determining their lattice and grain boundary diffusion coefficients. 2) CuAu has been used as a model system for short-range and long-range ordering studies as it has several ordered crystal structures at Cu₂₅Au₇₅, Cu₅₀Au₅₀, and Cu₇₅Au₂₅ alloy compositions. Both ordered and random solid solution states can be observed in CuAu alloys under different temperatures. 3) Cu and Au have very different masses and can be easily resolved using LEIS. 4) CuAu alloy thin films have high thermal stability and do not dewet

during thermal annealing up to 850 K. 5) Cu and Au are catalyst components in many heterogeneous reactions. Thus, understanding the kinetics of surface composition and surface structure change at various temperatures and initial conditions will guide future catalyst design.

Several types of experiments were conducted to study segregation kinetics in CuAu alloys. The first and most direct way of measuring kinetics would be monitoring the transition from one equilibrium state to another under various temperatures. Equilibrium states as both initial and final states are preferred due to their high reproducibility. A surface equilibrium state can be prepared by proper surface cleaning and prolonged annealing. In these experiments, a CSAF containing all possible CuAu binary compositions was loaded into the ThetaProbe and subjected to sputter-anneal cycles (> 700 K for more than 30 min) until no carbon or oxygen signal could be detected using XPS, at which point it was slowly cooled to target initial temperatures. Minimum He⁺ ion dose (5-40 nA sample current, circular beam spot with ~1 mm in diameter) was applied to get enough signal-to-noise level to detect the evolution between initial and final states.

Figure 8.19 shows one set of kinetic traces on 5 different CuAu alloy compositions. It is clear that, if we only focus on the normalized coverage of each specie using relative signal intensities between two components, the transition from initial to final state seem to be completed within 20 minutes. However, when we take a closer look at the signal of each component, both were changing over a much longer time scale. The cause of such phenomenon will be discussed in the

following sections, but the first lesson learned is that every detail should be carefully examined before reaching any conclusion in these kinetic studies.

Surface contamination has always been a big concern in UHV studies. The rate of adsorbate accumulation on metal surfaces from the UHV environment was already well-studied in a work using an almost identical ThetaProbe setup, which provides the timescale of metal surfaces being contaminated at room temperature²². Without checking surface cleanliness with XPS, which is sometimes timeconsuming for a complete composition-range scan and can cause more contaminants during XPS spectrum acquisition, surface cleanliness can also be estimated by ion yield across composition space. In Figure 4.1, the LEIS signals of Cu and Au on 13 different alloy compositions in a kinetic experiment (includes 37 cycles of LEIS spectra collection, with ~8 min per cycle) are plotted against each other; temperatures under which each data point was collected are used for color scaling. Since all CuAu alloys have FCC structures and LEIS does not have a 'matrix effect', a straight line should be observed when a set of compositions are measured under the same condition; the principle behind such a statement was explained in earlier chapters. For example, all red points collected at 600 K lie on the same line regardless of surface compositions, indicating a clean surface. Blue points were collected using the same ion dose but at room temperatures. Although signals on Au-rich surfaces were not affected by surface contamination, Cu-rich surfaces showed much lower signals, especially after prolonged exposure under low temperatures. Such deviation from a straight line indicates non-ideal surfaces, which could be caused by surface contamination of Cu or the preferential sputtering of Cu by He⁺ ions. This surface cleanliness checking method shows the advantage of conducting high-throughput experiments under identical conditions, since such minor differences could have been easily ignored or buried under noises if these 13 compositions were measured one after another, in which case He pressure, filament emission, or even the detector status could vary over time.



Figure 4.1 He⁺ LEIS signal of Cu and Au collected during one experiment in which 13 CuAu alloy surfaces were measured sequentially and repeatedly during a kinetic transition. Data points are colored by their iterations (time). Data points of the same color should stay on a straight line if the alloy surfaces are clean. Due to adsorption of CO, O₂ onto the CSAF surface, Cu-rich surfaces are partially covered by adsorbates at low temperatures and show low signal level.

4.3.2.1 Isothermal experiment

In an ideal non-destructive experiment, one measures the kinetics at a constant temperature. However, non-destructive surface analysis tools such as XPS and AES are either not surface-sensitive enough to capture the temporal change in surface composition, or achieving such compositional resolution sacrifices time resolution. LEIS serves as a surface-sensitive but invasive way of probing surface composition changes, because typically, 1-5% of all surface atoms under the beam

spot suffer a collision with incident He⁺ during the collection of one LEIS spectrum. Such a sputtering effect is usually negligible when only one spectrum is needed but can quickly become non-negligible when successive spectrums are taken at one point. To study the sputtering damage of He⁺ to the sample surface and surface reconstruction during sputtering, a set of experiments were carried out on a CuAu CSAF under isothermal conditions spanning alloy composition range, temperature and He⁺ ion dosage.

The CuAu CSAF sample was first sputtered by 3 kV Ar⁺ and then annealed at 800 K for ~20 min to reach a well-defined equilibrium surface termination. After cooling to a predetermined isothermal temperature in the range 300 - 700 K and held there for 30 min, LEIS spectrums were continuously collected on one CuAu alloy composition for 2-14 hours using various He pressures (He pressure ~ sample current/ion dose have linear relation). Such a procedure was repeated on different CuAu alloy compositions.

Figure 4.2 shows the composition changes over time on 3 CuAu alloys under temperatures from 300 K to 600 K using a 'high' He pressure and a 'medium' He pressure $(2.0 \times 10^{-8} \text{ mbar} \text{ and } 4.0 \times 10^{-9} \text{ mbar}$ above UHV background, respectively), which gave 200 nA and 40 nA sample current over a circular spot of ~1 mm in diameter with 0.75 keV primary beam energy. It is clear that the surface enrichment of Au was sputtered away within 30 min at room temperature; while under higher temperatures, although Au depletion was also observed compared to its equilibrium level, Au enrichment was partially preserved due to the active Au outward diffusion and segregation from the bulk lattice. At 600 K and above, the

surface composition did not change over time upon He⁺ sputtering even under a 'high' ion dose, indicating the surface damage was immediately compensated by the mobility of near-surface atoms. An upward tail was observed on all three alloys at 300 K after ~ 60 min, which was likely caused by surface contamination (CO, CO₂, and H₂O adsorption) of surface Cu atoms since the sputtered surfaces are likely to contain more lower-coordinated Cu atoms and being more active in adsorption of gas molecules. To reach the same total ion dose using a lower beam current, much longer sputtering time was needed while also allowing more effective 'repair' of surface damages. As shown in A and C, depletion in surface Au content was slower when using lower He pressure, even after the correction of total ion dose, which suggests that such a repairing process was still active at 300 K.



Figure 4.2 Kinetics of segregation on 3 CuAu alloys studied using He⁺ LEIS. Three temperatures and three He pressures were used to explore the interplay between sputtering/reconstruction/segregation.

The difference in initial composition at different temperatures was caused by their difference in equilibrium segregation, in which increasing temperature tends to decrease the segregation of surface-enriched species. The evolution of each component (Cu and Au) over time can be found in Appendix.

The collisions between He⁺ and CuAu alloy surfaces (0.75 keV, 45° incident angle) were simulated using SRIM software²³. The 'Monolayer Collision Steps / Surface Sputtering' damage estimation method was applied on uniform layers of CuAu alloys to estimate surface damage, including sputtering yield and vacancy generation in the near-surface region. It should be noted that although standard He⁺ LEIS (with only backscattered positive ions being detected) was shown to only give compositional and structural information of up to two atomic layers on the surface^{24,25}, sputter induced damage can exist over a much deeper region, although ions penetrating into deeper layers are efficiently neutralized and are not detected. It was suggested by the Monte Carlo simulation (in SRIM) of 10,000 He⁺ ions impacting the surface that, on average each incident He⁺ generates 1-5 vacancies in the near-surface lattice, with an exponential decay in vacancy concentration from top-surface to 10 nm below. More Cu vacancies are generated than Au vacancies due to their lower formation energy and more efficient momentum transfer between He^+ and Cu atoms than between He^+ and Au atoms. Sputter yield was calculated to be 0.5 Cu atom/He⁺ and 0.17 Au atom/He⁺ in pure metals, with a smooth transition as a function of alloy composition, as is shown in



Figure 4.3. It should be mentioned that the interaction between Cu and Au that causes the formation of several ordered alloys was neglected in simulations.

Figure 4.3 Monte Carlo simulation of collision between 0.75keV He^+ and $Cu_{0.5}Au_{0.5}$ alloy surface. The upper left figure shows the trajectory of He⁺ inside the $Cu_{0.5}Au_{0.5}$ lattice; the upper right figure summarizes the distribution of He⁺ appearance in all 10000 trajectories as function of depth; lower left figure shows the distribution of vacancies in $Cu_{0.5}Au_{0.5}$ created upon collision, while Cu vacancy concentration is higher than that of Au due to its lower formation energy and more efficient momentum transfer during collision; lower right figure shows the sputtering yields of Cu and Au as well as total vacancy yield as functions of CuAu composition.

A model that takes sputtering, vacancy site replenishment, and segregation was developed to describe the kinetic behavior of CuAu. Assuming that only sputtering occurred at room temperature while the other two repair mechanisms were 'frozen', the sputtering yield was estimated to be ~0.02 atom/ion by fitting the kinetic data collected at 300 K under the assumption that segregation is limited to the first atomic layer. Preferential sputtering was not observed as the steady-state surface compositions at 300 K on all three CuAu alloys reached their bulk compositions. This estimated sputtering yield was much lower than the SRIM simulation (shown in Figure 4.3). A 0 K temperature was assumed in the SRIM simulation, and thus the thermal effect was completely ignored, which may play a substantial role in some cases according to the software's handbook. According to fitted parameters, when a much lower ion dose is applied in kinetic studies using 0.75kV He⁺ LEIS (e.g. 5 nA with 1 mm spot size), it is safe to assume any sputter induced surface damage is immediately repaired through the migration of atoms from subsurface layers when the sample is held at 500 K or above.

The surface damage caused by He⁺ sputtering was also characterized by XPS. Starting from sputter-annealed surfaces (with 3 keV Ar⁺ and 800 K annealing for 15 min), the Cu $2p_{3/2}$ and Au $4f_{7/2}$ XPS spectra were taken after various ion doses of 0.75 keV He⁺ at room temperature. Other than the composition change caused by the removal of Au-enriched near-surface atomic layers, there was also a noticeable signal intensity drop of ~8% and ~3% on pure Cu and Au surfaces, respectively, indicating some vacancy formation caused by He⁺ sputtering. No peak position shift or valence band structure change was observed during He⁺ and Ar⁺ sputtering.

4.3.2.2 Temperature-ramp experiments

The most efficient way to estimate the temperature at which surface composition starts to change measurably is by increasing the sample temperature while measuring the surface composition to detect the onset of coverage changes. A set of experiments were conducted using CuAu alloys and in which the temperature of the sample was heated and cooled slowly (~0.01-0.04 K/sec) at a constant rate. Figure 4.4 and Figure 4.5 show the results of one such experiment, in which the surface compositions of 7 CuAu alloys were measured sequentially every 8 minutes using LEIS. The sample temperature was gradually decreased from 700 K to 400 K and then heated back to 700 K with and without isothermal pauses at intermediate temperatures. Raw Cu and Au LEIS signals can be found in Appendix. Figure 4.4 shows the temperature profile (solid red line) and the concurrent evolution of the Au coverage, θ_{Au} , (black squares) for CuAu alloys with bulk compositions having $x_{Au} > 0.50$. Figure 4.5 shows the same but for alloys with $x_{Au} \leq 0.50$. The equilibrium surface compositions, $\theta_{Au}(x_{Au}, T)$, have been determined by prior work. The horizontal dashed lines on Figures Figure 4.4 and Figure 4.5 indicate the equilibrium values of $\theta_{Au}(x_{Au}, T)$ at 500 K (red), 600 K (blue), and 700 K (magenta).

The first observation is that as the temperature decreases from T = 700 -500 K, the Au coverage, θ_{Au} , increases on the $x_{Au} > 0.50$ alloys. The second observation is that on all CuAu alloys, θ_{Au} decreases as the temperature decreases from T = 500 - 400 K. The third observation is that while the sample is annealed at 400 K, θ_{Au} continues to decrease, indicating the surface composition is still evolving with a time constant that is on the order of 30 min. The fourth observation is that when the CuAu alloys are heated from 400 K, θ_{Au} responds almost immediately, indicating that the time constant for Au segregation decreases rapidly with temperature to become lower than the sampling time of 8 min. The final observation is the asymmetric shapes of the surface composition profiles, $\theta_{Au}(t)$, resulting from cooling and then heating, revealing that the mobility of the atoms is insufficient to maintain equilibrium at heating rates of 0.04 K/sec. The starting and ending compositions at 700 K in this experiment matched very well with their equilibrium states.



