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Cu/Al Through Au Diffusion Characterized by KPFM

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Abstract

The nanometer scale characterization technique of Frequency Modulated Kelvin Probe Force Microscopy (FM-KPFM) will be used to assess a diffusion study on thin metal films that undergo accelerated aging. The KPFM technique provides a relatively easy, non-destructive methodology that does not require high-vacuum facilities to obtain nanometer-scale spatial resolution of surface chemistry changes. The KPFM technique will be exercised in an effort to explore its capacity to map surface potential contrast caused by diffusion in a manner that allows for a qualitative assessment of diffusion of Cu or Al through Au. Supporting data will be obtained from traditional techniques: AES, XPS and UPS.

An aging study was conducted on thin metal test specimens comprised of 500nm Cu or Al then 500nm Au on Si. The accelerated aging process was performed under inert conditions at aging temperatures of 100°C for Cu/Au film stack and 175°C for Al/Au film stack at aging times of 8 hours, 24 hours, 96 hours (4 days), and 216 hours (9 days).

A calibration method was developed using Au, Al and Cu standards to establish precision and repeatability of the KPFM technique. The average Contact Potential Difference (CPD)s and standard deviations for each metal were found and summarized.

Averages from surface roughness of the AFM topography images and roughness analysis of KPFM potential images which yield an average CPD of each area of unaged vs aged coupon surfaces were compared and show trends that indicate surface chemistry.

Introduction

Materials aging is a high-consequence failure mode in electronic systems. Typical aging mechanisms manifest themselves as diffusion, oxidation and or corrosion. Such mechanisms can degrade the electrical properties of connectors, relays, wire bonds, and other interconnections. Lost performance not only impacts the device in question, but also can affect the function and reliability of next-level assemblies. The detection of changes to materials surfaces at the nanometer-scale resolution, provides a means to identify aging processes at their earliest stages before they manifest into latent failures that affect system-level performance and reliability.

Exposure to elevated working temperatures can result in degradation of electrical conductivity due to growth of intermetallic regions or connection-failure due to the formation of voids and cracks due to Kirkendall effects. This is a common phenomena in the Au to Al wire-ball bonding process widely used throughout the semi-conductor industry [1] and thus is a material combination of interest in this study. Likewise, copper through gold diffusion is of interest because gold coating is used extensively in electrical contact and relays [2-5]. Electrical contacts rely on contacting surfaces to act as pathways for the transport of electrical current [6-8]. It is a common strategy to employ the use of multiple materials to meet material and performance needs. One such strategy is the plating of one metal onto another. A plating metal, gold for example, alters the interfacial properties such as nobility, interfacial shear strength, electrical conductivity and hardness of the contacts while the less costly and more readily available bulk material such as copper, maintains elastic modulus and strength [1, 9]. Application of the plating impacts the surface electrical properties by way of defects, grain structures and crystallographic characteristics. Electroplating is the most commonly used process for gold plating electrical components in mass production [2, 4], while physical vapor deposition processes such as sputtering [10] are popular environmental friendly alternatives to electroplating. These processes typically produce films with extremely fine grain structures, sometimes crystallographically textured, and a host of defect populations, which provide microscopic pathways for Cu diffusion through Au that will eventually lead to contact degradation[9].

Solid state diffusion in Au plated contacts has been the subject of numerous studies [2, 6, 10-12]. Pinnel [2, 13] summarized the major mechanisms in Au-Cu diffusion into three categories. The first one, which is called lattice or bulk diffusion, is a two-way process where Au diffuses into Cu while Cu into Au. The second mechanism relies on defects such as dislocations, twins and grain boundaries in Au films as rapid pathways for Cu diffusion. This mechanism, commonly referred as defect path or pipe diffusion, is more prevalent in thin film synthesized by physical vapor deposition processes or by electroplating because these processes create very fine grain structures and columnar grain boundaries. While bulk diffusion is highly temperature dependent, the defect path or pipe diffusion is less dependent on temperature; it is usually the more dominant mechanism at near ambient temperatures. The third mechanism results in the formation of intermetallic compounds between Cu and Au [2, 13]. Although the growth rate is relatively low, the intermetallic, which are typically brittle can potentially result in delamination of the Au films[9].

