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Work-function variation with alloy composition: Ag-Au[†]

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Auger electron spectroscopy has been used *in situ* to characterize the surfaces of evaporated silver-gold alloy films grown epitaxially on heated mica [(111) orientation]. The films were shown to be free of any detectable surface impurities. The known energy dependence of the electron escape depth in these metals was used to show that the alloy films had the same surface and bulk composition. The surface composition was determined by comparing Auger signals from the alloys with signals from pure metal reference standards evaporated simultaneously with the alloys. An electron-beam retarding potential method using the electron gun of the Auger spectrometer was used to determine the difference in work function between the alloys and the references. The measurements showed that the work functions of these alloys fall significantly below a linear interpolation between the values for the two pure materials. The change in work function with oxygen adsorption was found to be not linear in surface composition.

I. INTRODUCTION

The work function is one of the fundamental electronic properties of a metallic surface affecting both electron emission through the surface (photoemission, thermionic emission, and field emission) and electronic trajectories near the surface (via contact potential differences).[1–4] In the uniform-positive-background model for a metal the work function can be separated into surface and bulk contributions.[5–8] The bulk contribution arises from the free-electron Fermi energy and the exchange and correlation parts of the chemical potential of an infinite uniform electron gas. The surface contribution arises from the relaxation of the electron gas at the metal-vacuum interface. Dependence of the work function on crystalline orientation can be obtained either by considering a corrugated positive background[9] or by reintroducing the ion cores as a perturbation on the uniform positive background.[7] The latter procedure produces work-function values which agree fairly well with experiment for simple metals. There is, however, a considerable discrepancy between theory and experiment for the noble metals which has been attributed to the *d* electrons.[8]

Many applications of metals utilize alloys because of the possibility of varying properties with composition. Theoretical techniques for calculating the bulk properties of concentrated disordered metallic alloys are still being developed.[10,11] Several discussions of bulk alloy theory attempt to use the bulk contribution to the work function[12,13] as a generalization of the ideas of electronegativity that have found wide use in understanding the properties of molecules[14] and semiconductors.[15] Recently, Gelatt and Ehrenreich have calculated the variation in the bulk contribution to the work function of Ag-Au alloys as a function of composition.[16] In the absence of a first-principles calculation of the work functions of Ag and Au, they assumed that the surface contribution was the same for Ag, Au, and the alloys. This assumption permits a comparison of their bulk alloy calculations to the experimental data presented here.

Experimental measurements of the work function of metals are extremely sensitive to chemical and physical conditions at a surface.[2–4] When one is interested in the work function of a clean surface, small amounts of contaminants present at a surface can invalidate measurements. Even for a completely clean surface, the work function is different for different crystal faces, making measurements on polycrystalline samples of limited fundamental interest. Measurements on alloys are subject to the additional complication that the alloy surface composition can be appreciably different from the bulk composition.[17] In fact, measurements of the work function of Cu-Ni evaporated alloys indicated severe surface segregation attributed to a miscibility gap.[18] Bouwman has carried out photoelectric work-function measurements on Au-Pt,[19] Pt-Ru,[20] and Ag-Pd[21] evaporated alloys. Work-function measurements on refractory metal alloys using thermionic emission have been reviewed in the literature.[22] Although precautions were taken to ensure alloy purity in those studies, there was no direct method of determining the elemental composition of the surfaces or the crystalline orientation. As part of a diffusion study, Thomas and Haas have measured the work function of Au-Cr single-crystal alloy films as a function of bulk composition.[23]

Since the advent of Auger-electron-spectroscopy (AES) techniques[24–26] the experimenter can determine the identity and approximate quantity of all elements present in the surface region except H and He. AES has been used for systematic quantitative studies of alloy surface composition for

Cu-Ni[27,28] and Ag-Pd[29] solid alloys. In those cases there is evidence that samples can be prepared which have the same surface and bulk composition. In the experiments reported here AES has been used to ascertain the purity of the surfaces and to determine quantitatively the alloy surface composition.

The Ag-Au alloy system has long been a favorite for experimental and theoretical studies of bulk electronic properties because it is not complicated by miscibility gaps, structural changes, or large changes in lattice parameter. These alloys are also advantageous for studies of clean surfaces due to their low reactivity and the possibility of epitaxial growth on mica to give (111) surfaces. Especially important for this study are the large difference in work function and the separation of the Auger emission spectral lines for Ag and Au.

