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AUTHOR(S) T. N. Taylor, M. A. Hoffbauer, C. J. Maggiore and
J. G. Beery

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Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

The Growth and Stability of Ag Layers on Cu(110)

by

T. N. Taylor and M. A. Hoffbauer
Chemistry Division

C. J. Maggiore and J. G. Beery
Electronics Division

Los Alamos National Laboratory
Los Alamos, NM 87545

ABSTRACT

Combined surface science and high energy ion beam techniques have been used to characterize the composition, structure and thermal stability of Ag layers $< 900\text{\AA}$ thick on Cu(110). A uniform Ag/Cu surface composite is formed for one monolayer coverage. Analysis of its growth with LEED shows that the Ag is initially confined to the [110] troughs and that further deposition results in a Ag(111) layer exhibiting $c(2\times 4)$ symmetry. This surface science determination of Ag coverage is consistent with absolute coverages measured with Rutherford backscattering. Beyond one monolayer coverage, the deposition of Ag at 300K produces clustering (Stranski-Krastanov mechanism) in contrast to a poorly ordered but more uniform layering mode when deposited at 130K. Following nucleation for a deposition between one and two monolayers at 300K, Ag clusters $\sim 20\text{\AA}$ thick grow laterally across the surface up to 5 or 6 monolayers deposition. Continuous films grown cold at thicknesses $< 115\text{\AA}$ are found to agglomerate above 500K exposing a tenacious Ag-Cu interface like that formed by one monolayer Ag deposition.

Surface studies have been done on a wide variety of materials in order to characterize changes that occur in electronic, structural, and chemical properties as a function of monolayer adatom deposition. In some instances these studies have been extended to thicker layers in order to show the transformation of these properties to that of the bulk adatom material [1,2]. We have recently begun a fundamental study of bimetallic interfaces which is designed to tie atomic-level surface properties measured under UHV conditions to the materials behavior of more conventional thin films. Our approach couples surface science with ion beam analysis at the Los Alamos Ion Beam Facility.

One materials system which has recently received considerable interest in the thin film and optical sciences community involves the deposition of Ag on Cu substrates during the fabrication of optical and laser mirrors. Song et. al. [3] have published data that demonstrate the protective effect that a Cu surface layer can have on optical mirrors used at the Kitt Peak National Observatory. Their Rutherford backscattering data show evidence for a Cu surface layer which chemically passivates the underlying Ag film from atmospheric degradation. The origin of the Cu surface layer has been the topic of much speculation. Thin Ag-on-Cu films grown in UHV have recently been examined after heating using ISS and Auger depth profiling techniques by Pitts et. al. [4]. Major film composition changes were observed at temperatures in the 375-575K range. Studies such as these have led us to examine this bimetallic system at a more fundamental level in order to understand the physical limits placed on its growth and performance.

In the present study, we have used a Cu(110) face as the substrate for Ag film growth. In addition to serving as an atomically clean and well ordered support for Ag deposition, this corrugated low density face of Cu (1.09×10^{15} atoms cm^{-2}) offers the opportunity to study the role played by substrate structural factors in Ag growth morphology. In the following, we first discuss the growth of Ag on Cu (110) from submonolayer to 34 Å thick films. The remainder of the paper treats the thermal stability and degradation processes evident for these films and also for much thicker films grown under carefully controlled conditions.

II. EXPERIMENTAL

Silver layers on Cu(110) were grown and analyzed under UHV conditions ($< 2 \times 10^{-10}$ Torr base pressure) in a surface science chamber

connected via a differential pumping stage to a Van de Graaff accelerator beam line. In the present study Rutherford backscattering spectroscopy (RBS) was complemented by low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) using the LEED optics in a retarding field mode. Sputtering with energetic argon ions (1.5KeV) permitted in-depth measurements of the adlayer surface composition.

A near-circular (10 mm diameter x 1.5 mm thick) Cu (110) disc (oriented to $\pm 1^\circ$, > 99.999% Cu) was polished and etched to a mirror finish. The sample was then suspended between two strands of 0.25 mm tantalum wire passing through grooves cut on opposite edges of the disc. A thermocouple bead (chromel-alumel) was also captured in the center of one grooved edge. The sample could be cooled to 130K or resistively heated to >900K. Before starting these measurements, the crystal surface was cleaned below detectable AES surface impurity levels by repeated ion sputtering at 1.5 KeV followed by annealing to 825K. This treatment also gave an integral-order LEED spot pattern. Silver was vapor deposited at $< 3 \times 10^{-10}$ Torr using a collimated vapor source [5]. For each deposition the source temperature, as measured with a thermocouple, was stabilized to ± 1 K and the flow of Ag vapor to the substrate was controlled by opening and closing a shutter on the source.