Kelvin Probe Force Microscopy (KPFM) has been widely used to measure surface Contact Potential Difference (CPD) on various materials on the atomic and nanoscale. KPFM enables characterization of local electrical properties at remote and complex areas such as interfaces in nanomaterials and junctions in semiconducting devices because of its high spatial resolution[14]. Characterizing aging materials on the nanoscale is an important primary screening capability to identify potential material failure indicators. Two principal requirements challenge the quality of the intended CPD or work function measurements: reliability and high spatial resolution [14]. These nano-characterization requirements call for suitable tools and appropriate experimental protocols whose study and development form the basic core of this endeavor.

In this work, we focus on the use of Peak Force (PF) Atomic Force Microscopy (AFM) in Frequency Modulated (FM-KPFM) mode to measure the CPD variations simultaneously with topography measurements of the surface of thin film stacks, namely a binding metal followed by copper (Cu) then gold (Au) on the surface on top of an Si wafer. The objective of this investigation is the evaluation and improvement of FM-KPFM measurement capabilities under dry inert conditions (nitrogen) for better reliability and spatial resolution. Validation data will be obtained from traditional spectroscopy techniques: Auger Electron Spectroscopy (AES), UV-Photoelectron Spectroscopy (UPS), and X-ray Photoelectron Spectroscopy (XPS).

Thin film stacks in varying thicknesses will be fabricated and conditioned in a variety of temperatures to promote Cu grain boundary diffusion through Au which will be characterized with AFM PF-KPFM in an effort to explore its capacity to map surface CPD which indicates surface chemistry changes that may allow for a qualitative assessment of diffusion rate kinetics as well as topographical changes that may indicate aging phenomena.

Alternative methods for measuring CPD are Scanning Kelvin Probe (SKP) and UV-Photoelectron Spectroscopy (UPS). SKP provides CPD information on the macro scale without topographical or spatially resolved information. UPS is done under high vacuum and does not provide spatially resolved information. Thus, we explore using PF-KPFM to perform CPD mapping with higher spatial resolution of electronic properties and simultaneous surface topography/roughness. In this study we investigate whether the PF-KPFM in conjunction with AES, UPS and XPS could be used to characterize aging in materials and thus serve as an additional tool to identify material degradation when it is not readily evident in “bulk” measurement techniques.

Principal of KPFM

KPFM as a proof of principle was first reported by Nonnenmacher and coworkers [15]. Numerous developments to the method have been made to improve resolution and sensitivity. Many studies have identified extraneous factors affecting the measured surface potential and found mitigating techniques. Now, it is common to obtain spatial resolution on the nanometer scale, with a resolution on the order of a few mV[16-19]. In the most simplistic form, KPFM operates on the principal of measuring the contact potential difference between two parallel plate capacitors with a small spacing, at a periodic vibration of the two plates at a certain frequency ω. By applying an

external voltage to nullify the electric field between the two capacitors, the force exerted by the external field can be measured, and this force is the CPD[15]. In this method, the two parallel plate capacitors are the sample and the probe tip. The relationship is described below:

$$V_{CPD} = \frac{\phi_{tip} - \phi_{sample}}{-e}$$

where e is the electrical charge[20]. Thus, if the work function of the tip is known, the work function of the sample can be calculated.

In order to accurately measure the CPD between the surface and the tip, cantilever is mechanically driven at frequency ω. An AC tip bias with frequency ω is applied to the tip. Cantilever oscillation phase is measured by a lock-in amplifier. This phase signal is sent to a second lock-in amplifier to get its AC signal amplitude at the 2nd harmonic frequency ω_m. A feedback loop is employed to minimize this AC signal amplitude until it directly offsets the induced electric field gradient, as shown schematically in Figure 1. In addition, it is common practice to operate KPFM in an interleave mode in which the AFM will measure and record the topography for a line scan in the first pass, lift to a user-defined height, and measure the CPD on the second pass, using the topographical information to keep the lift height constant. This method is one of the main techniques to prevent topography correlated artifacts in the measurement[17], and is illustrated in Figure 2. Step 1 is the topographical pass, step 2 is the lift, and step 3 is the CPD measurement pass giving the output signal depicted at the top right.