II. EXPERIMENTAL PROCEDURE

Sample preparation and measurements of surface properties were carried out in a stainless-steel ultra-high-vacuum system having a 200-liter/sec sputter-ion pump. Titanium sublimation was also available and assisted in reaching a base pressure after bakeout of better than 5×10^{-11} Torr (measured with a Bayard-Alpert gauge). After each installation of new substrates and source metals, the entire system was normally baked for at least 12 h at a maximum temperature of 250 °C. The tungsten filament of the electron gun was operated during the last hours of bakeout to thoroughly outgas components within the electron gun and analyzer. The titanium sublimation feature was not used following the evaporation of the sample to avoid possible contamination problems.

Alumina-covered $100\times19\times0.25$-mm molybdenum boats were used for the evaporation sources. These boats required high operating power (about 500 W for the gold source); hence, water-cooled high-current feedthroughs were used. Variacs were used to control the power supplied through 3-V filament transformers.

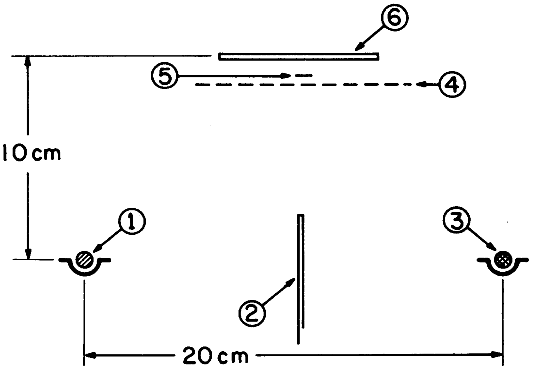


FIG. 1. Arrangement of evaporation sources, substrate, and shields (see text).

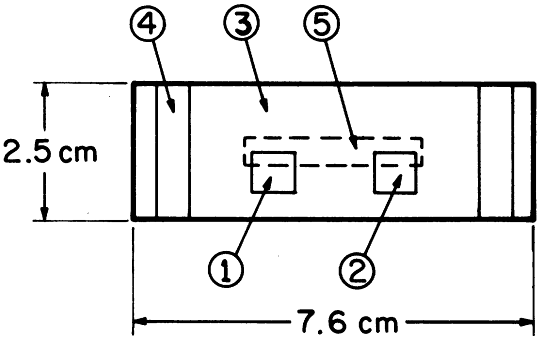


FIG. 2. Substrate geometry (see text).

The evaporation geometry is shown in Fig. 1. The sources [(1) and (3)] were placed as indicated to provide an alloy concentration gradient along the substrate. A shield (2) was used between the sources to prevent cross contamination. A movable shutter (4) that was located between the sources and the substrate (6) permitted extensive outgassing of the sources. The shutter provided a way to stop the evaporation from both sources almost simultaneously; thus, the vapor flux for the last layer was essentially the same as that of the preceding layers. A reference shield (5) shielded an area of the substrate from each source to provide pure metal references evaporated simultaneously with the alloy. The deposition rates were typically about 1 Å/sec from each source.

Figure 2 shows details of the substrate geometry. A gold reference (1), a silver reference (2), and a large area of alloy of varying composition (3) were produced. Silver stripes (4) evaporated near the ends of the bare substrate before mounting provided electrical contact to the sample. Work-function measurements were confined to the area inside the dashed lines (5) as explained below.

During the evaporation the background pressure rose slowly to at most 3×10^{-8} Torr. After the shutter was closed, the power to the sources was reduced and the pressure quickly dropped. No contamination occurred as a result of the brief exposure at the higher residual gas pressure during the evaporation for the relatively nonreactive silver and gold. This was confirmed directly by the fact that the results did not depend on the background pressure and by the fact that intentional exposures of clean samples to gases at even higher pressures and for longer times produced no work-function changes.

Most of the data reported here were obtained using air-cleaved mica substrates which were heated by a tungsten ribbon mounted in a substrate holder assembly patterned after one used by Christmann.[29,30] Thermocouple measurement of the temperature of a copper foil mounted under the mica substrate yielded 300 °C with 9 W supplied to the heater. Radiated power from the sources increased this to 350 °C. The temperature at the substrate surface was estimated to be between 400 and 450 °C during a typical evaporation. Glass substrates used in earlier experiments were heated only by the radiation from the sources during the evaporation of the films. Prior to the evaporations, the glass substrates were outgassed with a quartz-halogen heater lamp, and the mica substrates were outgassed by operating the tungsten heater at a higher power than that which was used during the evaporation. Heated mica substrates were used to produce epitaxial films with (111) planes parallel to the substrate. Glass substrates yielded polycrystalline films with bulk orientation which varied with composition.