Figure 4.4 (Part 1) Temperature-ramp experiment on 7 CuAu alloys. A temperature range of 400-700 K was covered by linearly changing sample temperature while iteratively measuring the surface composition of 7 alloys using

 He^+ LEIS. Equilibrium surface compositions at 500 K (orange), 600 K (blue), and 700 K (magenta) for each alloy are indicated by dotted lines.



Figure 4.5 (Part 2) Temperature-ramp experiment on 7 CuAu alloys. A temperature range of 400-700 K was covered by linearly changing sample temperature while iteratively measuring the surface composition of 7 alloys using He^+ LEIS. Equilibrium surface compositions at 500 K (orange), 600 K (blue), and 700 K (magenta) for each alloy are indicated by dotted lines.

The right-hand panels in Figure 4.4 and Figure 4.5 have temperature profiles from 700 to 400 to 700 K that include pauses at 400, 500, 600 and 700 K. The interesting feature for these segregation profiles is that for temperature above 400 K they reveal a response to the isothermal plateaus in which the segregation plateaus also. This suggests that equilibrium, or at least a stable structure representing local minima in chemical potential, is being established at these temperatures and with time constants less than the sampling time of 8 min. These plateaus are not perfectly aligned with the equilibrium Au coverages marked by dashed lines. However, considering that the full range of θ_{Au} is typically only about 5%, the matches with the prior equilibrium segregation experiment are not bad.

The decrease in θ_{Au} when the CuAu alloy was cooled below 500 K can be attributed to selective sputtering of the Au-enriched surface layers and insufficient Au outward diffusion rate to compensate, as shown in section 4.3.2.1. The cooling rate was high compared to the rate of surface 'repairment' and did not allow enough time for the sputter-reconstruct to reach steady-state at each temperature, which resulted in the asymmetric shapes of segregation kinetic profiles. According to the literature²⁶, diffusion of atoms out of the lattice is much easier than diffusion into the lattice of Cu₃Au alloy. The migration of Au, both the outward and inward migration, is the much slower than that of Cu. The immediate Au content increase upon heating from 400 K indicated that the rate of Au outward diffusion was still at an appreciable level, which in principle can be accurately determined if a much lower ion dose can be used. In alloys with Au content >50 at% in the bulk, surface Au concentrations reached their maxima at \sim 500 K on the heating-side of the profiles. That marked the points where the sputter-reconstruct pairs were balanced again.

A similar temperature-ramp experiment was conducted on a Cu-rich CuAgAu ternary alloy (since Cu is almost absent from other alloy surfaces). The bulk composition of this alloy was initially quantified to be close to Cu₃₃Ag₃₃Au₃₃. Due to material evaporation during oxidation and reduction treatment at >700 K, the bulk composition changed during the experiment, as discussed at the end of Chapter 3. Figure 4.6 shows the signal evolution of Cu, Ag, and Au in He⁺ LEIS. Immediate responses in Cu and Au upon heating from 400 K were also observed, but Ag increase occurred at ~ 440 K; plateaus in Cu, Ag and Au were found on the heating side at 500 K, which was not the case on the cooling side, which again indicated the difference in diffusion pathways during heating and cooling. The depletion of Ag and Au during cooling was likely due to the sputtering damage and exposure of underneath Cu-rich layers, since the ion dose was high (~200 nA), and the equilibrium segregation results also indicated that higher Ag content should be expected at lower temperatures.



Figure 4.6 An example of segregation kinetics on a ternary CuAgAu alloy studied using He⁺ LEIS. Cu and Au responded immediately upon heating from 400 K, while Ag started to diffuse out at a slightly higher temperature.

4.3.2.3 Temperature-jump experiments

Having searched for and identified the temperature range over which segregation kinetics can be measured using He⁺ LEIS, a set of temperature jump experiments were conducted to measure segregation kinetics under isothermal conditions. The sample was first sputter-annealed at elevated temperature (>700 K) to reach an equilibrium state, and then cooled to target temperatures.

Figure 4.7 shows one set of temperature-jump experiments that contains seven discrete CuAu alloy compositions. To simplify the problem, a temperature lower than 500 K was avoided in this experiment so that there wouldn't be a significant drop in Au content caused by sputtering during cooling, and the hysteresis would be less apparent. While only the surface compositions are shown in Figure 4.7, more details such as signal evolution of individual components can be found in Appendix. Monotonic temperature dependencies were observed on high-Au alloys (Au >50 at%), in which higher temperatures led to weaker enrichment of Au in the temperature range of 500 – 800 K. On the Cu₅₀Au₅₀ alloy, maxima in Au surface concentration can be found between 650 K and 700 K, which is consistent with its order-disorder transition temperature (T_c =683 K). The alloy behaves as a random solid solution above T_c , in which weaker segregation with increasing temperature is expected; while below T_c , the ordering tendency prevails, which leads to an ordered structure (zero segregation) at sufficiently low temperatures. The same observation was also found on the Cu₇₆Au₂₄ alloy since it has an order-disorder transition temperature of 663 K, while other alloys with Au <50 at% also behaved similarly to Cu₅₀Au₅₀ and Cu₇₆Au₂₄. Although the Cu₂₅Au₇₅ alloy also has an order-disorder transition with T_c~470 K, it is outside (below) the temperature range explored in this experiment, and thus alloys with Au >50 at% behaved as random solid solutions.

Due to the long stabilization time allowed for each temperature, segregation traces obtained in this experiment reflected more of the equilibrium characteristics of segregation than its kinetics, although some kinetic information can still be found in the details shown in Appendix.



Figure 4.7 Temperature-jump experiment on seven CuAu alloys.

4.3.2.4 Sputter-jump experiments

Since the difference between equilibrium states are usually small (~3-10 at% between 500 K and 800 K), accurate quantification of its transition kinetics is challenging. With the assumption that atom mobility is mainly a function of temperature rather than the initial state of surface composition and structure, the following experiments were designed: since segregation had been well-characterized on CuAu alloys in our earlier works, the equilibrium surface composition was known to differ from a bulk composition by 5-20 at%. Thus, by sputtering the surface of alloys with Ar^+ until a bulk termination is reached, we can study the surface transition from the bulk composition to its equilibrium surface composition at a given temperature, which would allow a wider transition window and be more tolerable to uncertainties. Although it should be noted that such transition represents kinetics in material with high vacancy concentration, part of which came from the initial Ar^+ sputtering and the rest from He⁺ sputtering during LEIS and thermal annealing.





Figure 4.8 Sputter-jump experiment on five CuAu alloys. Surfaces were sputtered with 3 $kVAr^+$ at room temperature, then heated to target temperature within 1 min.

Figure 4.8 shows such transition (from the as-sputtered surface at ~300 K to target temperatures of 375, 400, 425, 450, and 475 K) on 5 different CuAu alloys. All surfaces started from surface compositions close to the corresponding bulk compositions after 3 keV Ar⁺ sputtering at 300 K. The temperature was jumped – increased to target temperatures within 1 min – after collecting 3 LEIS spectra at 300 K. It is clear that when the target temperature is lower than 400 K, surfaces are trapped in low θ_{Au} states, especially on low x_{Au} surfaces. The differences between final states of an alloy at different temperatures are affected by the sputter-reconstruct competition, as discussed in section 4.3.2.1. The times needed to reach half of the transitions were determined by fitting first order curves to the data, and are plotted in Figure 4.9. Although the absolute differences between initial and final states are small at low temperatures, they took longer time to complete the

transition. The half-times of the transitions on Cu-rich alloys are longer than that on Au-rich alloys, which might be caused by the higher diffusion barrier of Au atoms in the Cu-rich lattice since it has smaller lattice constant. Although it was known that the ion bombardment during LEIS spectra collection may enhance diffusion through the generation of point defects²⁷, and thus, the composition dependent vacancy generation should enhance diffusion in Cu-rich alloys more than that in Au-rich allows due to the low generation energy barrier of Cu vacancies. However, the slow segregation kinetics observed on Cu-rich alloys shown in Figure 4.9 indicates that sputter-enhanced diffusivity did not play a major role in this experiment.



Figure 4.9 Half-times of 'sputter-jump' kinetics on five CuAu alloys.


Figure 4.10 Summary comparison plot between equilibrium segregation, steadystate 'thermostatic He⁺ *sputtering', and steady-state 'sputter-jump' experiments.*

Figure 4.10 compares the steady-state compositions in 'sputter-jump' experiments at T=310-500 K with that measured at equilibrium conditions and steady-state compositions in 'thermostatic experiments' discussed in section 4.3.2.1. Starting from the Ar^+ sputter-damaged surfaces, the segregation of Au was still active at room temperature (~310 K), which increased the Au concentration by ~2-3 at% within 5 hours of the experiment. Segregation at temperatures between 350 K to 500 K on all alloy compositions reached steady-states with Au concentrations lower than their equilibrium values at 500 K.

4.3.2.5 In-situ oxidation-reduction experiment

Segregation kinetics of alloys under UHV conditions provide valuable information on the mobility of atoms as a function of temperature, allowing direct comparison between experimental data with simulations as the alloy structures are well defined. When used as a catalyst in real reactions, more factors are involved, which determine not only the driving force of segregation in alloys but also the chemical states of components. To better approximate the kinetic behavior of alloy surfaces under catalytic conditions, an in-situ oxidation/reduction experiment was conducted on a CuAgAu alloy using near-ambient-pressure (NAP-) XPS at the Center of Functional Nanomaterials in Brookhaven National Laboratory. Details of sample description, as well as NAP-XPS, can be found in Chapter 3.



Figure 4.11 Evolution of Cu, Ag, and Au XPS signal during oxidation and reduction under near-ambient pressures. Cu peaks showed the emergence of Cu(I) upon oxidation and its disappearance upon reduction.

In brief, one point on a CuAgAu CSAF was selected for this study. Its bulk composition was initially determined to be ~Cu₃₃Ag₃₃Au₃₃ by EDX. However, it changed to Cu₄₆Ag₆Au₄₈ after a series of experiments in the NAP-XPS chamber as a result of Ag evaporation at elevated temperatures, and the exact bulk compositions when this particular experiment was performed is unknown. The sample was heated from RT to ~623 K during the oxidation period with 0.01 Torr O₂ inside the chamber, while Cu $2p_{3/2}$, Ag $3d_{5/2}$, and Au $4f_{7/2}$ were continuously tracked to monitor its composition change. O 1*s* signal was not monitored due to a time limitation, which could have provided valuable information. The evolution of metal signals is shown in Figure 4.7, in which the onset of Cu change was estimated to be 450-500 K; after the Cu signal reached a peak level, all signals started to drop as Cu oxide film started to grow thicker, until the film stopped growing (likely due to kinetic limitation). During the reduction period, the reappearance of all metallic components showed up at ~650 K, recovering to their initial levels after ~10 min at 700 K. Raw XP spectra of Cu, Ag, and Au during oxidation and reduction periods can be found in Appendix section 4.

While Ag $3d_{5/2}$ and Au $4f_{7/2}$ peaks did not show any observable peak shape/position change except for their intensity variations, the Cu $2p_{3/2}$ peak showed a clear position shift towards lower binding energy upon oxidation, as shown in Figure 4.7 B-D, and the reverse shift matched the start of oxide reduction. While the lowering of binding energy in Cu $2p_{3/2}$ can be caused either by alloying with Ag and Au or the formation of Cu₂O⁷, the latter can better explain our observation in this work. Denoting the peak position of Cu(0) as X, Cu(I) oxide locates at X-0.45 (eV) and Cu(II) oxide locates at X+1.1 (eV)⁷. Fitting of Cu spectra with Gaussian-Lorentzian (70%-30% sum) gave a fractional contribution of Cu(0) and Cu(I) in overall signals, as shown in Figure 4.7C, in which the Cu(I) appeared upon reaching 623 K and peaked at the end of oxidation period, contributing to ~30% of the observed signal. As suggested by Biesinger et al.⁷ and Hirsimaki et al.⁸, the addition of Cu Auger LMM peak can help identify the chemical state of Cu, which could be used in future experiments. The oxygen exposure at 623 K during the oxidation period was estimated to be $\sim 3 \times 10^7$ L, and the formation of Cu₂O under such exposure is consistent with the study on Cu surfaces⁹.

4.4 Conclusion

The kinetics of surface segregation on CuAu alloys was systematically studied in this work using He⁺ LEIS and NAP-XPS. Several types of experiments were designed to tackle the intrinsic problems with kinetics measurements using super surface-sensitive but surface destructive ion scattering technique, in which the surface damage as a function of ion dose, temperature, and alloy composition was quantitatively examined. The behavior of segregation during a temperature change was explained by the equilibrium segregation states, the long range ordering of the CuAu alloys, and the ion induced damages. While the changes between equilibrium states within a temperature range of <300 K are small and the kinetics are usually fast at above 500 K, a series of 'sputter-jump' experiments were performed to probe the segregation kinetics at low temperatures. The time scales of segregation kinetics as a function of temperature and alloy composition were measured. The segregation (oxidation/reduction) kinetics of a CuAgAu ternary alloy was also studied using NAP-XPS under 0.01 mbar of oxygen and 0.1 mbar of hydrogen at ~623 K. The results from these experiment can be used to help estimate the time and conditions needed for catalyst pretreatment steps.