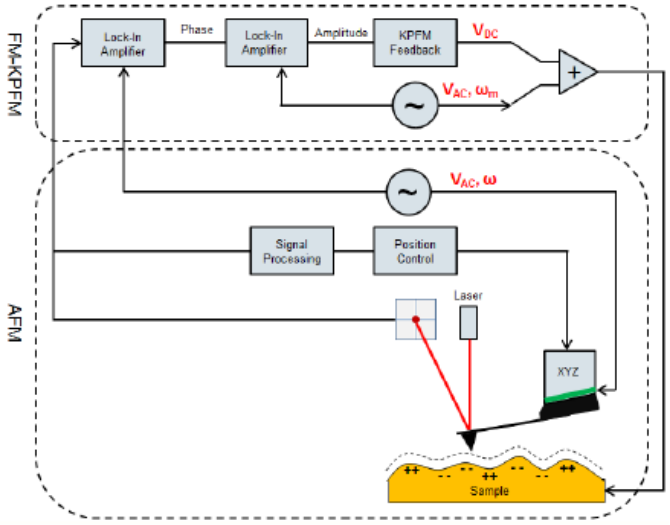

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Figure 1. Schematic of the feedback loop integrating FM-KPFM into the AFM. (Figure taken from Bruker training class handout).[21]

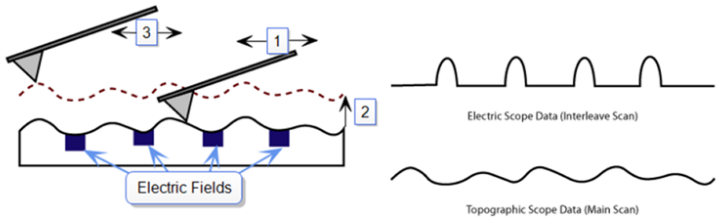

Figure 2. Depiction of expected signals when KPFM probes electric fields embedded in a surface. (Figure taken from Bruker training class handout).[21]

Two types of KPFM are amplitude modulated (AM-) and frequency modulated (FM-). In AM mode, the KPFM measures the force at ω, directly from the perturbation in amplitude of the cantilever oscillation, whereas in FM mode, the force is detected by the frequency shift at ω, and this shift is nullified by an applied voltage[20]. The differences in technique offer differing advantages. FM-KPFM offers higher spatial resolution due to the fact that the gradient in the electrostatic force is what is detected, rather than the force itself. AM-KPFM has a higher signal to noise ratio than FM- [14]; however, the surface potential measurement using AM- is significantly affected by the stray capacitance between the cantilever and surface, which induces an artifact in KPFM images[22].

It should be noted that KPFM is an inherently relative measurement technique: in order to determine sample work function, the tip work function must be known and invariable, which is not the case. Wearing of the tip as well as sample surface conditions change the tip composition, size and shape which can distort the measured CPD values [23]. These variables will be discussed in the following section.

In this work, we employ FM-KPFM to investigate the surfaces of thin film metal stacks in aims of providing a qualitative technique to provide indicators of possible aging phenomena that could be detrimental to their components.

Variables Impacting KPFM Surface Characterization

Tip Wear

Peak Force tapping AFM was employed as the topographical characterization method in this study. Peak Force tapping is a measurement where the probe tip periodically taps the sample at a set force multiple times as the probe rasters across the sample. The force is measured directly by the deflection of the cantilever. A feedback loop controls the force. Since the tip physically interacts

with the sample there is the possibility that the tip coating could wear over the course of the image acquisition; furthermore, contamination of the tip which could have a large impact on the CPD measurement. Tip wear was monitored by comparing the average CPD of an image of the same area over many images. No significant changes in the average CPD was detected after many images were acquired.