Work function measurements were made with the electron gun in the cylindrical mirror analyzer described below, and the procedure was a modification of Anderson's electron-beam retarding potential method.[31] A variable potential was provided by connecting the sample through a 0–12-V bias supply and 1 MΩ resistor to one end of the tungsten filament electron source (at negative 500 V). The electron gun was adjusted to give $I = I_0 = 3$ μA saturation current for 7 V applied potential; then, I-V curves were obtained at different positions on the sample by varying the bias supply voltage.

Since the I-V curves had the same shape, the displacement between two curves could be used to measure the difference in work function between two different parts of the sample. Normally the potential for $I = \frac{1}{10} I_0 = 0.300$ μA was recorded rather than complete I-V data, and the difference in potentials for this fixed reference current was taken as the work-function difference. The results in this method are differences in weighted averages of work functions at two beam positions,[2] and the exact form of the weighting depends on the size of any patches compared to the beam size, as well as on the relative magnitudes of the patch and external electric fields.[32] For the method to be successful, the electric field lines must be perpendicular to the sample. By evaporating only one metal onto a substrate, it was determined experimentally that, for the applied field (about 900 V/cm) and analyzer-sample geometry used, the area inside the dashed lines in Fig. 2 could be used for meaningful work-function measurements.

Differential Auger spectra were taken in the standard way introduced by Palmberg, Bohn, and Tracy[33] using a commerical cylindrical mirror analyzer with coaxial electron gun.[34] The sample was positioned perpendicular to the axis of the electron gun and analyzer unit using a commerical manipulator[35] modified to give 50-mm travel along the slide. The primary electron beam was normally 2000 eV and 25.0 μA with a diameter of about 0.1 mm, and the analyzer modulation was normally 2.0 eV. The electron multiplier potential was adjusted so that lock-in sensitivities of 100–500 μV full scale were used. Auger spectra were typically recorded at a rate of 1 eV/sec with a time constant of 0.1 sec. Analyzer resolution was about 0.5% of the electron energy.

The beam powers used for the Auger analysis were verified to be low enough not to affect the composition determinations. The procedures included observing the constancy of the Auger results as a function of time after moving the beam to a fresh spot on the sample, measurement of the work function before and after Auger scans, and monitoring the Ag/Au peak ratio while heating the sample. By preparing a sample known to have a variation in composition normal to the surface, it was possible to determine the limits of beam voltage and current which could be used on a nonuniform sample which was sensitive to heating or other beam effects. This confirmed the sensitivity of the procedures listed above to possible beam-induced changes in the uniform samples.

It is essential for accurate quantitative composition analysis using derivative spectra that the peak shapes do not change on alloying and that the peaks used for analysis do not overlap those of another constituent. These conditions were confirmed experimentally by comparison of the peaks at different compositions after normalizing them to the same height (by variation of the electron multiplier gain) and by examination of spectra made with expanded energy scales.

Some samples were exposed to oxygen and the work-function changes measured. In such cases, the ion pump was first turned off. Then, through a leak valve connected to a glass flask, oxygen was admitted at a constant pressure for a fixed time (2×10^{-6} Torr for about 30 min for the data reported here). The uncorrected Bayard-Alpert gauge reading was used, as only an approximate but reproducible measure of oxygen exposure was required. After the oxygen valve was closed, the ion pump was turned on again. Usually no measurements were taken until 24 h later, an arbitrary time long enough for the pressure to drop again to the low 10^{-10} Torr range before operating the analyzer.

One sample was analyzed by a low-energy electron-diffraction technique described in Sec III. Also discussed there are bulk analyses including x-ray diffractometer scans, back-reflection Laue photographs, and atomic absorption spectroscopy, which were made after all *in situ* measurements of surface properties were completed.