Rutherford backscattering measurements were done using a 2.3 MeV He^+ beam having a 1x1 mm cross-section and a beam divergence of $< 0.01^\circ$. A solid state barrier detector, capable of being cooled below 200K, was mounted on a rotary feedthrough which allowed ion measurements at scattering angles between 45° and 165° . Detailed interpretation of the Ag/ Cu(110) RBS spectra were made using a computer simulation program [6]. Absolute quantitation of elemental analysis in atoms cm^{-2} comes directly from the program modeling. Kinematic effects for Ag (Z=47) layers on Cu(Z=29), i.e. separation of Ag surface signal from that of the Cu substrate, simplifies interpretation of the data. All RBS data were taken under conditions which minimized channeling effects in the Cu substrate. The depth resolution of the present RBS measurements was between 100 and 200 Å, depending on the trajectory of the incident and backscattered ions relative to the substrate normal.

III. RESULTS

A. Deposition and Growth Modes

Silver was vapor deposited on clean Cu(110) at substrate temperatures of 130K and 300K. Silver adatom, Ag(355eV), and copper substrate, Cu(63eV), Auger peak-to-peak signals in $N'(E)$ were recorded as a function of deposition time (coverage) as shown in Fig. 1. The correspondence between deposition time and absolute coverage in Ag(111) monolayers (ML) was found using the Auger versus RBS data of Fig. 2.

The initial linearity in Fig. 1 of the Ag(355eV) and Cu(63eV) signals with Ag deposition at both 130K and 300K shows that a monolayer thickness is maintained up to a Ag(111) surface density (1.39×10^{15} atoms cm^{-2}). Subsequent deposition at 130K gives a smoothly increasing behavior where a pure Ag(355eV) signal is attained after 12 minutes (~ 13 ML) deposition. In contrast, deposition at 300K gives a pronounced break in the Ag(355eV) and Cu(63eV) Auger signals above one monolayer coverage. There is a less than one monolayer transition before a second near linear Auger region begins, extending up to 5 or 6 monolayers deposition. The Cu(920eV) peak, not shown in Fig. 1, exhibits the same trend as the Cu(63eV) peak for 130K versus 300K substrate growth temperatures. However, its relatively low surface sensitivity and signal-to-noise ratio give poor resolution of monolayer breakpoint features. The pronounced monolayer breakpoints seen in the Ag(355eV) and Cu(63eV) data at 300K are strong indications of 3D Ag crystallite formation during film growth. An effect like this resulting from compound formation is deemed unlikely due to the immiscibility of the two materials at these temperatures. Given that the atom density of Ag is 5.86×10^{22} atoms cm^{-3} , the final thicknesses of the films grown in Fig. 1 are $\sim 34 \text{ \AA}$.

The data shown in the RBS coverage calibration of Fig. 2 were taken in a manner which minimized any chance that the 2.3 MeV He^+ ions might effect the Ag growth process. Silver was never deposited on a region of the Cu(110) sample that had been exposed to the He^+ beam since the last sputter/anneal cleaning treatment. The effect that Ag crystallite shadowing has on the postmonolayer data of Fig. 2 was not investigated[7].

Our LEED results are in good agreement with the coverage data shown in Figs. 1 and 2. The early growth stages of Ag on Cu(110), up to Ag(355eV) ~ 0.2 , give LEED satellite spots which are indicative of Ag located in [110] troughs. The satellite spacing noticeably narrows as the coverage approaches 9.62×10^{14} atom cm^{-2} , consistent with a Ag-Ag

distance in the troughs which is the same as that for the Ag(111) plane of 2.88 Å. Near this coverage, shown by the arrow in Fig. 2, the LEED pattern begins transforming into a c(2x4) array which is completed at the calibrated Ag(111) monolayer coverage. Small expansion (< 2%) of a Ag(111) hexagonal layer can be seen to place it in (2x4) registry with the Cu(110) substrate; $5 \times 2.88 \text{ Å}$ for Ag-Ag $\approx 4 \times 3.61 \text{ Å}$ for Cu along [001]. An increase in Ag coverage above one monolayer leads to more complex diffraction features which require further investigation. More disorder is seen in all the LEED patterns at the lower temperature. These diffraction data will be treated in detail in a separate publication.