Surface Charges

Variations in CPD may be due to surface preparation, to the uneven distribution of adsorbates, crystallographic orientation or variation in surface local geometry. These variables are known as Patch Charge [23].

Many surface phenomena impact surface characterization, especially electrical characterization. Two major contributors are surface dipole layers and adsorbates, including humidity. The surface dipole layer can form by a charge distribution forming and then the opposite charge distribution being created to balance overall surface charge. A dipole layer induces an energy step that must be overcome for electrons to escape the surface [23]. This is an intrinsic phenomenon that occurs in conducting materials and may vary substantially depending on composition, environmental and surface conditions.

Adsorbates can create surface dipoles which form from the transfer of charge between the adsorbate and the substrate. The composition and quantity of the adsorbate may induce a large degree of variability in the CPD measurement.

In order to minimize patch charges all experiments were performed at controlled low (~4% relative humidity by running dry nitrogen through the AFM enclosure.

Experimental

Thin Metal Film Fabrication

Thin metal test specimens of 5nm titanium or chromium (adhesion layer) followed by 500nm copper followed by 500nm - 4µm gold (Ti or Cr/Cu/Au) films were deposited by evaporation on polished silicon substrate wafers cleaned with a Lenium degrease, followed by acetone and then IPA. This was followed with 20 minutes of UV/O3 single crystal.

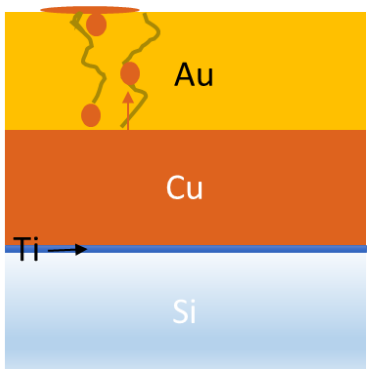

Figure 3. Evaporated deposition samples. Si followed by 5nm Ti adhesion layer, 500nm Cu and 500 - 4µm Au. Cu atoms migrating up through Au grain boundaries.

Aging Study

Typical maximum operating temperatures for electrical connectors in industrial applications range between 80°C and 135°C [2], while the temperature requirements in geothermal drilling and military aircraft applications can be significantly higher [24]. In the current study, heating experiments were conducted up to 125°C . An aging study on thin metal test specimens was conducted on Ti or Cr/Cu/Au films deposited by evaporation on single crystal, polished silicon substrates. The Ti or Cr/Cu/Au layer thicknesses are 50nm/500nm/500nm up to 4µm respectively. The accelerated aging process, which was performed in air, at aging temperatures of 60°C, 100°C, and 125°C and aging times of 8 hours, 24 hours, 96 hours (4 days), and 216 hours (9 days). The below matrix shows coupon number for each condition for record keeping purposes (Table 1).

60C						
	500nm	1um	2um	3um (Au only)	4um	3um
8hr	51	52	53	54	55	56
24hr	57	58	59	60	61	62
96hr	63	64	65	66	67	68
216hr	69	70	71	72	73	74
100C						
	500nm	1um	2um	3um (Au only)	4um	3um
8hr	2	6	10	14	18	22
24hr	3	9	11	15	19	23
96hr	4	8	12	16	20	24
216hr	5	9	13	17	21	25
125C						
	500nm	1um	2um	3um (Au only)	4um	3um
8hr	27	28	29	30	31	32
24hr	33	34	35	36	37	38
96hr	39	40	41	42	43	44
216hr	45	46	47	48	49	50

Table 1. Time, Temperature, Au thickness sample matrix.

Instrumentation

Atomic Force Microscopy

AFM measurements were performed using Peak Force KPFM mode on a Bruker Dimension Icon Atomic Force Microscope equipped with a standard tip holder operated under dry nitrogen environment with a closed loop scanner having a maximum horizontal scanning range of 90 x 90 μm^2 and a vertical scanning range up to 8 µm.