4.5 References

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Chapter 5 Oxygen adsorption across structural space

5.1 Introduction

Many heterogeneous catalytic reactions involving metal catalysts are structure sensitive, in which the activity and selectivity depend on the atomic structure of the metal surfaces on which reactions occur. By synthesizing nanoparticles with controlled shapes and exposed facets^{1–3}, researchers have been able to tune their catalytic properties^{4,5}. DFT calculations on different metal surface orientations also provide support and guidance to catalyst design⁶. Although the importance and possibility of utilizing surface structure sensitivity are understood, most studies in this area only compared reactivity and selectivity between a few low Miller index surfaces, since these surfaces are usually easier to synthesize and also require less modeling effort. The study of high Miller index surfaces is challenging in the sense that it is almost impossible to synthesize nanoparticles with only one type of high index surface. In addition, large unit cells are also needed for their simulations, and surface reconstructions under reaction conditions further complicate the problem.

First established in the 1940s by Gwathemey^{7–9}, the use of Surface Structure Spread Single Crystals (S⁴C) as high-throughput libraries of surface orientation and structure has served as an efficient tool for continuous screening of metals across surface orientations¹⁰. S⁴Cs are an excellent tool in the sense that they bridge the gap between the studies on flat single crystals under UHV and those on nanoparticles; the continuous distribution of surface orientations on S4C contains well defined high index surfaces, which have the key features of surfaces on a nanoparticle: high density of low-coordinated atoms and active sites, while monoatomic steps and kinks are their most basic forms.

As a model system in UHV studies, oxygen adsorption on Cu has been extensively examined utilizing experimental tools as well as computational methods, and a summary of the existing literature can be found in Chapter 1.3. Based on the oxygen exposure, pressure and temperature, oxidation on Cu surfaces can be classified into 3 stages. 1. For exposures less than $10^4 - 10^5$ L, a disordered chemisorbed layer of oxygen atom is observed on Cu (111) surfaces. 2. Formation of a Cu₂O thin film¹¹ occurs at exposure $> 10^5 - 10^6$ L at $10^{-7} - 10^{-5}$ Torr.3. Finally, a prolonged exposure at $10^{-5} - 10^{-3}$ Torr leads to further oxidize the surface to CuO, in the form of an oxide layer up to ~100 nanometers thick. As indicated by several experimental studies conducted under UHV conditions, molecular oxygen¹² and molecular precursors¹³ only exist on the Cu (111) surface at T<170 K, while only chemisorbed oxygen can be found on the surface at above room temperature. Oxygen dissociation is more active on Cu (100) and Cu (110) surfaces than on $Cu(111)^{12,14}$. The oxygen atom adsorption site on the Cu (111) surface was identified to be the three-fold hollow site by HR-EELS¹¹, SEXAFS¹⁵ as well as DFT¹⁶, whereas top-site and bridge-site-adsorption sites are comparably unstable¹⁶ and only occupied at $\sim 100 \text{ K}^{13}$. The differences between atomic oxygen adsorption energies on hcp- and fcc- hollow sites are within 0.1 eV¹⁶. Surface reconstruction upon oxygen adsorption is generally agreed to occur ^{10,17,18}, but the exact structure as a function of oxygen uptake and temperature is unclear.

In terms of studying structure-sensitive adsorption on Cu, pioneering work was done by Armitage and Woodruff¹⁹, in which they used a cylindrical Cu single crystal and showed that the rates of initial dissociative O₂ adsorption on low Miller index surfaces vary in the order (110) > (100) > (111) at room temperature. Lawton et al¹⁰ studied oxygen adsorption along major high symmetry axes of the Cu(111) structure using a dome-shape Cu(111) S4C combined with spatial resolved XPS and STM. Theyshowed the reconstruction of step sites into (100) steps regardless of their initial orientations. Schilling et al²⁰ later used STM to study the surface oxide structure its chirality on Cu(111) S4C.

To further explore the adsorption behavior of oxygen on Cu on high Miller index surfaces, especially those not lying along major symmetry axes and containing kink sites as well as more than one type of step site, this model system was studied using a Cu(111) S4C in this work. We have focused on measuring and describing the kinetic behavior of initial-stage oxygen adsorption across a continuous region of Cu surface structure space vicinal to the Cu(111) plane.

5.2 Experimental procedures

A Cu (111) S4C with a 10 mm diameter and 21 mm radius of surface curvature was prepared following the procedures described in Chapter 2.3. The Cu(111) S4C was vacuum brazed onto a $14 \times 14 \times 3 \text{ mm}^3$ Cu block using a thin foil of CuAg alloy flashed to 1100 K. A K-type thermocouple was spot welded to the side of the Cu block. A pyrolytic BN heater underneath the Cu block was controlled using a PID program to stabilize sample temperature with accuracy within 0.1 K. The crystalline orientation of the S4C was determined using EBSD. Two cycles of 3 kV Ar^+ sputtering and subsequent annealing to 900 K were used to reproducibly clean the surface, which was then cooled to 500 K within 5 min for oxygen adsorption experiments.

The oxygen pressure in the UHV chamber was monitored using an ion gauge, and a mass spectrometer was calibrated to convert mass spec signal readings to real-time O₂ partial pressures. Figure 5.1 shows a picture of the sample-doser geometry inside ThetaProbeTM. The two leak valves could direct O₂ flow to the sample surface are labeled as 'flood gun leak valve' and 'ion gun leak valve'. The first one was close to the sample (~2 cm) and the second was further away (<10 cm). Both were angled by ~45° with respect to the surface normal. The uniformity of oxygen exposure was first tested by using the two leak valves separately. While the 'flood gun leak valve' resulted in a faster oxygen uptake (determined by O 1*s* XPS) on the side of the surface closest to the doser, the 'ion gun leak valve' gave a much more uniform exposure, as is discussed in the next section. Therefore, the ion gun leak valve was used for this experiment.



Ion gun leak valve as doser



Figure 5.1 Oxygen dosing geometry in UHV chamber. Oxygen can be introduced into the chamber through two leak valves integrated with a flood gun and ion gun, respectively. The Oxygen uniformity test showed that while both dosing directions are angled (not from top-down of the sample), the doser from the ion gun leak valve is further away from the sample and thus gave relatively uniform oxygen coverage.

The oxygen pressure was controlled to be 2E-8 to 5E-7 mbar, with exposure time from 5 min to 1 hour to give target total exposures from 1 L to 1000 L (1 L = 10^{-6} Torr sec). After a 1000 L exposure, the Cu $2p_{3/2}$ and O 1s XPS signals were collected on 169 surface orientation across the Cu(111) S⁴C surface. These spectra were used to determine the near-surface compositions locally. For the smaller exposures used to measure oxygen uptake only O1s peaks were collected. The O 1s/Cu 2p_{3/2} ratio of Cu (111) surface after 900 L exposure at 650 K was used to define the absolute oxygen uptake. This is based on the known 29-oxide structure formed using these exposure conditions²⁰. All oxygen uptakes at other oxygen exposures were normalized by the saturation (1000 L) oxygen signal at 500 K. A 250 - 300 eV pass energy was used to obtain the O1s XP spectra, and gave a reasonably high signal-to-noise level at the expense of energy resolution. Since there wasn't a second distinguishable oxygen species within the kinetic energy range of 527 – 533 eV, such loss in energy resolution did not affect the quantitative estimation of total oxygen uptakes. Depending on the number of points measured on the S⁴C surface, one cycle of O1s XPS took 50 to 130 min. After each XPS mapping, sputter-anneal cycles were performed to restore clean Cu surfaces. The sequence of oxygen exposures was randomized to exclude any effect caused by constant drift in time (potential signal loss due to exposure of channel plate detector

to the oxygen environment, although the detector did not function in the presence of oxygen).

5.3 Results

Figure 5.2 shows the oxygen uptake maps across 169 surface orientations after various exposures to oxygen at 500 K. Major axes along (100) and (110) directions were labeled by solid and dotted lines, respectively. Three-fold symmetry can be observed on surfaces after exposures in the range 80 -150 L, in accordance with the symmetry of the FCC (111) surface. This confirms the uniform oxygen exposure (not affected by the 45° angled doser). Exposures labeled in Figure 5.2 were estimated using the steady-state pressure and overall exposure time without a calibrated mass spectrometer, since the main goal of this experiment was to demonstrate the uniform oxygen uptakes after 300 L exposure were already close to saturation levels. Details of the mass spectrometer calibration and exposure estimation are included in the Appendix section 6 for reference.



Figure 5.2 Oxygen coverage across Cu(111) S4C surface after various exposures (0-1200 Langmuir) at 500 K. 3-fold symmetry in oxygen uptake can be observed due to symmetry in FCC (111) surface structure

Due to the curved surface and X-ray source – sample – detector geometry, the absolute XP signal on one side of the sample (close to the detector side) is higher than on the other side. Since three-fold symmetry demonstrated, the 63 surfaces on the high-signal-side of the sample covering one-third of the whole surface were used to perform the detailed adsorption kinetic study. Figure 5.3 shows the fanshape region containing the selected 63 surfaces as well as the ideal surface termination (without reconstruction) of selected surfaces. Details of the definition of step, kink sites, and their densities will be discussed in the following chapter.



Figure 5.3 Map of linear step density as a function of the ideal surface structure covered in this study using (111)-centered curved single crystal; [1 0 0] and [1 0 0] directions are labeled along dotted lines. s1/(1 1 0) and s0/(1 0 0) types of steps as well as kinks composed of s1 and s0 steps are labeled on corresponding ideal structures. Angular kink density distribution is shown as a colored arc, in which blue represents zero kink density and red represents maximum density.

Figure 5.4 shows the normalized oxygen uptake maps (by comparing to 1000 L exposure) obtained at exposures in the range of 1 to 500 L with the surface at 500 K. Surfaces further away from (111) center have higher adsorption rates than center points. Surfaces with high Miller indices and lying on the left- and right-sides of the fan are chiral; however, they cannot exhibit enantiospecific interactions with achiral O₂. This is born out of the symmetry of the uptake data across the high symmetry direction indicated by the dashed black lines in Figure 5.4.

Figure 5.5 compares oxygen uptake on surfaces lying along both major symmetry axes and marked with the solid and dashed black lines. Surfaces along the (100) step direction clearly have higher adsorption rates than those lying along the (110) step direction with the same step density, while both being higher than the (111) surface with only terrace sites. Such an observation is consistent with data presented in Figure 5.2 and obtained across 169 surfaces, although the exact exposures in the earlier dataset had higher uncertainty and cannot be compared directly. A similar experiment was performed by Lawton et al¹⁰ in 2012 using a hand-polished Cu(111) S4C, in which the surface oxygen uptake along 4 major axes was compared upon 30 L exposure at 300 K; although it was confirmed that surfaces with higher step density were more active than (111) surface, the differences between $[11\overline{2}]$ and $[\overline{1}\overline{1}2]$ directions (corresponding to boundary/solid and dotted line directions in this work) were small compared to the noise level. Two reasons might have caused the difference in conclusions between this work and the mentioned literature: 1) the S4C used in this work was nano-machined and gave better structural accuracy compared to the hand-polishing method; 2) since the structural dependency of oxygen uptake is only clear within a narrow exposure window (i.e. ~30-120 L), a slight miscalculation (either in this work or the literature) in oxygen exposure is enough to make the difference between different axes less obvious, which was enhanced by a higher noise level of data in the literature.



Figure 5.4 Surface oxygen uptake at various oxygen exposures at 500 K. [1 0 0] direction is indicated by dashed lines; oxygen exposures in the unit of Langmuir (1 $L=10^{-6}$ Torr·sec) calculated with calibrated Mass Spectrometer are labeled next to each map. Saturation coverages are defined by oxygen uptakes at 1000 L exposure, while the difference in oxygen uptake between 500 L and 1000 L is within experimental error.

Figure 5.6 presents the same dataset in another form: oxygen uptake on 63 surfaces as a function of exposure were colored by the step site density (defined by the fraction of step site among all sites on each surface).



Figure 5.5 Oxygen uptake along (100) and (110) directions at various exposures. (100) steps show higher activity in dissociating oxygen than (110) steps, while both are higher than that on terrace sites.



Figure 5.6 Surface oxygen uptake on 63 surfaces studied in this work at various oxygen exposures from 0.76-1000 L. Step edge density is used to color data points without distinguishing the type of step. Surfaces with low step density showed slower adsorption kinetics.