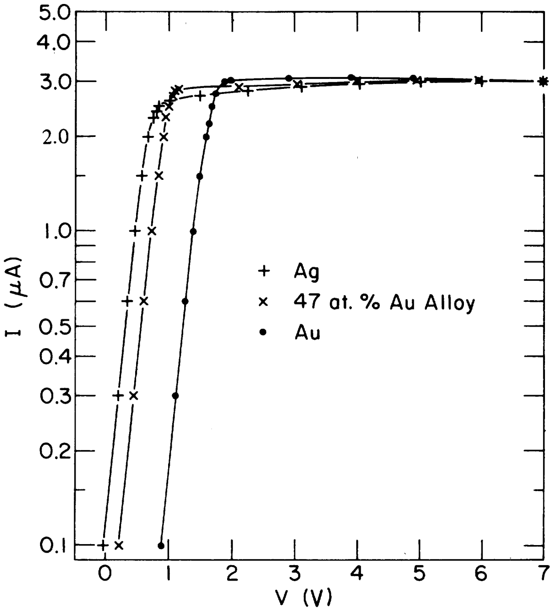


FIG. 3. Current-voltage curves from retarding potential measurements.

III. RESULTS

Examples of the *I-V* curves produced by the electron-beam retarding potential technique which was used to determine work-function difference are shown in Fig. 3. The curves are parallel in the retarding field region. An example of a derivative Auger electron spectrum is presented as Fig. 4. The compositions indicated in Fig. 4 were obtained by dividing the peak-to-peak height in the scan shown by that obtained from the references from the same evaporation; the silver and gold compositions were determined independently from their respective references.

Besides its use for alloy composition analysis, an important application of AES in this work is the detection of surface impurities. Ag, Au, and alloy films reported here, as well as several other metals, were examined following contamination by exposure to the atmosphere or to high residual gas pressures. This procedure verified sensitivity to elements such as Cl, S, and C and permitted the precise location of the positions at which impurities would produce peaks if present on the samples. It was possible, for example, to show that a peak observed at 195 eV was characteristic of clean silver and to distinguish it from a chlorine peak which appeared about 10 eV lower. This was accomplished by examining Auger scans on fresh Ag samples and on samples having various amounts of adsorbed Cl. No peaks attributable to impurities were observed in the Auger spectra of the samples as evaporated for work-function measurements.

The results for simultaneous evaporations on heated mica substrates are given in Fig. 5, which is labeled for clarity as work-function difference, relative to gold, versus surface composition. The graph actually is the difference in applied potential between an alloy position and the gold reference obtained by the electron-beam retarding potential method plotted as a function of the 72-eV Auger peak-to-peak height normalized to the signal from the gold reference. A plot obtained by using the 352-eV Ag peak instead of the 72-eV Au peak is

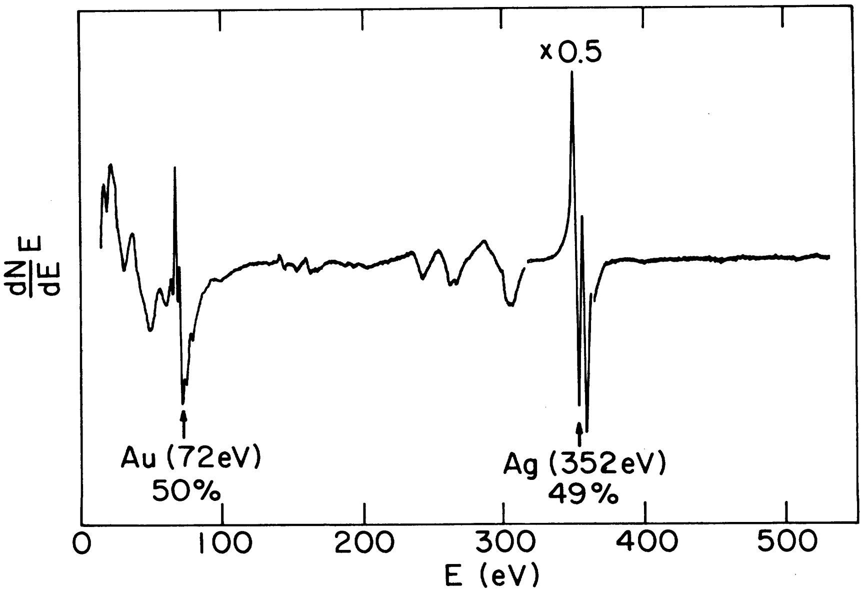


FIG. 4. Derivative Auger electron spectrum from silver-gold alloy.