All samples were mounted on stainless steel AFM pucks and electrically grounded using silver paint making sure the paint created a continuous path between area of interest and puck. The integrity of this grounding was verified using a multimeter prior to imaging.

Kelvin Probe Force Microscopy

Scans were collected at a speed of 0.1Hz with a 512 line scan resolution. The FM-KPFM analysis parameters were: varying scan sizes, lift height of 80nm, drive3 amplitude of 6000mv and auto phase lock in. Data was processed using NanoScope software. Plane fit correction was applied to all height sensor images. A first order Flattening correction was applied to KPFM images in order to account for slow axis variability such as electronic drift and particulate artifacts. Roughness

analysis was applied to height sensor and potential images to work out the average roughness and average potential values for areas of interest.

The SCM-PIT AFM probe by Bruker was selected for use. It is a Platinum-Iridium coated Antimony doped Si probe/cantilever with cantilever specifications of: thickness of 2.5 – 3.5µm, length of 200-250 µm, frequency of 60-100kHz and spring constant of 1-5N/m. The probe specifications are: tip height of 10-15µm and radius ~20nm with Platinum-Iridium coating.

Auger Electron Spectroscopy

AES was performed with a Physical Electronics 690 Auger spectrometer. Operating pressures were less than $2 \cdot 10^{-9}$ Torr. The instrument utilizes a double-pass cylindrical mirror analyzer. Images and spectra were obtained using a field-emission tip with beam energy of 10 kV at 10nA. Data was processed using the Physical Electronics Multi-Pack software.

X-Ray Photo Electron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed with a Kratos AXIS Supra instrument. X-ray excitation was from a monochromatic Al Kα (1486.7 eV) source. Individual spots analyzed were an elliptical area of 300 x 700 microns. Survey spectra were recorded at either 80 eV or 160 eV pass energy. High resolution spectra were taken at 20 eV pass energy. Base pressures were less than $5 \cdot 10^{-9}$ torr.

Results

Au and Cu are very miscible even at room temperature [25]. Grain sizes and grain boundaries for each metal vary greatly throughout literature and are highly dependent on deposition conditions. There was no published literature exploring the use of KPFM to characterize diffusion of thin metal films.

KPFM Calibration

The Instrument parameter settings were optimized in order to provide data that is free of artifacts and other signal degradation behaviors. It was determined that an interleave lift height of 80nm and a drive amplitude of 6000mv maximizes KPFM signal.

A calibration method was developed using Au, Cu, Al and Ni standards to characterize precision and repeatability of the KPFM technique. CPD averages and standard deviations for each metal were found and summarized below (Table 2).

Standards	Average CPD [V]	Standard Deviation
Au	0.0239	0.0257
Ni	0.0068	0.0063
Unaged Au samples	0.0195	0.0060
Cu evaporated	0.0169	0.0003
Au evaporated	0.0157	0.0002

Table 2. CPD averages and standard deviations

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Kelvin Probe Force Microscopy/Auger Spectroscopy

Data analysis

Roughness and KPFM images were flattened then roughness data analysis was applied to produce the average roughness values (Ra) for the height sensor images and the average CPD values (Ra also used) on the KPFM image. The Average value for each image was averaged over 3 images – average CPD value along with standard deviation is presented for each sample and aging condition.