5.4 Ideal surface structures

The ideal structures of the surfaces across the Cu(111) S4C consist of (111) terraces and monoatomic steps, and the density of steps is only a function of the

distance between a surface and (111) pole; the structure of steps depends on surface orientations, as illustrated in Figure 5.3. In the azimuthal angular direction, the kink density along the step edge is zero in the high symmetry directions and maximum along the direction that bisects the high symmetry directions.



Figure 5.7 Ideal structure of surfaces vicinal to Cu(111). Two types of step sites are shown by rectangles and labeled as (110) and (100) steps. A kink site is composed of one (110) step and one (100) step.



Figure 5.8 Calculation of areal surface site coverage. α_c is the angle between the (111) plane and (110) or (100) planes, e.g., $\alpha_{c(100)} = 54.7^{\circ}$, $\alpha_{c(110)} = 35.3^{\circ}$. α is the angle between the (hkl) plane and the (111) plane ($0 \le \alpha \le 12^{\circ}$ in this work).

$$\frac{L_1}{L_1 + L_2} = \frac{\tan(\alpha)}{\tan(\alpha) + \sin(\alpha_c) - \cos(\alpha_c)\tan(\alpha)}$$

$$\rho_{s100} = \frac{2\tan\alpha}{\sqrt{3} + \tan\alpha} \frac{2\tan\theta}{\sqrt{3} + \tan\theta}$$
$$\rho_{s110} = \frac{2\tan\alpha}{\sqrt{3} + \tan\alpha} \frac{\sqrt{3} - \tan\theta}{\sqrt{3} + \tan\theta}$$
$$\rho_t = 1 - \rho_{s100} - \rho_{s110}$$

The density of one type of site can be defined by its number density, area density, or their corresponding fraction after normalization. The normalized area fraction is the most useful one in kinetic modeling and will be used by default in this context.



Figure 5.9 Relative concentration of sites calculated for the ideal surfaces along the edge of the S⁴C sample studied in this work. Depending on the definition of sites, one can either see a kink site being one pair of (110)-step and (100)-step sites, or a kink site as an independent site.

5.5 Kinetic modeling of oxygen adsorption

As described in earlier sections, oxygen dissociatively adsorbs on Cu surfaces above room temperature, forming nanoclusters of oxide on Cu (111) surfaces, which turn into ordered 44'- and 29'- structures upon annealing 423 and 673 $^{21-24}$. While on (100) and (110) surfaces, $(\sqrt{2} \times \sqrt{2})$ R45° and (2 × 1) superstructures^{25–27} are formed, respectively, at room temperature.

Several kinetic models for the mechanism of Cu(hkl) initial oxidation have been tested and will be discussed in the following sections; the fitting results using different kinetic models are illustrated in Figure 5.7, Figure 5.8, and Figure 5.12 with three representative surfaces: Cu (111), Cu (322), and Cu (332). A more detailed description of fitting can be found in Appendix section 5.

5.5.1 First-order adsorption

As the simplest adsorption model, first-order kinetics adequately describe a variety of processes. Non-dissociative Langmuir-Hinshelwood adsorption is described by first-order kinetics, while other adsorption mechanisms can also exhibit first-order kinetics under certain conditions. To provide a baseline for further comparison with more complex models, first-order adsorption kinetics taking the form of Equation 5.1 were fit to experimental oxygen adsorption data on 63 Cu surfaces vicinal to (111).

Equation 5.1
$$\frac{d\theta}{dt} = k_{ads1}^{(hkl)} P_{02}(1-\theta)$$

By assuming that there is only one type of 'average site' on each of the 63 surface orientations and allowing only one adsorption rate constant per surface orientation, $k_{ads1}^{(hkl)}$, the entire dataset containing 63×14 data points can be described using 63 independent variables. Fits to data from 3 selected surfaces are shown in Figure 5.7 (blue curves). On the Cu(111) surface, first-order kinetics gave a reasonable fit to experimental data, while the deviations are more evident at low coverages (<30%) on Cu (322) and (332) surfaces.



Figure 5.10 Fittings of oxygen adsorption on Cu (111), (322), and (332) surfaces using the 'one-site' assumption. Precursor-state model, 1st order model, and 2nd order model are compared.

5.5.2 Second-order adsorption

It is known that oxygen uptake on Cu(111) surface increases linearly with exposure when oxygen coverage is relatively low (up to $\theta \approx \frac{1}{2}\theta_{sat}$) and surface temperature is higher than room temperature^{28,29}. Second-order kinetics have been used to describe the adsorption process on low Miller index Cu surfaces at room temperature²⁹. A second-order equation with a single rate constant for each surface orientation has been examined in this section, defined as:

Equation 5.2
$$\frac{d\theta}{dt} = k_{ads2}^{(hkl)} P_{O_2} (1-\theta)^2$$

This simple model assumes that an 'average' type of adsorption site represents all sites on each surface. The fitting results from 3 representative surfaces are shown in Figure 5.7 (red curves). It is clear that the low exposure region of data on (322) and (332) surfaces are under-predicted by second-order kinetics, and this site-averaged model is an oversimplification of reality. It should be noted that regular 2nd order kinetics fittings overlap with precursor-state fittings on (322) and (332) surfaces.

5.5.3 Single-site precursor-state model

As described in several published papers ^{29,30}, the precursor-state kinetic model can describe oxygen adsorption behavior on Cu (111) surface in a submonolayer coverage regime. In this model, it is assumed that there exists a 'preadsorbed' state in which oxygen molecules can diffuse randomly on the surface before being chemisorbed onto one site. Upon visiting each site, the precursor can either adsorb, desorb or migrate to another site. The parameters in this model include P_{ads} , P_{des} , and P_{dif} representing probabilities of adsorption (from precursor-state to chemisorbed state), desorption, and diffusion between sites. Derivation and discussion of the precursor-state model can be found in the Appendix section 5. Adsorption geometries of precursors were discussed in Mavrikakis' work¹⁶.

On the Cu (111) surface, the oxygen sticking coefficient measured in this work over the exposure range of 0 to 150 L is roughly constant, $S \cong 2.1 \times 10^{-3}$, for $\theta < 0.65$. This is consistent with the literature²⁹, in which the initial sticking probability was determined to be $S_0 \cong 2.5 \times 10^{-3}$ at 500 K. In comparison, on Cu

(100), $S_0 \cong 2.0 \times 10^{-2}$ at 500 K as determined using ellipsometry and AES³¹ On Cu (110). is $S_0 \cong 0.2^{31}$.

Figure 5.7 already included the precursor-state fitting (black curves) on Cu (111), (322), and (332) surfaces, compared with 1st order and 2nd order fitting results. The precursor-state model showed the best performance on Cu (111). Not surprisingly, when a single site is assumed in the precursor-state model, it fails to describe the oxygen adsorption kinetics on surfaces such as (322) and (332) with high step densities.

The inclusion of the second type of surface site into the precursor-state model will be discussed in the following sections.

5.5.4 Multi-site first-order adsorption

As it is clear that when assuming the distribution of different site types on a surface can be represented by an 'average site' we are neglecting complexity, and failing to reproduce the structure sensitivity of oxygen adsorption on Cu(hkl). Thus, multi-site models will be tested with the following assumptions and constraints: 1) all 63 surfaces examined in this study have *n* common site types; 2) each type of common site (e.g. terrace site, type-1 step size, type-2 step site, and kink site) is associated with an adsorption rate constant that is not a function of surface orientation, while the only difference between surfaces is the areal fraction of site types; 3) all sites are distributed randomly across the surface. It should be noted that 3) is only assumed so that for adsorption requiring more than one empty surface site (not necessary for first-order kinetics), the possibility of finding adjacent empty sites can be estimated to be proportional to the product of concentrations of each site. As an example, we might assume that there exists one type of terrace site, t_1 , and two types of step sites, s_1 and s_2 , on all *hkl* surfaces. On an ideal (111) surface, t_1 terrace site account for 100% of all adsorption sites, $\theta_{t1} = 1$. On a high Miller index surface, the fractions of s_1 and s_2 sites are higher: $\theta_{t1} < 1$, $\theta_{s1} > 0$, and $\theta_{s2} > 0$. We assume that all sites of a given type have the same kinetic behavior for oxygen adsorption, regardless of surface orientation. However, the fractions of each site type differ across surface orientations. In this way, we can significantly reduce the degrees of freedom in data fitting and get a more robust estimation of adsorption kinetics across all surfaces examined in this work.

The distribution of sites is allowed to vary independently at each surface, while the rate constants of common sites are shared parameters across all surfaces. The fitting results on Cu(322) and Cu(332) are shown in Figure 5.8. While three types of common sites were assumed on the 63 surfaces examined, only two of them are present on these two surfaces. 'Component-3' represents the contribution from a highly active site for oxygen adsorption with a sticking coefficient of 0.68, while its fractional abundance is correlated with step density, as is shown in Figure 5.10. Compared to simple 'average site' models described in previous sections, this multi-site model clearly better approximates the experimental data without any apparent deviation trend.



Figure 5.11 3-site 1st order fitting results on (322) and (332) surfaces. Three common sites are assumed to be dominant sites on all 63 surfaces, while their relative abundance is allowed to vary on each surface. Adsorption follows 1st order behavior on each site with a rate constant k. The 'type-1' site is absent from 322) surface and the 'type-2' site is absent from (332) surface. k_1 =0.0069, k_2 =0.020, k_3 =1.36; corresponding to sticking probability of ~0.34%, 0.95% and 68%.

The fitting results of all 63 surfaces are shown in Figure 5.9 as parity plots with adsorption rate constants labeled alongside. Figure 5.10 shows the example of site distributions of the '3-site model' and their uncertainties, estimated using a Monte Carlo approach. More information on site distribution fitted from different kinetic models is in the Appendix section 6.





Figure 5.12 Parity plots of 1st order fittings by assuming 1-4 common sites are shared among 63 surfaces.



Figure 5.13 Fitted site distribution and corresponding uncertainties. 3 types of common independent sites are assumed, all sites have 1st order kinetic behavior. Color bars corresponding to the site distributions and uncertainties are shown in the bottom row.

Site distributions in Figure 5.10 show a clear mirror symmetry w.r.t. to the dotted line, with a slight offset of $\sim 2.5^{\circ}$ towards the right, which is likely to be a result of an error in surface orientation determination in EBSD. The first type of site dominates Cu (111) surface as well as surfaces along [110] directions, representing terrace site; the second type of site is concentrated on surfaces along [100] direction and with high step densities, with the highest fraction concentration of 70%, indicating step sites with much higher adsorption activity; and the distribution of the third type of site is in accordance with the step density, regardless of the type of sites. Uncertainties in site distributions are much smaller than their concentrations.

5.5.5 Multi-independent-site second-order adsorption

By assuming adsorption can only take place on two adjacent empty sites of the same type, a simple model taking the linear combination of individual types of sites can be developed: apparent adsorption rate constant on each site can be fitted using the following definition

$$\frac{d\theta_i}{dt} = k_{hkl}^i P_{O_2} (1 - \theta_i)^2$$
 Equation 5.3

While total coverage:

$$\Theta = \sum_{i} x_i \theta_i$$

In which x_i denotes the fraction of site *I* among all sites on surface *hkl*; Θ and θ_i range from 0 to 1, and $\Theta = 1$ corresponds to the saturation oxygen coverage of each surface in the initial stage of oxygen adsorption. The surface temperature and oxygen exposure rang used in this work should be well within the initial oxygen adsorption stage as described in literatures^{11,31}.



Figure 5.14 Parity plots of 2^{nd} order fittings by assuming there are 1-4 common sites shared among 63 surfaces.

Similar to the treatment in first-order and second-order kinetics, we first assume there exist two different types of sites, while dissociative adsorption can only occur on two adjacent sites of the same type. Kinetic parameters, including adsorption, desorption, and diffusion probabilities on each site are shared parameters across 63 surfaces, while the distribution of sites is allowed to vary on each surface.

5.5.6 Multi-site precursor-state model

Following the same method applied in sections 5.5.4 and 5.5.5, we assume there are a few types of independent sites shared commonly among all 63 surfaces examined in this work, and fit their site distribution as well as kinetic parameters on each of the sites. Figure 5.12 shows fitting results on Cu (322) and (332) surfaces, in which 3 common types of sites are assumed, and only 2 of them showed up on each surface, similar to the results shown in Figure 5.8 using first-order assumption.



Figure 5.15 3-site precursor-state fitting results on (322) and (332) surfaces. 3 common sites are assumed to be dominant sites on all 63 surfaces, while their relative abundance is allowed to vary on each surface. Adsorption follows precursor-state behavior on each site with initial sticking coefficient S₀ and desorption/diffusion terms K_1 , K_2 . 'type-1' site is absent from (322) surface and 'type-2' site is absent from (332) surface. Initial sticking probabilities on 3 sites are ~0.26%, ~1.3%, and ~100%. The chance of precursor desorption from empty sites of 'type-1' and 'type-3' without another available site nearby is high, whereas it is low on 'type-2' sites.