B. Stability

Silver films, grown 34, 115, and 900 Å thick on clean Cu(110), were heated in five minute increments at progressively higher temperatures while being observed with AES and/or RBS.

Changes observed in the Auger sputter profile of a 34 Å thick film after heating to 575K are shown in Fig. 3. As seen in the previous section, films of this thickness exhibit a Ag(355eV) signal characteristic of the pure material. Sputter profiles of films grown at 130K and 300K exhibit the same qualitative behavior. As depicted in Fig. 3 for a 300K film, the profiles initially show a smoothly increasing rate of change in Ag(355eV) and Cu(630eV) Auger signals as a function of sputtering time. For this case, an inflection point is found near the three minute mark followed by a gradual approach to the clean Cu(110) condition. The 130K film has an inflection point near two minutes sputtering time.

After heating a 34 Å film to 525K the Cu Auger signals begin to increase with an accompanying decrease in the Ag(355eV) signal. These changes are much more developed for the unsputtered 575K condition (time=0) of Fig. 3. The sputter profile for this heated film exhibits a relatively rapid decrease (increase) in the Ag (Cu) Auger signals during the first 30 seconds of sputtering. This temporal behavior correlates well with the rate of removal for a Ag monolayer from this surface (see insert Fig. 3). Sputtering for six minutes longer does not appreciably change either the Ag or Cu contribution. These data clearly indicate thick and thin (monolayer) Ag regions on the surface, consistent with a Ag agglomeration mechanism. Surface enrichment of Cu is ruled out as a contributing possibility because the initial stages of the sputter profile for such a

segregation process would show increasing Ag and decreasing Cu Auger signals.

Evidence that a Ag monolayer exists over a portion of the surface (between agglomerates) is supported by LEED data on the heated film which shows a $c(2 \times 4)$ - like monolayer pattern where the extra features are split, plus diffraction beams from crystallite faces nonplanar with the Cu(110) substrate. Given that the initial monolayer thickness of Ag for the heated film in the sputter profile is ~ 80 percent as large as the completed monolayer signal (Fig. 1), we conclude that Ag agglomerates (with an average thickness ~ 160 Å) cover ~ 20 percent of the surface.

This agglomeration phenomenon was further examined for a 115 Å thick film using RBS analysis. For these measurements the detector was set at 10° relative to the substrate plane, giving a depth resolution of ~ 100 Å. Figure 4 shows RBS spectra for a 115 Å film grown at 130K and after a five minute anneal at 525K. With this heating the Ag peak is found to decrease in intensity and broaden while the Cu leading edge broadens and develops a secondary edge. As a result, the spectral minimum near 2.0 MeV increases in intensity well above its previous baseline value; with the onset at ~ 500 K. These changes are consistent with a surface which contains thick Ag agglomerates that have formed from most of the Ag originally covering the rest of the substrate. The backscattered spectrum is, as a good approximation, a composite formed by superposition of spectra from a clean and heavily covered Ag surface. For the heated case in Fig. 4, a RBS scattering simulation shows that the "bare" Cu component covers approximately half the surface and is responsible for the secondary edge in the Cu portion of the spectrum. Due to the limited RBS resolution the "bare" Cu component could include a ~ 10 Å film of Ag without appreciably changing the fit. The remainder of the spectrum is attributable to a distribution of Ag agglomerate heights with a maximum thickness near 350 Å as determined from the energy position of the topmost edge of the Cu signal. For this agglomerated surface, LEED showed a sharp split $c(2 \times 4)$ pattern with superimposed 3D crystallite features; thus attesting to the fact that large regions of "bare" surface exist with only a monolayer Ag coverage undetectable by RBS.

Preliminary RBS studies of this nature on a 900 Å thick Ag film grown at 300K show no film degradation after five minutes of annealing at temperatures as high as 725K. Film changes seen above this temperature have been tentatively assigned to interface roughening effects like those

previously reported by Schoen et. al. [8] in a RBS study of Cu on Ag thin films.