AFM topography and KPFM images of unaged vs aged surfaces were compared and showed some indication of topographical change in surface microstructure and an observable enlargement of features in the aged potential image as well as increase in potential image range (figure 3). (edit)

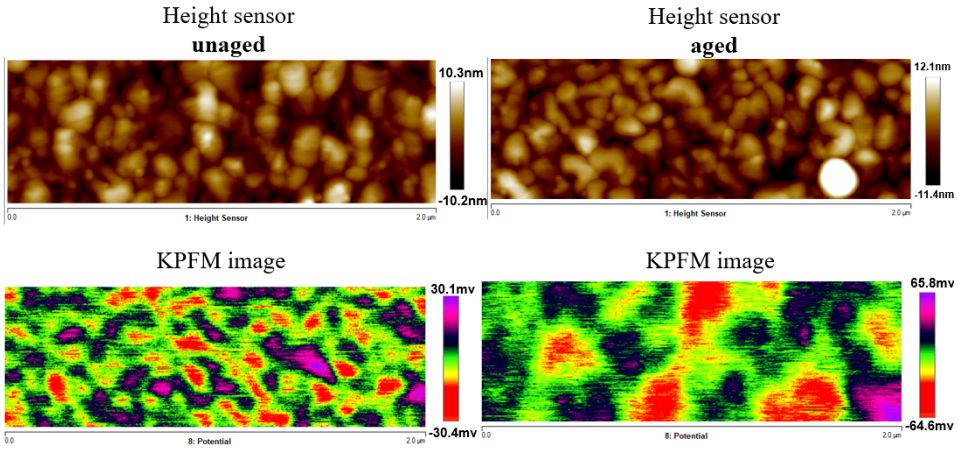

Figure 3. Height sensor and KPFM unaged images (right top and bottom). Height sensor (left top) shows coarsening and KPFM aged images (left bottom) shows enlargement of features. Causes for enlargement are unknown presently.

Morphology/roughness/CPD changes

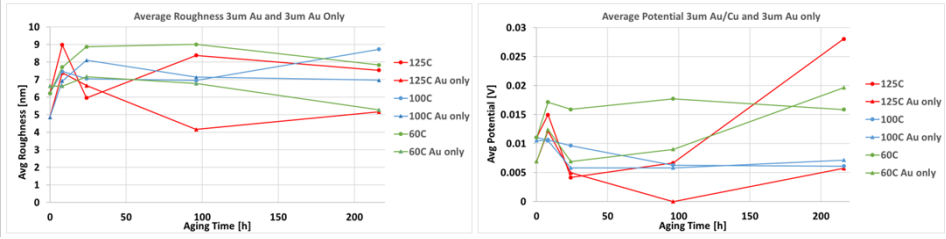

Figure 4. Plot on the left shows average roughness trends for 3 µm Au with and without underlaying Cu at all temperatures over 0 – 225hours. Plot on the right shows average CPD trends for 3 µm Au with and without underlaying Cu at all temperatures over 0 – 225hours. We observe that roughness and CPD values are higher in samples with Cu underlayer.

Possible reasons for roughness changes:

Diffusion

Oxidation

Annealing

Grain coarsening

The results of aging study showed increased roughness on all thickness of Au. There was also a change in roughness on the 3um thickness where Cu was not present underneath. An interesting trend observed is that the roughness for all samples seemed to converge at the longer aging times. Roughness changes may be due to Cu coming up through Au grain boundaries and possibly covering the surface. An copper oxide film may have formed on the surface which would have a CPD different from Cu used in the calibration study. Oxide film on Cu was found in previous Au-Cu diffusion studies [9]. Roughness change may also be attributed to annealing effects, that is, the atoms are rearranging to a more stable surface conformation with time and heat. Fictious contamination may also be the source of roughness changes.

Average potential difference changes

Possible reasons for potential contrast and changes in potential contrast:

Diffusion

Oxidation

Annealing/coarsening

Work function anisotropy

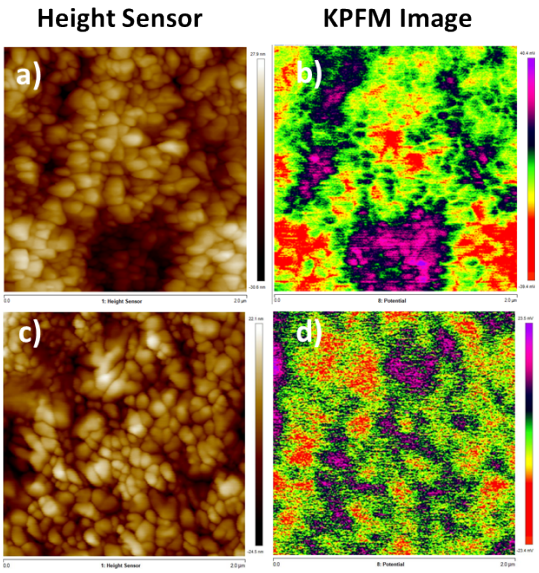

Figure 5. a) topography b) KPFM image of the 2µm Au/Cu stack aged at 60°C for 24h. c) topography, d) KPFM image of the 2µm Au/Cu stack aged at 100°C for 8h. figure demonstrates contrast inversion

The above figure demonstrates contrast inversion on the KPFM image where low points in the topography image a) are areas of high CPD values in the KPFM image b). Where we see high points in the topography image c) are areas of high CPD values in the KPFM image b). This inversion may be due to patch charging.

Auger Electron Spectroscopy

Auger spectroscopy was done on a series of samples at varying degrees of aging. Whether copper was present on the surface or not KPFM images of same samples showed contrast therefore contrast is not due to copper diffusion through gold top layer. For future analysis, samples will be marked and AES and KPFM analysis will be done on the same area to eliminate variability.

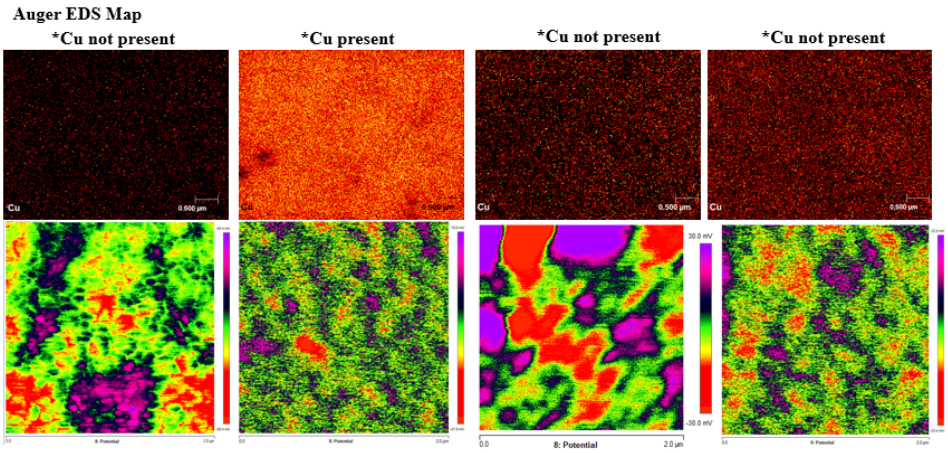

Figure 6. Auger EDS images (top row) indicate presence or absence of copper on a number of samples varying in aging conditions. KPFM images (bottom row) whether aged or not show contrast. Therefore contrast observed in KPFM images in not due to the presence of copper on Au surface but some other surface phenomena

X-Ray Photoelectron Spectroscopy

An unaged sample was analyzed via XPS with in situ sputtering and heating. Cu, C, and O were observed on the as-received Au surface. Sputtering removed C and O, but the trace Cu took some time to be completely removed. Heating the sample to 57°C under vacuum lead to only a re-adsorption of adventitious C contamination. Increasing temperature lead to diffusion of Cu to the surface along with adsorption of adventitious C (figure 4).