Figure 5.16 Site distributions along high symmetry directions. A) Terrace site, (100)-step and (110)-step sites on the ideal surface structures. B) Sites 1-3 on reconstructed surfaces predicted by the precursor-state model.

5.5.7 Summary of complexity and performance of all models discussed above

Table 5.1 summarizes key parameters of the above-discussed kinetic models, including overall performance in terms of adjusted R-square, average absolute offset in fitting (in a unit of normalized oxygen coverage), and complexity of the model in terms of *#* of parameters.

	Model	DOF (composition)		Offset %	Adjusted R ²
1 st order	2-site	65	2+63	4.92	0.962
	3-site	129	3+63×2	3.15	0.983
	3-site*	12	3+9	4.07	0.973
	4-site	193	4+63×3	2.91	0.985
Langmuir-	2-site	65	2+63	6.39	0.936
Hinshelwood	3-site	129	3+63×2	5.34	0.952
2 nd order	4-site	193	4+63×3	5.17	0.955
Precursor-	2-site	69	6+63	4.17	0.974
state 2 nd order	3-site	135	9+63×2	2.72	0.985
	3-site*	18	9+9	3.10	0.983

Table 5.1 Summary of adsorption model fittings, including their degree of freedom in fitting, average absolute offset as well as adjusted R^2 . [* represents the linear decomposition and interpretation of fitted sites using known surface sites on ideal surfaces, as discussed in section 5.5.8]

Adsorption rates at various temperatures on Cu (111) were given in literatures³², with the conclusion that oxygen incorporation into sublayer as well as

sublayer oxygen diffusion out of lattice is only becoming evident at above 600 K. Thus, measuring oxygen uptakes using XPS after oxygen evacuation (a procedure used in this work) should not have caused a deviation in results.



Figure 5.17 Summary of model performance

Figure 5.13 compares the performance of models described in section 5.5, in which the left column figures show the trend lines of how much model

predictions deviate from measured results, and the right column figures show the 68% confidence intervals (corresponds to '1-sigma'). Trend lines and confidence intervals were calculated using a Monte Carlo method: with known uncertainty in oxygen signal determination (~4% of maximum coverage), Gaussian noises were added to the original dataset, and model fittings were performed; such noise adding and model fitting were repeated 100 times for each model, and then a Gaussian Process Regression model was applied with optimized hyper-parameters to give trend line, confidence interval as well as uncertainties on each kinetic parameter.

When 1st order kinetic models are compared with 2nd order kinetic models, it is clear that with the same number of parameters (same degree of freedom), 1st order models outperform corresponding 2nd order models in terms of absolute offset value; 2nd order models also consistently fail to predict 100% coverage at 1000 L oxygen exposure. Thus, data measured in this work excludes Langmuir-Hinshelwood 2nd order kinetic being the dominant pathway on Cu surfaces vicinal to (111) orientation at 500 K. When more parameters are included in the model, the additional flexibility will inevitably improve the fittings; such improvement is obvious when the type of common site increases from 1 to 3, but becomes marginal thereafter. Given ~4% of uncertainty in raw data acquisition, the 3-parameter model and 4-parameter models are already indistinguishable, and further complication of the model is meaningless.

Precursor-state model describes the kinetic behavior better than 1st and 2nd order models when a similar degree of freedom is allowed in fitting, but due to its flexibility, especially when more number of sites are included, accurate

157

determination of model parameters that describe all 63 surfaces is challenging. And its marginal improvement compared to 1st order models is not sufficiently significant to preclude the latter.

It should be noted again that 'multi-site' models in section 5.5.5 - 5.5.7 have an 'independent site' assumption, which means oxygen atoms adsorbed onto one type of site cannot migrate to another type of site, and in both 2^{nd} order kinetics, molecular oxygen dissociation requires two adjacent sites of the same type. Such assumption may not be accurate, while the inclusion of some site-interaction terms can further improve the fitting, but the quality of data collected in this work in terms of uncertainty is not enough to allow the fitting of a very flexible model. Thus, fitting parameters qualitatively reflect the existence of multiple sites and their natures in oxygen adsorption, but care should also be taken when comparing these numbers to other works quantitatively.

5.5.8 Interpretation of kinetic model fitting results

While many kinetic models have been examined and compared in previous sections in terms of their fitting performance and flexibility, it is important to interpret these fitting results in a physically meaningful way to help understand this adsorption reaction. As discussed in section 5.5.7, '3-site' 1st order kinetics and '3-site' precursor-state kinetics gave reasonably well fittings with fitting offset comparable to experimental uncertainty level. Thus, the fitting parameters in these two models were further examined and are discussed in this section.

In each of the two models, 3 sets of kinetic parameters (rate constant k for 1st order kinetics; rate constant S₀, desorption/diffusion terms K₁ and K₂ for precursor-

state kinetics) were given by the fitting, as well as a set of 63×3 parameters describing the relative abundance of sites (with DOF = 63×2). Although each surface was fitted separately, the distribution of sites showed smooth variation across the structural space with mirror symmetry; thus, it is natural to relate them to the site distributions on ideal surface structures (discussed in section 5.4). Sites on ideal surfaces vicinal to (111) orientation can be described by 3 most basic sites: terrace site, (111)-type step site, and (100)-type step site. The abundance of kinks can be expressed by the linear combination of the basic sites. By counting the density of sites on each surface, we can easily get a distribution of basic sites on ideal surface terminations, denoted as D_{ideal} (3×63 matrix), as shown in Figure X. Then we can use a 3×3 matrix *A* to relate this distribution to the fitted distributions $D_{fitting}$:

 $A * D_{\text{ideal}} = D_{\text{fitting}}$

$$\begin{bmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{bmatrix} * \begin{bmatrix} terrace \\ (100) - step \\ (111) - step \end{bmatrix} = \begin{bmatrix} site - 1 \\ site - 2 \\ site - 3 \end{bmatrix}$$

In this way, we can greatly reduce the flexibility of the model by cutting free variables describing site distributions from 63×2 to 3×3 . Matrix A describing both '3-site' models are shown below:

$$A_{1^{st} order} = \begin{bmatrix} 1.05 & -3.93 & 0.20 \\ 0.06 & 3.71 & -0.37 \\ -0.11 & 1.22 & 1.17 \end{bmatrix} \pm \begin{bmatrix} 0.03 & 0.20 & 0.15 \\ 0.03 & 0.20 & 0.17 \\ 0.01 & 0.07 & 0.08 \end{bmatrix}$$
$$A_{precursor} = \begin{bmatrix} 1.12 & -3.51 & 0.00 \\ -0.03 & 3.53 & -0.10 \\ -0.08 & 0.98 & 1.09 \end{bmatrix} \pm \begin{bmatrix} 0.02 & 0.13 & 0.12 \\ 0.02 & 0.10 & 0.11 \\ 0.01 & 0.06 & 0.06 \end{bmatrix}$$

Fitting performance using $A_{1^{st} order}$ and $A_{precursor}$ are also shown in Table

5.1, labeled in *. Both fittings showed reasonably low offset considering their

reduced DOF compared to corresponding '3-site' models, especially in the case of the precursor-state model.

Take Apprecursor as an example: density of site-3 is the summation of all the monoatomic steps on the corresponding ideal surface, independent of its type; density of site-2 is 3.5 times of the (100)-step; and density of site-1 is the summation of terrace sites subtracted by 3.5 times of the (100)-step. We can think of it as each (100) step turns 3.5 terrace sites into 3.5 type-2 sites, while this newly formed type-2 site is different from both terrace and step sites in oxygen adsorption kinetics. Uncertainties were estimated by calculating $A_{precursor}$ using 2/3 of all the surfaces that were randomly selected, and this process was repeated 100 times to get the standard deviation in parameters. $A_{1^{st} order}$ is very similar to $A_{precursor}$ although different kinetic models were applied, which again supports the interpretation above. What exactly this type-2 site is and how terrace sites reconstruct into type-2 sites are unable to tell from this work, but several existing papers^{33–36} may help understand the possible reconstructed structure: it was found that Cu(410) and equivalent surfaces are the most stable facets after reconstruction upon initial stage oxidation on many $Cu(h \ 1 \ 1)$ (h>3) surfaces, while the size of the new facets were affected by the temperature and oxygen pressure during oxidation. It would be interesting to see if future STM works on Cu(h 1 1) surfaces with h < 3can help explain the reconstruction observed in this work.
5.6 Conclusion

The kinetics of initial oxidation of Cu surfaces vicinal to (111) orientation was mapped out in this work at 500 K. 1st order adsorption kinetics, Langmuir-Hinshelwood 2nd order adsorption kinetics, and precursor-state 2nd order kinetics were fitted to the data, and their performance was compared. '3-site' 1st order kinetics and '3-site' precursor-state kinetics both showed good fitting to experimental data, and the fitted site distributions showed clear mirror symmetry w.r.t. the [100] direction, in line with surface symmetry. The fitted three sites represent adsorption sites with low, medium, and high activities, which can be related to the site distribution on ideal surface structures by a simple matrix *A*. Although surface reconstruction under the presence of adsorbates/reaction environment³⁷ is recognized in many literatures, this work provides a way to interpret the structure after reconstruction without the use of STM.

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Chapter 6 Catalytic oxidation reaction evaluation across composition space

6.1 Introduction

To further utilize CSAFs and enable their characterization in another dimension, microreactor array systems have been designed and assembled under the effort of several Ph.D. students (Gamze Gumuslu, Irem Sen, Nick Golio) and a postdoc (Peter Kondratyuk) in our group¹. Its ability to be used as a tool for screening the catalytic performance of alloy catalysts in hydrogenation reactions across alloy composition space was successfully demonstrated².

The direct oxidation of isopropyl alcohol (IPA) with molecular oxygen has been used as a probe reaction to determine the nature of active surface sites of catalysts3,4. The oxidation of alcohols is also important for the synthesis of fine chemicals and their removal from waste water5, as IPA is widely used as washing agent in semiconductor and precision machinery industries6. Depending on the catalyst and reaction conditions, dehydration, partial oxidation as well as full combustion products can be produced, forming propene, acetone, and carbon dioxide, respectively. The dehydration activity of a catalyst used to be a good measure of its acidity4.

While reactions involving hydrogen dissociation/recombination, and olefin hydrogenation have been already studied using the microreactor array, demonstrating its high efficiency in catalytic activity screening, its potential to be used for more types of reactions is still yet to be explored. There are several intrinsic advantages in studying hydrogen-related reactions using the microreactor array relative to other reactions: 1) quadrupole mass spectrometers typically have high sensitivity towards light fragments such as hydrogen, which enables more accurate quantification towards conversion; 2) hydrogenation reactions typically do not leave residues on catalyst surface (although hydrogen may cause the formation of metal hydrides and destabilize the thin film), so CSAF samples can stay relatively clean over a long period, and activity measured can represent steady-state performance; 3) hydrogen activation has very high TOF on Pd-based catalysts, and maximum conversion can be reached below 600 K, which is the operation limit for the glass-made microreactor. These are challenges to the studying of oxidative reactions and need to be studied.

6.2 Experimental procedures

6.2.1 Catalysts preparation

Several metal wires and CSAFs were prepared to test the activity of IPA decomposition/oxidation on various pure metals and their alloys. Pd, Ag and Pt wires were 2-inch long with 0.05 inches in diameter, and folded to 1-inch long, Cu wire was 8-inch long and folded to 1-inch long with 0.01 inch in diameter.

6.2.2 Catalytic activity tests

Details of the microreactor array, including its fabrication method, material, dimension, and its sampling system as well as its connection to mass spectrometer were described in earlier publications^{1,2,7} and dissertations. In brief, the microreactor system consists of a feed-gas control unit, a channel-splitting unit, a reaction zone, a product gas sampling system, and a detection unit, as are shown in

Figure 6.1. The specially designed glass microchannel block in Figure 6.2 segments the CSAF surface into 100 independent reaction zones/cells, each having a volume of $800 \times 600 \times 100 \ \mu m^3$. The same reactants are fed into each microreactor cell, and after reactions take place upon contact with the heated CSAF surface, products are directed to the outlet and sampled by a moving capillary that sucks product molecules into a UHV chamber for analysis with a mass spectrometer. Since there is a composition gradient across the lateral direction of the CSAF, the microreactor array acts as 100 reactors with different catalyst compositions in each and produces catalyst-dependent products that allow an efficient catalytic screening.



Figure 6.1 Schematics of microreactor system consists of mass flow controllers, microreactor array, reaction zone, sampling system, and mass spectrometer.