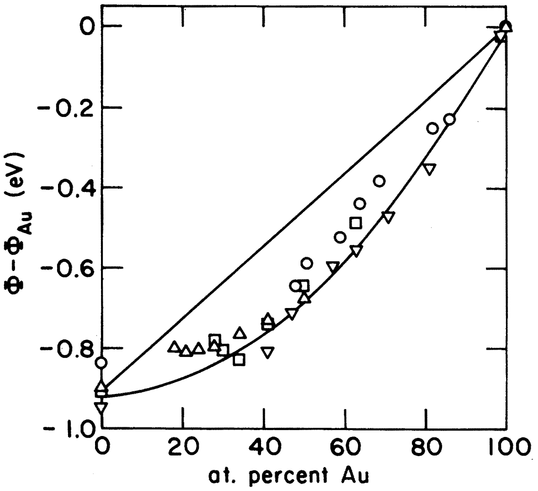
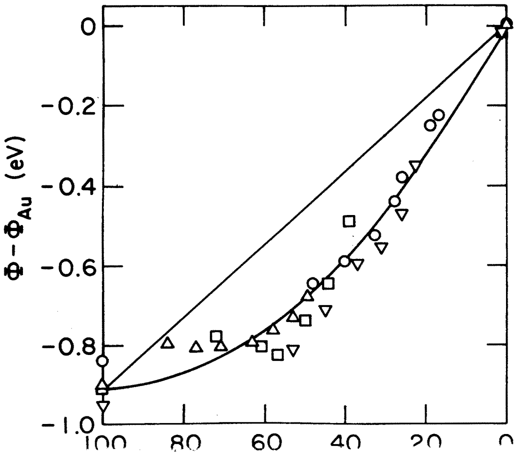


FIG. 5. Work-function difference as a function of surface composition (obtained from the 72-eV transition in gold) for evaporations on heated mica substrates for samples E1(○), E2(△), E3(□), and E4(▽). Solid lines are described in text.

given in Fig. 6. The curves drawn for comparison with the data are the linear interpolation between silver and gold ($\Phi = \Phi_{Ag} + 0.91x$, where $\Phi_{Ag} \equiv \Phi_{Au} - 0.91$ and x is the fractional gold content at the surface) and a quadratic interpolation ($\Phi = \Phi_{Ag} + 0.91x^2$) which approximately describes the experimental data both for the epitaxial films and our earlier results for polycrystalline films.[36] The data for the evaporations of polycrystalline films on glass substrates are presented in Fig. 7.



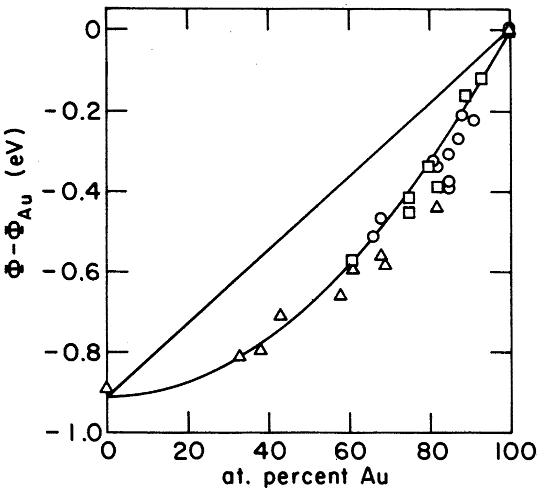


FIG. 7. Work-function difference as a function of surface composition for evaporations on glass substrates for samples P1(○), P2(△), and P3(□). Solid lines are described in text.

Repetition of measurements on a particular sample yielded agreement within about 0.010 eV, or about 1% of the silver-gold difference, for the contact potential difference and better than 2% for normalized Auger peak heights. The estimated absolute accuracy of these measurements is about 5%. The work-function accuracy is limited by possible systematic errors in the method, such as those associated with any varying patch distributions. The composition determination is subject to systematic errors discussed in Sec. IV inherent to quantitative Auger analysis.

As a result of multiple bounces of atoms in the vapor streams against the vacuum system walls, some cross contamination of the reference metals could occur. Most samples had less than 0.5% gold in the silver reference and less than 0.5% silver in the gold. Due to variations in the evaporation rates and size of the sources, some references indicated no cross contamination, but two gold references (on samples E3 and E4) contained about 1% silver. For these last samples a small correction was applied by augmenting the reference Auger amplitude to compensate for the 1% loss of signal caused by the additional constituent, and the work-function versus composition curves were extrapolated at the experimental slope to obtain the applied potential which would have resulted from pure gold (a 2% correction). For two evaporations