IV. DISCUSSION

Analysis of the data plotted in Fig. 1 gives further insight into the growth properties of the Ag on Cu(110) system. Due to its low kinetic energy the Cu(63eV) Auger signal is very sensitive to Ag deposition, being attenuated to approximately 0.30 of its clean substrate value by a monolayer coverage. For an attenuation factor, $\alpha = \exp[-d/\lambda \cos\phi]$, where d is the Ag layer thickness of 2.57 Å and $\cos\phi = 0.74$ for a LEED optics axially aligned along the sample surface normal [9], one calculates an electron inelastic mean free path λ of 2.90 Å. Similarly, the Cu(920eV) Auger signal (not shown in Fig. 1) is only reduced to 0.75 of its original value, giving a λ of 12.1 Å. One can also get an estimate of λ for Ag(355eV) through use of the relation $I/I^\infty = 1 - \alpha$, where I/I^∞ is the ratio of monolayer to pure material Auger signals. For the monolayer value of Ag(355eV) in Fig. 1 of 0.32 ± 0.025 , one obtains $\lambda = 9.0$ Å. All these determinations for λ fall well within the range of tabulated values in the literature [10].

The growth mechanism for Ag on Cu(110) at 130K gives a Ag(355) signal intensity as a function of coverage which agrees very well with that for a layer-by-layer (Frank-van der Merwe) growth mode. Given the above values for α , the equation $I_{Ag}^N(\text{adatom}) = 1 - \exp(-0.39N)$ defines the N layer endpoints for the Ag(355eV) signal which closely approximate the data of Fig. 1 (see solid line segments in the figure). Using the same layering model, the Cu(63eV) signal for N layers attenuation is given by $I_{Cu}^N(\text{substrate}) = \exp(-1.20 N)$ relative to the clean Cu(63eV) substrate value. Note that the 130K data for this peak fall markedly below the envelope found from the above equation (see solid line segments for inset in Fig. 1). Such a departure is inexplicable from layered attenuation, and is most likely an experimental artifact resulting from the large secondary slope in $N'(E)$ at this energy. The disorder encountered in LEED at 130K shows some statistical departure from an ideal layering sequence. Such imperfect layering, which may also be viewed as the low temperature limit for Stanski-Krastanov growth (see below) [11], has recently been

shown by Springer [12] to give a near approximation to the ideal layer-by-layer case.

The difference in Ag and Cu Auger signals for deposition at 300K compared to that at 130K after one monolayer coverage clearly represents a case where there is an appreciable increase in self shadowing of the Ag with reduced effectiveness in substrate covering per Ag adatom deposited. This behavior is consistent with the formation of 3D Ag islands or clusters in a Stranski-Krastanov mechanism. The dashed line in Fig. 1 represents an idealized clustering mode where no intermediate growth processes are encountered between one monolayer and the formation of an 9 layer thick continuous film. For this case clusters protruding 8 layers ($\sim 20 \text{ \AA}$) above the Ag/Cu monolayer composite are nucleated near one monolayer and grow laterally to give a continuous film. The Ag on Cu(110) data nearly duplicates this line up to 5 or 6 monolayers deposition. The transition region between one and two monolayers (see Fig. 2) allows for cluster nucleation and rapid growth to an effective thickness of < 8 layers. Data points above the idealized case at two monolayers are consistent with a thinner than 8 layer average cluster thickness. Above two monolayers, the clusters appear to grow laterally at ~ 8 layers thickness up to 5 or 6 monolayers deposition. Such lateral cluster spreading (thick growth) as contrasted to between-cluster filling (thin growth) is further substantiated by the continued existence of the very surface sensitive Cu(63 eV) Auger signal ($\lambda = 2.9 \text{ \AA}$) beyond 5 monolayers deposition. At this point, where the clusters cover more than half the surface, departure from the idealized clustering line presumably results from coalescence as a thick ($> 20 \text{ \AA}$) continuous film begins to form.

By requiring the initial clusters to be hemispheres (radius of 8 layers or $20.6 \text{ \AA}$) one can get a coarse estimate of the cluster density during the early stages of growth. Assuming nucleation is complete and using the atomic density of bulk Ag, a cluster density of $1.3 \times 10^{12} \text{ cm}^{-2}$ is found for two monolayers deposition. At this point in the growth process the clusters cover approximately 1/8 of the surface.