Figure 6.2 Microchannel glass block with 100 inlet channels and 100 outlet channels. Each pair of channels together with one rectangle region of the gasket consist a reaction zone that is isolated from neighboring zones and acts as an independent reactor when combined with a CSAF.

In all catalytic testing experiments, Ar was used as a carrier gas for IPA vapor, which was saturated in the vapor phase in a flat bottom flask by bubble-flowing Ar through liquid IPA at room temperature (~296 K, 4.4% IPA at saturation concentration) at a flow rate of <5 ml/min (Ar flow rate). Oxygen was used as a second feed gas in oxidation reactions. All gas flows were controlled using a set of mass flow controllers calibrated by a Baratron pressure gauge. The residence time inside each channel was estimated to be ~0.1-0.2 sec, depending on the flow rate. The catalyst surface area in each channel was ~0.5 mm².

Experiments were conducted on two separate microreactor array systems, with the only difference being the mass spectrometers: an SRS Residual Gas Analyzer (RGA) mass spectrometer was used in one setup, while an Extrel mass spectrometer was used in another setup.

Two types of experiments were conducted in this work: in the first one, the sampling capillary tube was kept stationary inside one channel with certain alloy composition and steady flow condition, while the temperature was increased from room temperature either stepwise or with a constant (usually ~0.03 K/sec) rate. Mass spectra covering m/z of 10-60 a.m.u. were collected continuously with an m/z step of 0.1 every 1-5 sec. The steady flow condition both inside the microreactor channel as well as in the mass spectrometer chamber can help reduce the fluctuation in signal and allow a more accurate background/baseline subtraction. In the second type of experiment, a selected number of channels (usually ~10 for binary CSAFs) were sampled sequentially and iteratively at a constant flow condition and temperature, and typically the sampling capillary would stay for 1-2 min in each channel to make sure steady-flow was developed so that products in earlier channels were completely pumped out.

6.3 **Results and discussion**

6.2.3 Activity on pure metal wires

While the combination of CSAF and microreactor provides an efficient platform for catalytic activity screening across alloy composition space, it is not ideal for quick estimation of activity on pure metals, since the thermal-induced dewetting of thin-film may expose substrate and introduce the substrate-metal interface and complicate the interpretation of results; as mentioned in previous sections, the small contact area and short contact time also put a higher requirement on the sensitivity of the mass spectrometer. Thus, before jumping into the fabrication of CSAFs and tedious sample loading, alignment, leak test, etc., it is more time-efficient to study the catalytic behavior of pure candidate elements by running reactant gas over pure metal wires. Calibration channels are already integrated into the microreactor system and does not require separate calibrations. Just to provide a reference for future efforts on this project, the activity/selectivity of several metals are listed in Table 6.1. An example of mass spec data of IPA oxidation catalyzed by Pt wire is shown in Figure 6.3, in which the formation of acetone, CO₂, and H₂O can be observed during the temperature ramp. Species that most likely contributed to the signal are labeled in plots of corresponding m/z values.

Metal	Flowrate	Т	IPA	O2	Acetone	CO2
	(Ar/IPA +	(K)	conversion	conversion	selectivity	selectivity
	O2)		(%)	(%)		
Ag	9.5+1	600	87	65		
Ag	9.5+0.5	500	1.7	2	100	0
Ag	9.5+0.5	540	33	10	100	0
Ag	9.5+0.5	570	66	29		
Ag	9.5+0.5	600	84	76		
Ag	4.75+0.25	600	87	87		
Ag	9.5+0	600	42		100	0
Cu	9+1	500	100		100	0
Pt	9+1	500	>90	36		
Pt	9.5+0.5	500	>95	>70		
Pt	5+1	530	>95	18		

Table 6.1 Catalytic activities of Cu, Ag, and Pt in IPA oxidation reactions.



Figure 6.3 IPA oxidation catalyzed by a 2-inch Pt wire. 5 ml/min Ar/IPA, 1 ml/min O_2 , 300-530 K. Reactivity (IPA consumption) started at ~ 415 K and approached maximum at ~ 530 K, leading to the formation of acetone and CO_2 , while the selectivity towards CO_2 increased significantly at above 500 K.

6.2.4 Mo catalyzed IPA dehydration

Mo has been routinely used as the substrate for CSAF depositions in our lab as it does not alloy with transition metals to a great extent under normal annealing conditions <800 K (phase diagrams of Mo-X systems are attached in Appendix section 1). However, Mo oxide is also known to have reactivity towards IPA dehydration. Before exploring the activity of alloy components in CSAFs in IPA decomposition/oxidation, the role of substrate material Mo has to be first studied.

A Mo block of $14 \times 14 \times 3$ mm³ in dimension was loaded into a microreactor assembly, with a glass gasket used to isolate adjacent channels. A total flow rate of 5 ml/min was used in all Ar/IPA and O₂ flow combinations. The activity of IPA decomposition without oxygen was first tested at 300-600 K, and oxygen was added in later experiments to study its effect on the activity/selectivity.

Pure Mo surface exhibited activity towards IPA dehydration with and without the presence of oxygen, and deactivation was also observed at 550 K and above.

The morphology of the Mo surface after reactions was characterized in SEM and shown in Figure 6.4. Color contrast can be observed between zones exposed to reactant gases and that under glass gasket as a result of MoO_x crystal formation, as depicted in the last row of Figure 6.4; whereas the region protected by glass gasket (and thus not in contact with oxygen) did not show the formation of any micron-sized crystal.



Figure 6.4 SEM/EDX images of Mo surface after used as catalyst in IPA oxidation reaction. A) Array of channels spaced at 1 mm. B) Zoom-in on one channel. C) Pieces of MoO3 formed inside channel region. D) Surface under glass gasket where no MoO3 crystals formed. E) MoO3 nanocubes. F) EDX-SEM overlapped image of MoO3 nanocubes, red-Oxygen, green-Mo.

6.2.5 Mo-Pd catalyzed IPA dehydration/oxidation

While Mo is identified to belong to the 'acidic' group of metals that give dehydration product (propene), Pd is among the 'redox' group of metals that have high activity towards partial oxidation reaction yielding acetone at low temperature. In this work, we explored the combination of Mo-Pd in the catalysis of IPA conversion. Since Pd-Mo can form alloys at up to 20 at% Pd (80 at% Mo), and Pd thin film tends to dewet and form Pd nanoparticles, it is expected that some extent of alloying can be achieved after annealing of Pd thin film on Mo substrate.

A Pd-on-Mo CSAF with a thickness gradient from 0 to 38 nm was prepared by e-beam evaporation as described in earlier chapters. After sampling loading and position alignment, 10 channels were selected along the thickness gradient direction with Pd thickness ranging from 3 to 38 nm. The activity of 10 channels was monitored while increasing sample temperature stepwise from 300 K to 600 K. Activity towards acetone formation was first observed on high-Pd channels at 400-450 K with up to ~75% IPA conversion, which disappeared upon further heating. As shown in Figure 6.5, IPA conversion reappeared after 500 K is reached with 100% selectivity towards propene formation, and the gradual decay in IPA conversion as Pd content increased was also observed, indicating the activity only came from the exposed Mo substrate. It should be noted that due to gasket misalignment, the high-Pd channel that showed activity towards acetone formation had a lower flowrate and thus higher residence time than others; and since it did not show activity towards propene formation, it was not compared with other channels in Figure 6.5. SEM images of the reaction zones were taken after the experiment to estimate Mo exposure, and are shown in Figure 6.6. No thin-film dewetting was observed (e.g., nanoparticle or 2-D porous structure formation).

After the temperature peaked at 600 K, the sample was gradually cooled to room temperature in the same stepwise manner, while the activity of Pd did not

reappear. CSAF was treated with pure H_2 flow at 600 K with the hope to recover Pd activity, but the low-temperature activity towards acetone formation was not restored.



Figure 6.5 IPA oxidation conversion on Pd-Mo catalysts.



Figure 6.6 SEM images of Pd-Mo surfaces after used as catalyst in IPA oxidation reaction.

6.3 Conclusion

Isopropyl alcohol oxidation reactions catalyzed by Cu, Ag, Pd, Pt, and Mo were studied in this work. While all metals showed catalytic activity either towards acetone formation (Cu, Ag, Pd, Pt) or towards propene formation (Mo), the activity measured from a single channel was usually too low to be accurately determined due to the low catalyst loading and short contact time. A Pd-on-Mo CSAF was also tested, while the pure Pd surface showed transient activity towards acetone formation, it quickly deactivated and did not regenerate its activity after H₂ treatment. A gradual activity change was observed across the thickness gradient on the CSAF, only showing propene formation activity as a result of thin-film dewetting and subsequent exposure to Mo substrate.

IPA oxidation activity catalyzed by Cu, Ag, Pd, Pt, Mo measured in this work qualitatively agrees with literature, but the attempt to study its activity on binary/ternary alloys across composition space was not successful, mainly due to the low catalyst loading and short contact time in our microreactor design. If similar reactions are to be studied in the future, modifications on the microreactor sealing, both at the block-CSAF interface and at the sampling region, will be needed to allow a lower reactant gas flow rate and thus longer contact time as well as higher conversion.

6.4 References

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Chapter 7 Discussion on Angle-resolved XPS (AR-XPS)

7.1 Motivation

XPS and He⁺ LEIS have been routinely used in this thesis for quantitative composition determination of alloy surfaces. Although XPS is often regarded as 'surface-sensitive' compared to other tools such as EDX, XRD, etc., the information depth (e.g. inelastic mean free path - IMFP) of standard XPS in alloy materials is usually larger than 2 nm, which contains ~ 10 atomic layers. When surface segregation occurs in the top 2-3 atomic layers, the top surface composition changes can be quickly swamped out by signals from deeper layers. Thus, XPS usually gives alloy compositions very close to that determined by SEM-EDX on CSAFs. He⁺ LEIS is probably the most surface-sensitive tool, especially for heavy atom determinations due to He⁺ having a relatively high ion yield (less efficient momentum transfer and lower neutralization probability), but it suffers from being destructive – sputtering damage effects always needs to be considered, including the high concentration of vacancies generated in the near-surface region. There are 3 ways to collect more surface sensitive information using XPS: 1) changing the incident photon energy, which is usually achieved by using synchrotron sources and cannot be readily available in lab-scale instruments; 2) using emission lines with higher binding energies, which result in lower kinetic energy of electrons and thus in general shorter IMFP; 3) collect emission signal from grazing angles w.r.t. sample surface rather than perpendicular to the surface, so that under the same IMFP, the effective information depth can be cut shorter by the sine of the grazing emission angle.

While the synchrotron resources are rare, which makes the first option less valuable to most surface science groups, the other two options were explored in this work with the hope of quantifying the top-most surface composition from AR-XPS data, so that it can be both top surface-sensitive as well as 'non-destructive'.

It should be mentioned that IMFP is used in this work only for a rough estimation of effective attenuation length, mean escape depth, and information depth, and a detailed discussion on their meanings and differences can be found in Powell's work¹.

7.2 Experiment design

While the surface segregation in several ternary alloy systems has been systematically studied in this thesis, yielding exact bulk-surface relations using EDX and He⁺ LEIS, it would be convenient to use these data as benchmarks and see if AR-XPS can 'predict' the same information on the same alloys. The idea is that when XPS is collected at several different angles with respect to the surface normal simultaneously, each angle contains information from a different effective depth, or in other words, the summation of information in each atomic layer weighted by their effective depth. If the number of collecting angles is denoted as *n*, then the decomposition of up to *n* layers is possible without further information input; e.g., when n = 2, we can assume that the material consists of 2 layers with thickness h_1, h_2 ; then their composition θ_1, θ_2 can be solved deterministically. When more information is available, such as bulk composition is known from EDX or top-surface composition known from LEIS, compositions of more layers can be solved. To explore option 2 and option 3 mentioned in Chapter 7.1, the number of different collecting angles and the number of emission lines from each element needs to be decided. Using the example of the CuAgAu alloy system, 3 emission lines were selected for each element based on their binding energies, overlapping with other components and signal intensities: Cu) $2p_{3/2}$, $3p_{3/2}$ and Auger *LMM*; Ag) $3d_{5/2}$, $3p_{3/2}$ and Auger *MN*; Au) $4f_{7/2}$, $4d_{5/2}$ and $4p_{3/2}$. Details of emission lines are listed in Table 7.1 and survey XPS spectra on pure Cu, Ag and Au surfaces are shown in Figure 7.1.

Cu	2 <i>p</i> _{3/2}	LMM	3 <i>p</i> _{3/2}
BE (eV)	932	570	75
Signal (a.u.)	1	0.6	0.16

Ag	MN	3 <i>p</i> _{3/2}	3 <i>d</i> 5/2
BE (eV)	1130	573	368
Signal (a.u.)	0.83	0.6	1

Au	$4p_{3/2}$	4 <i>d</i> _{5/2}	$4f_{7/2}$
BE (eV)	546	335	84
Signal (a.u.)	0.33	0.97	1

Table 7.1 Peak positions and signal intensities of selected lines of corresponding elements.