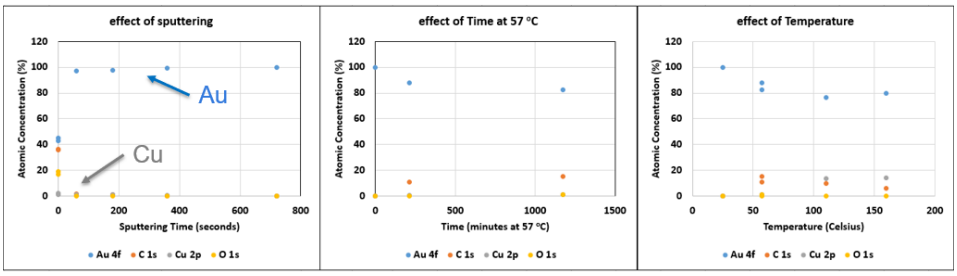

Figure 4. XPS sputtering removed C and O, but the trace Cu took some time to be completely removed (left). Heating the sample to 57°C lead to a re-adsorption of adventitious C contamination (middle). Increasing temperature lead to diffusion of Cu to the surface along with adsorption of adventitious C (right).

Ultraviolet Photoelectron Spectroscopy

UPS sputtering analysis was done on an unaged sample and yielded two work functions around 5.35eV and 4.75eV which presumably belong to Au and Cu respectively. The same sample was analyzed under constant 57°C for 24 hours. The work function decreased over this time. This decrease may be due to re-adsorption of adventitious C contamination on the surface. Finally, the sample was exposed to a steady increase in temperature from RT to 160°C. The work function decreased again due to re-adsorption of C contamination.

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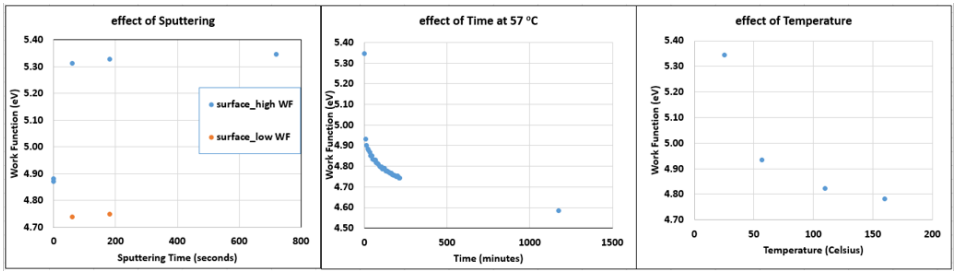

Figure 6. UPS sputtering analysis of unaged sample reveals two work functions which indicate the presence of Au and Cu(left). Work function decreased over time at constant 57°C (middle). Work function decreases as temperature increases (right).

Conclusion

Thin metal film stacks were fabricated as well as sample preparing, and handling techniques established. KPFM calibration has been done in order to understand repeatability and variance

within the instrument and samples of interest. A large aging study has been conducted to probe diffusion kinetics at 60°C, 100°C and 125°C at varying Au thicknesses. Optimizing KPFM data analysis was accomplished. Understanding diffusion phenomena using KPFM proved to be a challenge that was not well resolved.

Where changes in roughness observed? What did they indicate?

Where changed in CPD observed? What did they indicate?

Roughness changes were observed over the aging study with minimal meaningful trends found. It appears the roughness converged for longer aging times for all temperatures

What did we see in XPS? What does it mean with respect to diffusion and what does it point to in my conclusions for KPFM analysis?

What did we see in Auger? What does it mean with respect to diffusion and what does it point to in my conclusions for KPFM analysis? ***talk about the time scales expected of diffusion (since gold and copper readily mix in ambient. refer to the article you cited above and make a statement whether accelerated aging was actually needed or if its expected that mixing already exists before you would even receive a sample.

Future Work

TEM cutouts of thin metal film stacks were prepared using FIB. KPFM analysis was done on these cross sections to see if Cu mobility through Au grain boundaries is observable. Additional aging analysis at 150°C will be done. AFM analysis on FIB cutout was incomplete because getting the appropriate area to image was not possible because the sample floated out from a welded side. Too much force broke the weld and centering the AFM on the cutout was a tremendous challenge that was not accomplished.

Insitu heating experiment (add)

Consider heating samples/tip to remove adsorbed water – 120C for 1 hr under dry N2. Cool for 10min in glovebox before analyzing

(section on experimental improvements)

Acknowledgements

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