With reference to previous studies such as those on Ag/Si(111) [7,11] and Ag/W(110) [13,14], it is not unexpected that the growth of thick coherent Ag films on Cu can result from cluster coalescence at 300K. The unknown ingredient in these Ag/substrate systems is the nature of the template upon which the clustering occurs and the affect that it has on the growth kinetics[15]. In the present study, we have shown that there is a

stable or tenacious Ag/Cu monolayer composite which serves as the growth template. We have found that this composite layer is preserved when a uniform Ag film is heated to the point where it heavily agglomerates.

One of the most thoroughly analyzed Stranski-Krastanov systems from a surface science perspective is the growth of Ag on Si(111). Clustering at this interface has been critically examined by Van Loenen et al. using high resolution (3-4 Å in depth) Rutherford backscattering spectroscopy [7]. Their study shows that after formation of a Ag/Si template layer approximately 4×10^{12} clusters cm^{-2} are nucleated. The Ag/Si template layer is completed at $\sim 2/3$ of a Si(111) monolayer coverage or 5.20×10^{14} atom cm^{-2} as contrasted to a Ag(111) monolayer coverage for Ag on Cu(110). After the first two Ag(111) monolayers of deposition on the Ag/Si template the clusters have reached ~ 10 Å average thickness. This is followed by a slower increase in thickness as lateral growth with some coalescence commences to give ~ 20 Å average thickness after deposition of ~ 7 Ag(111) monolayers on the template. These data are qualitatively similar to the growth scheme we have deduced from our Auger data for Ag on Cu(110). Van Loenen et al. have also estimated a small height to width ratio (~ 0.2) for the early growth of individual clusters. Assuming that the same general shape restraints hold for Ag clusters on Cu(110), our estimate of cluster density ($1.3 \times 10^{12} \text{ cm}^{-2}$) is clearly an upper limit.

The presence of a chemically passivating Cu surface layer on Ag thin film mirrors [3] has led to speculation that the Cu naturally segregates during the Ag deposition process on the underlying Cu substrate. In agreement with predictions of surface segregation for Ag and Cu mixed systems [16], our data clearly dispute this idea. Evidence that Ag is the segregant for this mixture of elements has also been experimentally verified in work on heated Cu on Ag bilayers studied by Pitts et. al.[4] and Schoen et.al.[8]. The former work, using ISS depth profiling, also shows an "apparent" massive motion of Cu through Ag without surface enrichment for a Ag (200Å) on Cu (500Å) thin film bilayer heated up to 575K. Given the perspective gained from our study of 34 and 115 Å Ag thin film stability on Cu(110), we believe that their data are most consistent with agglomeration of the 200 Å Ag overcoat.

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FIGURE CAPTIONS

- Figure 1 - Plot of Ag (355 eV) and Cu (63 eV) Auger signals versus Ag deposition time (coverage) on Cu (110) at 130 and 300K. Straight line segments between dots are for layer-by-layer modeling (see text). Dashed line shows idealized clustering mode from $N=1$ to $N=9$. For AES: $E_p = 2500$ eV, $I_p = 10$ μ A, modulation = 10 V_{pp}.
- Figure 2 - RBS coverage calibration of the Ag (355 eV) Auger signal for Ag deposition on Cu (110) at 300K. Inset shows RBS spectrum for several monolayers Ag deposition. For RBS: 2.3 MeV He⁺, scattering angle = 90°, detector angle with respect to surface plane = 30°. Errors associated with the data points are less than 10%.
- Figure 3 - Auger sputter profiles from Ag films grown 34 Å thick on Cu (110) as a function of annealing. Ag (355 eV) and Cu (63 eV) Auger signals versus sputtering time are shown for a continuous unheated film (1) and a film grown at 130K and agglomerated (2) by heating at 575K for 5 minutes. Inset shows Ag (355 eV) and Cu (63 eV) depth profiles for approximately one monolayer Ag coverage. For (1) at $t = 0$, Ag (355 eV) is the near bulk value of Fig. 1. Sputtering done with 1500 eV Ar⁺.
- Figure 4 - RBS spectra from a Ag film grown 115 Å thick on Cu (110) as a function of annealing. Transition to an agglomerated surface is shown after heating at 525K for 5 minutes. Computer simulation of the pure Cu contribution to the RBS spectrum after heating is shown for agglomerates covering 48 percent of the surface. For RBS: 2.3 MeV He⁺, scattering angle = 90°, detector angle with respect to surface plane = 10°.

Fig. 1
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Fig. 2
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AUGER SPUTTER PROFILE

Fig. 3
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Fig. 4
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