A CuAgAu CSAF was used in this work to collect data along three binary composition lines in one single experiment, which makes data collected on different alloys directly comparable without the need to correct signal drift caused by X-ray source or off-focusing. All experiments were conducted in the ThetaProbe (Thermo Fisher) UHV chamber, and a detailed description of XPS-sample geometry can be found in the literature².

7.3 Results and discussion

The first step of using AR-XPS data is determining the relative sensitivity factors between emission lines at various angles³. Figure 7.2 shows the data collected on ~20 alloys along each binary (CuAg, CuAg and AgAu) composition line. The use of 20 alloys rather than only the pure components enhances the robustness of parameter estimation, and also revealed any non-linearity in composition due to alloying.

A summary of the sensitivity factors (RSF) between emission lines can be found in Table 7.1, which is in qualitative agreement with the literature. As stated in Jeurgens' paper³, the dependency of RSF on collection angle in parallel data acquisition mode is due to the combined effects of the anisotropies of the photoionization cross-sections and the elastic scattering of the detected photoelectrons within the solid. Tasneem's work⁴ discussed the necessity of including surface excitation in AR-XPS quantification.



Figure 7.1 XPS survey scan on pure Cu, Ag and Au surfaces. Peaks of high intensity and different binding energies were selected to represent signal from different information depth in order to probe the near-surface composition with AR-XPS.



Figure 7.2 Relative sensitivity factor (RSF) determination using AR-XPS signal collected on binary CuAg, AgAu alloys at 4 different collection angles. \sim 20 alloy compositions were used along each binary composition line at 700 K. Ag MN refers to Ag M4N45N45 Auger emission line.



Figure 7.3 Relative sensitivity factor (RSF) determination using AR-XPS signal collected on binary CuAu alloys at 4 different collection angles. \sim 20 alloy compositions were used along each binary composition line at 700 K. Cu LM refers to Cu L₃M₄₅M₄₅ Auger emission line.

Emission	Angle-4	Angle-3	Angle-2	Angle-1
Lines				
Cu 3p _{3/2}	1.00	1.00	1.00	1.00
Cu LM2	3.47	2.78	2.51	2.40
Cu 2p _{3/2}	6.28	4.98	5.47	7.18
Ag 3d _{5/2}	5.17	4.45	4.54	5.33
Ag 3p _{3/2}	2.69	2.52	2.62	2.82
Ag MN	3.95	3.63	3.24	2.10
Au 4f _{7/2}	4.99	4.62	4.64	5.19
Au 4d _{5/2}	4.63	4.58	4.48	4.47
Au 4p _{3/2}	1.54	1.46	1.48	1.61

Table 7.2 Sensitivity factors in AR-XPS normalized to $Cu_{3p_{3/2}}$. Angle-4 shows the most surface sensitive information.

A quick way of estimating near-surface compositions from AR-XPS was applied, similar to that used in LEIS quantification:

Denote
$$m_{i,j} = \frac{I_{i,j}}{RSF_{i,j}}$$
 $c_{i,j} = \frac{m_{i,j}}{\sum_i m_{i,j}}$

e.g. in a CuAu alloy: $c_{Cu2p3,j} = \frac{m_{Cu2p3,j}}{m_{Cu2p3,j} + mean[m_{Au4f7,j}, m_{Au4d5,j}, m_{Au4p3,j}]}$





Figure 7.4 Comparison of segregation profiles of CuAu alloys determined by LEIS versus Angle-resolved XPS using different emission lines. 'Angle-4' refers to the most surface-sensitive angle; Cu 2p_{3/2} has the highest binding energy and thus being the most surface-sensitive among the 3 Cu emission lines selected.

Figure 7.4 shows segregation profiles of Cu_xAu_{100-x} calculated using different emission lines from Cu and Au. Although all emission lines were able to capture the Au enrichment in the near-surface region, and AR-XPS estimations lay between EDX and LEIS, which is consistent with their surface sensitivities, quantitative prediction of top-surface compositions (defined by LEIS) using only EDX and AR-XPS seems to be challenging.

Although Cu 2p_{3/2} has the shortest IMFP (~ 1 nm in Cu, Ag and Au) among all 3 Cu emission lines while Cu 3p_{3/2} has the longest IMFP, the latter predicted the strongest Au surface enrichment similar to that given by LEIS. Au 4f_{7/2} and 4d_{5/2} lines also showed similar profiles as that given by Cu2p_{3/2} and Cu LM2: strong surface enrichment of Au in low-Au alloys and weaker enrichment as Au content increases in the bulk alloy. Angle-dependent variation can be found in some alloys with slightly higher Au prediction in grazing angles, but the differences were small compared to noise level, which made the sophisticated deconvolution model meaningless. The angle-dependency in the segregation profile predicted by Cu 3p_{3/2} is interesting, as the most and least surface-sensitive angles gave a similar estimation of surface compositions, while the middle angles showed stronger Au enrichment.

Segregation profiles of CuAg alloys are shown in Figure 7.5. As in the case of CuAu, enrichment of Ag was observed in AR-XPS due to the super-strong Ag enrichment on the top surface; angle-dependency was also clear, with the most surface-sensitive angle showing the highest Ag enrichment. Cu 3p_{3/2} and Ag MN lines have relatively weak intensity and thus suffered from high uncertainties. Ag MN (Auger peak) line has the highest binding energy (~1130 eV) among all peaks used in this work and thus being more surface-sensitive than other Ag lines, and it also predicted stronger Ag enrichment than that given by Ag 3d_{5/2}, proving the feasibility of using different emission lines to probe different depth underneath the top surface.



Figure 7.5 Comparison of segregation profiles of CuAg alloys determined by LEIS versus Angle-resolved XPS using different emission lines. 'Angle-4' refers to the

most surface-sensitive angle; Cu LM2 and Ag 3p3/2 lines suffered from peakoverlapping issue and thus not presented here.

Due to the weak segregation in AgAu alloys in which EDX and LEIS measured results only differ by <5 at%, not surprisingly, AR-XPS gave the same surface compositions as that determined by the other two methods without any angle dependency.

The typical AR-XPS quantification model assumes the measured XPS signal can be decomposed into the summation of signal from all atomic layers from the top surface to the bulk. The mean free path of electrons in the material, together with all the corrections mentioned previously, have to be carefully taken into account in such a signal reconstruction process¹, and an ideal near-surface crystalline structure is usually assumed. Efforts ware devoted to the quantitative analysis of AR-XPS using the dataset shown in this chapter and other datasets on CuAuPd and NiPdAu alloys following the method applied in several papers³⁵. However, nevertheless, most of them failed to predict the top-surface compositions measured by LEIS, and the few successful ones might be due to coincidence since hundreds of cases were tested.

7.4 Conclusion

A comprehensive angle-resolved XPS dataset on binary alloys consisting of pairs of Cu, Ag, and Au was collected in this work, which spans both alloy composition space and binding energy range. The AR-XPS dataset was in qualitative agreement with the surface segregation results using EDX and He⁺ LEIS, in which the surface enrichment of Au in CuAu alloys and the enrichment of Ag in CuAg alloys can be detected. The choice of emission lines in AR-XPS was shown to affect its quantification, even after the RSF is corrected. When the top-surface composition is very different from that in the bulk, such as in the case of CuAg alloys under UHV, or the situation discussed in Chapter 3 (oxygen-induced Cu segregation in CuAgAu alloys), AR-XPS is capable of telling the change. In order to use AR-XPS as a more reliable tool for top-surface composition quantification, efforts will be needed in the following aspects: 1) Improve the sensitivity of AR-XPS in its parallel data acquisition mode since the quality of data is the basis of all analysis. 2) Theoretically explore how imperfections can be included in the model, both in crystalline structure (such as defects) and surface impurities. 3) Develop a convenient toolbox that includes not only all necessary database and corrections, but also sensitivity analysis, which will allow the identification of the major uncertainty sources and thus improving the experiment design.

7.5 References

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Appendix

8.1 Section 1 Alloy phase diagrams

Several alloy systems were studied in this thesis, in which elements such as Ni, Cu, Mo, Pd, Ag, and Au were used as CSAF components, substrate, and active components in catalysts. The phase diagram of an alloy determines its structural stability and thus should be carefully examined in experiment design and data analysis. The phase diagrams of several alloy systems from the ASM database are shown in this section as a reference to help understand the topics discussed in the main context.



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Figure 8.1 Phase diagram of Mo-Ag alloy



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Figure 8.2 Phase diagram of Mo-Au alloy



Figure 8.3 Phase diagram of Mo-Cu alloy



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Figure 8.4 Phase diagram of Mo-Ni alloy



Figure 8.5 Phase diagram of Mo-Pd alloy



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Figure 8.6 Phase diagram of Mo-Pt alloy



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Figure 8.7 Phase diagram of Cu-Pd alloy



Figure 8.8 Phase diagram of Cu-Pd-Au alloy



Figure 8.9 Phase diagram of Ni-Pd-Au alloy


Figure 8.10 Phase diagram of Cu-Ag-Au alloy

8.2 Section 2 Images of CSAF surfaces

CSAFs with various alloy compositions were used in this thesis to accelerate material screening. Due to its thin-film nature, CSAF surfaces may undergo structural changes after exposure to conditions such as thermal annealing or chemical treatments. Some images taken by digital camera and SEM are included in this section to help understand the main context.



Figure 8.11 SEM images of AgAu alloys after vacuum thermal annealing. The field of view in each image is $68x51 \text{ um}^2$



Figure 8.12 SEM images of CuAu alloys after vacuum thermal annealing. The field of view in each image is $68x51 \text{ um}^2$



Figure 8.13 SEM images of CuAg alloys after vacuum thermal annealing. The field of view in each image is $68x51 \text{ um}^2$



Figure 8.14 25×25 SEM images across Cu-Ag-Au composition space.



Figure 8.15 (1-13) SEM images of CuAgAu CSAF after oxidation; index matches that labeled in Figure 3.27. (lower-right) Photo of sample surface and the analyzer cone taken by a side-camera used for sample position alignment. Scale bar: 20 um.



Figure 8.16 Microscopic images of annealed CuAgAu CSAF surface before contrast enhancement. Annealing conditions: 1) 700 K, 3 hour. 2) 750 K, 3 hour. 3) 800 K, 3 hour. 4) 800 K, 5 hour.

8.3 Section 3 EBSD on CSAFs

CSAFs are polycrystalline alloy thin-films. Although single crystals are usually favored in UHV surface science studies for its simplicity, they give quantitatively different results than that measured on real catalyst surfaces, which are usually polycrystalline, if not nanoparticles. When we compare results of surface segregation, adsorption, and catalysis collected on a CSAF with existing literature using single crystals, it is important to know the distribution of grain orientations, while EBSD is an ideal tool for the efficient mapping of grain orientations on polycrystalline thin-film surfaces.

The EBSD determined pole figures of surfaces on a CuAu CSAF are shown in this section for reference.



Figure 8.17 Pole figures of EBSD indexing on selected alloy compositions from pure Cu to pure Au. At each point, a region of \sim 63x40 um was mapped out using a step size of 2 um and spot size of 320 nm; EBSD patterns were matched to the Cu lattice to determine surface orientations, which gave almost identical results as that given by matching to the Au lattice due to their similarity in lattice constants and both being FCC lattice; on average \sim 50% of all EBSD patterns were successfully indexed, while the rest were either blurry or contained overlapping patterns from different grains. All alloy compositions on CuAu CSAF show FCC (111) being the dominant surface orientation.



Figure 8.18 EBSD indexing of annealed CuAu CSAF



Figure 8.19 EBSD indexing of annealed CuAu CSAF

8.4 Section 4 Segregation kinetics

Kinetics of segregation was discussed in Chapter 4, in which He⁺ LEIS and XPS were routinely used to keep track of metallic components. Although these raw data is usually converted to atomic fractions by normalizing the signal, the raw signal of each component also contains information worth studying. Ion scattering is destructive to the material surface that causes the formation of vacancies in the near-surface region and the roughening of the surface, and the ion yield will be affected during this process. Other than the reason mentioned above, ion yield in LEIS is also affected by surface contaminants, and the examining of the raw signal can help verify the surface cleanliness during the experiment.

The raw data of several experiments discussed in Chapter 4 will be shown in this section to help understand the details of these kinetic experiments.