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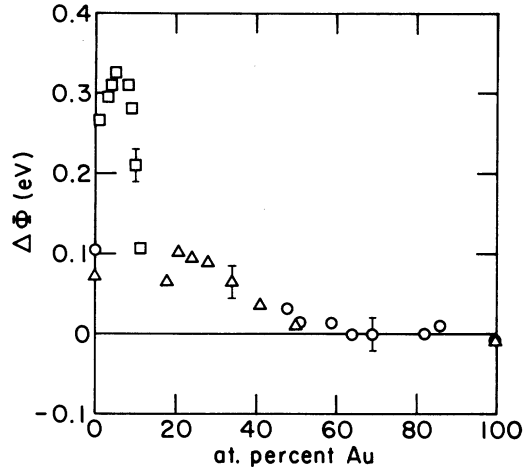

FIG. 8. Change in work function due to 3.6×10^{-3} Torr sec exposure to oxygen for samples E1(○), E2(△), and D1(□).

to ±0.035 eV. The alignment corrections were obtained by overcoating the alloy sample with a thick layer of silver and repetition of retarding potential measurements. The validity of the cross contamination and alignment corrections was empirically verified on other samples.

In addition to the fact that a similar variation of work function with composition was found in both the epitaxial and polycrystalline films relative to their respective references, the two types of gold reference were observed to have approximately the same work function. This observation is consistent with x-ray diffractometer results discussed below which indicated that the polycrystalline gold references were highly (111) oriented. The difference between the epitaxial and the polycrystalline gold references was 0 ± 0.035 eV as judged by the potentials required to produce the standard 0.300 μA current in the contact potential measurements using similar sample holders in the same physical configuration. The uncertainty given for the difference is due to variations, between the different experiment runs, in the current setting for the tungsten analyzer filament and the associated effects on its emission properties and on the voltage drop across the filament.

Presented in Fig. 8 are results for work-function changes following the $(3.6\pm0.1)\times10^{-3}$ Torr sec exposure of epitaxial samples to research grade (99.995%) oxygen from a glass flask. Since no residual gas analyzer was used, the work-function change observed could include some small effects due to other gases. The interpretation of the nonlinear variation of work-function change with composition will, therefore, be limited in this paper as described in Sec. IV. The low-energy electrons incident on the sample during contact potential measurements did not affect the adsorbed oxygen; however, the 2-kV 25-μA beam used for Auger measurements desorbed oxygen and could not be employed for its detection. The work-function changes shown have been calculated assuming constant analyzer filament properties; therefore, the magnitudes of the changes are uncertain by 0.020 eV. Independent measurements by the Kelvin vibrating capacitor method using the same oxygen flask and an oxidized tungsten reference indicated that the contact potential difference between the pure gold films and the reference did not change with oxygen exposure. An alternative method for presenting the data, which would shift the points in Fig. 8 by about 0.010 eV, would be to assume that the work-function change for gold was zero; however, no usable gold reference was obtained for one of the samples as discussed below.

The alloy sample D1, ranging from 1% to 11% gold, was prepared by diffusing a silver layer of roughly 100 Å into a silver-rich alloy sample which had been prepared by simultaneous evaporation of silver and gold. The diffusion was accomplished by annealing at about 300 °C for 2 h. No usable references were created; hence, the composition was determined using an electron multiplier calibration from the other experiment runs. The work-function change following oxygen exposure for this sample is characterized by a peak at 5%. There is agreement with the other samples in the adjacent composition regions. Besides that agreement, justification for presenting the data for sample D1 in Fig. 8 with that for the simultaneous evaporations includes the following: Another sample prepared in a similar manner in the gold-rich region yielded work-function versus composition data lying within ± 3% of the best fit to the data shown in Fig. 5, with no systematic difference from the results for those films. Second, the diffusion experiments discussed below indicate that no surface segregation problems should occur with such an annealing preparation method. Similar composition dependence, but larger work-function changes, were obtained with the exposure to oxygen of the polycrystalline samples on glass substrates.

The bulk orientation of some of the films was determined by measurement of peak area ratios in x-ray diffractometer scans and by the presence or lack of six-fold symmetry in back-reflection Laue photographs. Qualitatively, a (111) orientation was found for the gold and silver references, as well as the alloys, deposited on heated mica substrates. For the polycrystalline films on glass substrates, the orientation was predominantly (111) for gold references. The orientation decreased rapidly as the gold content decreased to 80% and was much more random for the rest of the alloy compositions and for the silver references. That is, epitaxial growth was obtained on heated mica substrates, but a monotonically varying composition-dependent bulk orientation was obtained on glass substrates.

To study specifically the surface structure, the last epitaxial sample, E4, was examined *in situ* by a low-energy-electron-diffraction (LEED) technique which utilized the cylindrical mirror analyzer.[37] The primary beam energy and the mirror voltage were varied simultaneously to yield azimuthally integrated diffracted beam currents at a fixed angle as a function of primary beam energy. The method does not give the symmetry of the reciprocal lattice directly as does conventional LEED, and the data are somewhat complicated by effects associated with the large analyzer acceptance angle, but it was possible to interpret the peaks obtained as due to the unreconstructed atomic arrangement of the (111) surface. The diffraction curves obtained for silver, gold, and the alloys were similar.

Two portions of epitaxial films were analyzed by atomic absorption spectroscopy with the result that a relatively thin (800 Å) film grown in a 600-sec evaporation had a bulk composition of 52 at.% gold in agreement with the surface composition of 51%, but a 4000 Å film deposited in a 900-sec evaporation had 25% for the bulk average and 40% for the surface. Slowly varying compositions normal to the surface produced by changes in the source sizes which occurred at higher rates and longer evaporation times were not diffused out quickly with the sample preparation method employed. However, experiments using ionization rate monitors, observation of the stability of the work function over long periods of time, and diffusion experiments with intentionally large composition gradients near the surface indicated that no significant gradient would be present in the last few atomic layers of the samples reported here. This was confirmed on sample E4 by obtaining the surface composition separately using the 72, 239, and 2024-eV gold peaks which result from electrons with approximate escape depths of 4, 8, and 30 Å, respectively.[26,38] The different peaks yielded agreement for the composition within the experimental errors of a few percent. Earlier samples were tested similarly using only the 72- and 239-eV peaks.

An additional experiment relating to composition variation with depth and to diffusion or surface segregation was the following: Compositions were calculated using the different gold Auger peaks on an epitaxial alloy region. A silver coating of about two layers (as estimated from the evaporation time) was deposited at room temperature, and the analysis was repeated. Finally the sample was annealed, and the composition analysis was performed again. Some of the results are summarized in Table I in which the compositions are accurate relative to other entries in the table to about 2%. The data in Table I demonstrate the sensitivity of the use of different energy gold peaks to the presence of a silver overlayer and show that the overlayer diffuses into the bulk with annealing. These observations are consistent with other experiments performed in this laboratory, using a Kelvin vibrating capacitor technique for contact potential difference measurements, which indicated that both silver-rich and gold-rich alloy surfaces, relative to the underlying layers, diffuse toward the bulk composition.

TABLE I. Alloy composition results using different Auger transitions in gold (a) after simultaneous evaporation, (b) after deposition of silver overlayer at room temperature, and (c) after annealing overlayer at approximately 300 °C.

Electron energy	72 eV	239 eV	2024 eV
Approximate escape depth	4 Å	8 Å	30 Å
Normalized peak heights (± 2%)			
(a) as deposited	73%	72%	72%
(b) 1 day after ~6 Å Ag overlayer	16%	30%	55%
(c) after 1-h anneal at ~300 °C	69%	68%	67%

IV. DISCUSSION

Although it is known experimentally that silver and gold have a large difference in work function, the difference has not been explained theoretically. The dominant parameter which enters existing work-function theories[7] is the electron density as determined by the valence, which is 1 for both metals, and by the lattice constant, which is different by less than 0.3%. The possibility that the undetermined source of the difference in work functions will be a nonlinear function of composition in the alloys should also be considered.

The *d* electrons of the noble metals have been viewed as important for a complete treatment of their work functions[8] and have been included in a treatment of the bulk alloy problem for the Ag-Au system by Gelatt and Ehrenreich.[16] Their bulk Fermi energy calculation, coupled with the assumption of equal surface dipole layers for the two metals, predicts a work function for the alloy lying below a linear interpolation between Ag and Au with a deviation from linearity which is about one third the experimental result reported here. At least some part of the variation of the work function with alloying may be due to details of the surface dipole layer not included in an analysis of the bulk problem. It is interesting to note that the work-function measurements on annealed Pt-Ru and Ag-Pd alloys[20,21] also fall below a linear interpolation.