Figure 8.20 0.75 keV He⁺ *LEIS signal evolution on 3 CuAu alloys at 300 K, 400 K and 500 K using 200 nA sample current with 1 mm circular spot.*



Figure 8.21 0.75 keV He⁺ *LEIS signal evolution on 3 CuAu alloys at 300 K, 400 K and 500 K using 40 nA sample current with 1 mm circular spot.*



Figure 8.22 Raw LEIS Cu and Au signal evolution during the temperature-ramp experiment, corresponding to data shown in Figure 4.3.2.2 - 4.3.2.3. ~40 nA



Figure 8.23 Raw LEIS Cu and Au signal evolution during the temperature-ramp experiment, corresponding to data shown in Figure 4.3.2.2 - 4.3.2.3. ~40 nA



Figure 8.24 LEIS signal of Cu and Au corresponding to surface composition data shown in Figure. The last plot shows the total LEIS signal, defined by the summation of Cu and Au multiplied by its sensitivity factor (1.8 in this case); data before first reaching 700 K had lower ion yield, which was likely due to initial surface contaminant at 500 K and eventually sputtered away by 1 kV He⁺. ~40 nA



Figure 8.25 NAP-XPS spectra of Cu $2p_{3/2}$, Ag $3d_{5/2}$ and Au 4f during oxidation and reduction periods.

8.5 Section 5 Derivation of equations

Derivation: Equilibrium segregation

$$\begin{aligned} Ag^{bulk} + M^{surf} &\rightleftharpoons Ag^{surf} + M^{bulk} & eq.0 \quad K_{AgM} = \frac{\theta_{Ag} x_M}{x_{Ag} \theta_M} \\ Ag^{bulk} + Au^{surf} &\rightleftharpoons Ag^{surf} + Au^{bulk} & eq.1 \quad K_{AgAu} = \frac{\theta_{Ag} x_{Au}}{x_{Ag} \theta_{Au}} \\ Ag^{bulk} + Cu^{surf} &\rightleftharpoons Ag^{surf} + Cu^{bulk} & eq.2 \quad K_{AgCu} = \frac{\theta_{Ag} x_{Cu}}{x_{Ag} \theta_{Cu}} \\ 1Ag^{bulk} + aCu^{surf} + (1-a)Au^{surf} \\ &\rightleftharpoons 1Ag^{surf} + aCu^{bulk} + (1-a)Au^{bulk} \end{aligned}$$

eq. 0 can be written as a combination of eq. 1 and eq. 2

$$eq. 0 = a * eq. 1 + (1 - a) * eq. 2$$

$$K_{AgM} = (K_{AgAu})^{a} (K_{AgCu})^{1-a}$$

$$\frac{\theta_{Ag}}{x_{Ag}} \frac{x_{M}}{\theta_{M}} = \left(\frac{\theta_{Ag}}{x_{Ag}} \frac{x_{Au}}{\theta_{Au}}\right)^{a} \left(\frac{\theta_{Ag}}{x_{Ag}} \frac{x_{Cu}}{\theta_{Cu}}\right)^{1-a}$$

$$\frac{x_{M}}{\theta_{M}} = \frac{x_{Au} + x_{Cu}}{\theta_{Au} + \theta_{Cu}} = \left(\frac{x_{Au}}{\theta_{Au}}\right)^{a} \left(\frac{x_{Cu}}{\theta_{Cu}}\right)^{1-a}$$

$$\frac{x_{Au} + x_{Cu}}{\theta_{Au} + \theta_{Cu}} / \frac{x_{Cu}}{\theta_{Cu}} = \left(\frac{x_{Au}}{\theta_{Au}} / \frac{x_{Cu}}{\theta_{Cu}}\right)^{a} = (K_{CuAu})^{a}$$

$$(K_{CuAu})^{a} = \frac{\frac{x_{Au}}{x_{Cu}} + 1}{\frac{\theta_{Au}}{\theta_{Cu}} + 1} = \frac{\frac{x_{Au}}{x_{Cu}} \frac{\theta_{Cu}}{\theta_{Au}} + \frac{\theta_{Cu}}{\theta_{Au}}}{1 + \frac{\theta_{Cu}}{\theta_{Au}}} = \frac{K_{CuAu} + \frac{\theta_{Cu}}{\theta_{Au}}}{1 + \frac{\theta_{Cu}}{\theta_{Au}}}$$

$$ln\left(\frac{x_{Au} + x_{Cu}}{\theta_{Au}} + \theta_{Cu}\right) = a \ln\left(\frac{x_{Au}}{\theta_{Au}}\right) + (1 - a) \ln\left(\frac{x_{Cu}}{\theta_{Cu}}\right)$$

$$a \ln\left(\frac{x_{Au}}{\theta_{Au}} / \frac{x_{Cu}}{\theta_{Cu}}\right) = ln\left(\frac{x_{Au} + x_{Cu}}{\theta_{Au}} + \theta_{Cu}}\right)$$

$$a = \log_{K_{CuAu}} \frac{K_{CuAu} + \frac{\theta_{Cu}}{\theta_{Au}}}{1 + \frac{\theta_{Cu}}{\theta_{Au}}}$$

$$-\frac{E_{AgM}}{RT} = a\left(-\frac{E_{AgAu}}{RT}\right) + (1 - a)\left(-\frac{E_{AgCu}}{RT}\right)$$

Derivation: precursor-state model

Based on the occupation state, all sites on the surface can be categorized into empty sites available for adsorption (there is another empty site nearby), empty sites not available for adsorption (no other empty site nearby), and filled sites not available for adsorption. Upon visiting a site, a precursor may either adsorb (if allowed), desorb, or diffuse to another site, as illustrated by the schematic below:



$$k'_{d}$$
 k''_{d}

 $P'_{d} = \frac{\kappa_{d}}{k'_{d} + k'_{dif}}, P''_{d} = \frac{\kappa_{d}}{k''_{d} + k''_{dif}}$ Without specifying which type of site is visited, the probability of adsorption and

desorption can be expressed as the following:

$$P_{a1} = P_a f(\theta)$$
$$P_{d1} = P_d f(\theta) + P_d'' [1 - \theta - f(\theta)] + P_d \theta$$

Sticking coefficient S' can be derived:

$$S' = \sum_{i}^{\infty} P_{ai} = P_{a1} \left[1 + P_{dif1} + (P_{dif1})^{2} + (P_{dif1})^{3} + \dots + (P_{dif1})^{n} + \dots \right]$$

= $\frac{P_{a1}}{1 - P_{dif}} = \frac{P_{a1}}{P_{a1} + P_{d1}}$
 $S'_{0} = \frac{P_{a}}{P_{a} + P_{d}} = \frac{k_{a}}{k_{a} + k_{d}}$

$$\frac{S'}{S'_0} = f(\theta) \left(f(\theta) + \frac{P''_d}{P_a + P_d} [1 - \theta - f(\theta)] + \frac{P'_d}{P_a + P_d} \theta \right)^{-1}$$

For dissociative adsorption, $f(\theta) = (1 - \theta)^2$

Denote

$$K_{1} = \frac{P'_{d}}{P_{a} + P_{d}}, \quad K_{2} = 1 - \frac{P''_{d}}{P_{a} + P_{d}}$$
$$\frac{S'}{S'_{0}} = \left(1 - \theta K_{2} + K_{1} \frac{\theta}{1 - \theta}\right)^{-1} (1 - \theta)$$

Now the seven k parameters have collapsed into three parameters: S'_0, K_1, K_2

$$K_{1} = \frac{P'_{d}}{P_{a} + P_{d}} = \frac{1 - P'_{dif}}{1 - P_{dif}}$$
$$K_{2} = 1 - \frac{P''_{d}}{P_{a} + P_{d}} = 1 - \frac{1 - P''_{dif}}{1 - P_{dif}}$$

When $K_1 \rightarrow 1, K_2 \rightarrow 0$, precursors on sites not available for adsorption have the same probability of diffusing to adjacent sites as those on empty sites.

When $K_1 \rightarrow 0, K_2 \rightarrow 1$, precursors on sites not available for adsorption have higher probability of diffusing to adjacent sites rather than desorbing from the surface, and the sites not immediately available for desorption now serve as a reservoir of precursors. When the surface coverage is high, the effective sticking coefficient can be increased through the continuous supply of precursors to the empty sites from surrounding sites.



8.6 Section 6 Oxygen adsorption on Cu(111) S⁴C

Figure 8.26 O_2 P-T traces during exposure experiments measured by a calibrated mass spectrometer. Title in each subplot indicates the date of experiment as well as the initial exposure target, while cumulative exposures calculated by the integral under curve are labelled on the bottom of each subplot. The mass spec data in one of the experiments (labelled as '32 L' in Figure 5.3.7) was missing, and 32 Langmuir was the target exposure, while the actual exposure was likely to be slightly higher than the target.



Figure 8.27 A) bulk compositions of 146 points across the CuAgAu CSAF on ternary diagram. B) deviations in bulk compositions if the probing beam position is off by 100 um. C) the effect of position offset in x-direction. D) the effect of position offset in y-direction. E) 2-D colorbar indicating the offset value and direction.



Figure 8.28 Fitted site distribution and corresponding uncertainties. 3 types of common independent site are assumed, all sites have 2^{nd} order kinetic behavior. Color bars corresponding to the site distributions and uncertainties are shown in the bottom row.



Figure 8.29 Fitted site distribution and corresponding uncertainties. 4 types of common independent site are assumed, all sites have 1st order kinetic behavior. Color bars corresponding to the site distributions and uncertainties are shown in the bottom row.



Figure 8.30 Fitted site distribution and corresponding uncertainties. 4 types of common independent site are assumed, all sites have 2^{nd} order kinetic behavior. Color bars corresponding to the site distributions and uncertainties are shown in the bottom row.



Figure 8.31 (left) first order, (right) second order; color-bars: (left) site distributions, (right) uncertainties

Chapter 9 General conclusions

In this thesis we have demonstrated the use of high-throughput methodologies in the studies of surface segregation, oxygen adsorption, and catalysis.

In the first part of my thesis, we focused on the topic of surface segregation in transition-metal alloys, in which we studied the equilibrium surface segregation in CuxPdyAu1-x-y alloys, NixPdyAu1-x-y alloys, and CuxAgyAu1-x-y alloys as a function of alloy composition, temperature, crystalline structure, and oxygen environment. These were the first demonstrations of comprehensive segregation study across ternary alloy composition spaces. An extended Langmuir-McLean model was derived to describe segregation in ternary alloys and calculate segregation free energies. We have shown that under UHV conditions, the segregation tendency of elements follows the order of Ag>Au>Cu>Pd>Ni in general. We showed the existence of B2 structure near Cu₅₀Pd₅₀ composition suppressed segregation of Cu, and the ordering tendency of CuAu alloys resulted in a peak of segregation at corresponding order-disorder transition temperatures. We have quantified the influence of oxygen on segregation in CuAgAu alloys, in which oxygen-induced segregation of Cu resulted in Cu-dominant surfaces at a pressure of ~1 Torr.

In the second part, we have inspected the kinetic aspect of surface segregation in Cu_xAu_{1-x} alloys under UHV in response to temperature changes, and the segregation/oxidation kinetics of a CuAgAu ternary alloy under oxygen environment. The critical ion dose – temperature range within which the

destructive aspect of LEIS can be neglected was identified. A set of experiments were designed to study the low temperature near-surface transitions in alloys upon a temperature change, which complements the traditional grain boundary diffusion studies at higher temperatures based on add-layer diffusion method. The time scale of transition from one surface state to another was shown to depend on both temperature and alloy composition.

In the third part of my thesis, we examined the kinetics of initial-stage oxygen adsorption on Cu surfaces vicinal to Cu (111) at 500 K. While we got consistent results on Cu (111) with existing studies, some interesting behavior was observed on high Miller index surfaces. Several kinetic models were fitted to the dataset, and the two best-performing models indicated the existence of at least three type of common sites on the surfaces examined. The fitted site distribution was also compared to that on the ideal clean surface structures, and the correlation between the clean surfaces and the reconstructed surfaces during oxidation was interpreted.

In the fourth part of my thesis, we explored the potential of the catalytic microreactor array being used for oxidation reaction studies with the example of IPA partial oxidation. The activity and selectivity of several metals, including Mo, Cu, Ag, Pd, and Pt were measured. Mo showed sufficient catalytic activity towards propene formation to be quantified by mass spectrometry at T>500 K, while Pd only showed transient activity towards acetone formation at T<400 K, and none of the rest showed detectable activity at T<600 K. The thin layer of Pd deposited on

Mo only lowered the activity of Mo. We showed that currently our high-throughput microreactor is more suitable to the studying of reactions with high intrinsic activity.

In the last part of my thesis, we collected the most comprehensive dataset of angle-resolved XPS on binary alloys, including Cu_xAu_{1-x}, Cu_xAg_{1-x}, and Ag_xAu_{1-x}. We have quantified the relative sensitivity factors between different elements and different emission lines. We showed that the AR-XPS was capable of qualitatively predicting the segregation in alloys, while the selection of emission line affects its quantification, and higher quality data and more sophisticated models are needed to predict the top surface compositions from just AR-XPS data.