In addition to the main result, shown in the graphs in Figs. 5–7, that the work function is approximated by a quadratic interpolation rather than the composition average of Ag and Au, additional systematic effects are apparent on examination of the work-function data for particular samples in the graphs. Even with the observed relatively high diffusion rates and with the low evaporation rates used, it is possible that the non-normal angle of incidence of the vapor streams during the evaporation affected some details of the surface structure of the films. The sums of the Ag and Au compositions determined independently using their respective references were observed to vary systematically with position on the substrate. Since different samples had different ranges of composition and different compositions at the same manipulator position reading, this variation with substrate position does not correspond to a variation with composition which would enter into an explanation of the general result of the deviation of the work function from a linear interpolation. The sums of Ag and Au compositions for the epitaxial films varied from a low of 91 to a high of 104. The average sum for the alloy at the center of each slide was low at about 93 while the average near the ends was high at about 102. Regarding the lack of correspondence of the sum to the composition, note that the interpolated results for the sum for the 50% Au alloys were 91, 99, 94, and 92 for samples E1, E2, E3, and E4, respectively (see Figs. 5 and 6).

Since more accurate quantitative Auger composition analysis would have to include consideration of the backscattering contribution to the Auger signals for both the references and the alloy, it is to be expected that the sum of the Ag and Au compositions normalized to the individual references do not add exactly to 100%. Although surface segregation of one constituent affects the value of the sum, this was found not to occur in Ag-Au alloys as discussed elsewhere in this paper.

The possibility of oxygen adsorption in both molecular and atomic states makes a unique interpretation of the oxygen exposure results difficult, and complicated effects have been observed with silver-gold alloys used as catalysts for ethylene oxidation.[39] Nevertheless, the data for the change in work function with oxygen exposure as a function of composition presented in Sec. III (Fig. 8) seem consistent with existing results for oxygen adsorption on silver. It is known that bulk diffusion of oxygen into silver occurs, and the smaller work-function change on pure Ag than on the 5% Au alloy can be interpreted as the decrease in surface potential due to diffusion of some adsorbed oxygen atoms from the surface into the bulk. The lack of significant work-function change above about 55% is consistent with the requirement of several adjacent silver atoms on the surface for the adsorption of an oxygen atom[40]; few such sites without gold atoms would be present in a disordered alloy with a large gold content. The peak at 5% Au suggests that bulk diffusion of oxygen into the Ag-rich alloy does not proceed when an oxygen atom would not be completely surrounded by silver atoms in the bulk.

The absence of work-function change at higher gold contents is evidence that the samples were actually solid solutions rather than small patches of the pure metals. The change with oxygen exposure in the latter case, for patches which are large relative to atomic dimensions, would be a linear function of the silver content. The lack of any work-function change on pure gold and gold-rich alloys is some indication of the purity of the oxygen. Gold does not adsorb oxygen but does adsorb other gases, such as CO, and these would produce work-function changes if present.

Results presented in this paper indicate that surface segregation of Ag does not occur in the Ag-Au alloy system. The simplest theory (ideal solution) and a more complete treatment[17] both predict surface segregation of the element with the lower surface tension or heat of vaporization. However, the experimental observations here imply that the heat of formation of about 1.1 kcal/mole[41] for the 50-50 alloy is large relative to the difference in surface energy between (111) crystal faces of silver and gold. Significant surface segregation would be prohibited for the free-energy minimization if it were favorable for the unlike constituent atoms to be adjacent and the surface energy difference were small.

The unexpected result that the polycrystalline and the (111)-oriented epitaxial alloys had similar work functions for the preparation methods used in this study could be explained by the fact that a (111) face is the lowest surface energy plane for an fcc metal. The interpretation would be, then, that the polycrystalline samples had facets which were oriented with respect to the substrate in the manner needed to produce the low-energy planes at the vacuum-metal interface, even though the bulk orientation of those samples was different from that obtained for the epitaxial films.

V. SUMMARY

Clean single crystal (111) Ag-Au alloys have been prepared by simultaneous evaporation onto heated mica substrates. Auger electron spectroscopy has been used to confirm the purity of the crystals, to show the lack of a composition gradient perpendicular to the surface for the top layers, and to measure quantitatively the alloy surface composition. The variation in work function of these alloys falls significantly below the linear interpolation between the two pure metals and is described approximately by $\Phi = \Phi_{Ag} + 0.91x^2$, where x is the fractional gold content of the surface. How much of this nonlinearity is due to the surface contribution to the work function arising from the relaxation of electrons at the surface is not known.

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