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Ordered Au(111) layers on Si(111)

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Ordered Au films are grown on top of a thin (seven-layer) Cu film acting as a buffer between Au and a Si(111) substrate and characterized with synchrotron radiation photoemission spectroscopy. A sharp Shockley surface state characteristic of Au(111) is seen in the valence band spectra together with structures in the *sp* part of the band that disperse toward the *sp* band edge for growing film thickness. These structures are ascribed to quantum well effects. The Au film shows sharp (111) low energy electron diffraction patterns for a film thickness above eight layers. © 2007 American Vacuum Society. [DOI: 10.1116/1.2715964]

I. INTRODUCTION

Gold surfaces are often used as substrates in studies of organic structures on surfaces, since they are stable in various biochemical environments and allow attachment of biomolecules through thiol groups. Thus a large number of studies of the interactions between molecules and Au surfaces have been performed.¹ Typically, surfaces of bulk Au crystals or thin films on mica are used. However, formation of well-ordered thin Au films on Si would be a step in the direction of direct integration of biosensors on wafers containing Si electronics.² Deposition of Au directly on Si leads to formation of a disordered surface layer containing a mixture of Si and Au that floats on top of the Au layer even for relatively thick films. Various models of the Au–Si system have been suggested over the years. Early experimental results were interpreted in terms of a thick reacted layer at the interface.^{3,4} Later experiments, using synchrotron radiation photoemission, have led to a model where a pure gold layer is sandwiched between the Si substrate and a reacted layer at the free surface.^{5,6} Yeh *et al.*⁶ found that the reaction between Au and Si starts from the initial deposition and after 4 ML (monolayer) pure Au grows below the reacted surface layer. Investigations of the metallic Au part of the Au/Si system are thus complicated by the presence of this reacted layer. For instance, no low energy electron diffraction (LEED) pattern is observed after the loss of the 7×7 structure during the deposition of the first few Au layers. Moreover, the surface state usually found on the (111) surface of noble metals is absent and Au core level spectra instead show a reacted component. Reconstruction of the Si(111) surface into a $\sqrt{3} \times \sqrt{3}$ -Au structure prior to growth of thicker Au films im-

proves the quality of the Au film compared to the growth directly on the 7×7 surface.⁷ However, LEED patterns and the Shockley surface state are still absent.

Previous investigations have demonstrated that Cu buffer layers improve the growth of Ag (Refs. 8 and 9) and Al (Ref. 10) relative to the growth directly on clean Si(111) 7×7 . For both Ag and Al, the Cu buffer layer leads to improved sharpness of both quantum well (QW) peaks in the *sp* bands and the surface states. The goal of the present work is to demonstrate that Au films with large domains and electronic properties resembling those of bulk Au(111) surfaces can be grown on Si(111) when a thin Cu film is used to prevent the reaction between Si and Au. Our previous work with Au on Si (Ref. 9) using a Cu buffer layer demonstrated the appearance of the Shockley surface state, but without an ordered surface layer seen by LEED or QW states in the valence band spectra. In the present work, the growth techniques have been improved. Core and valence band photoemission spectroscopy, LEED, and atomic force microscopy (AFM) are used in combination to characterize the Au surface properties as a function of the thickness. A sharp Au(111) LEED pattern is now observed, and the Shockley surface state characteristic of Au(111) surfaces appears even for films that are only a few layers thick. Furthermore, a structure that is interpreted as QW levels in the Au *sp* band appears.

II. EXPERIMENTAL RESULTS

The photoemission experiments were performed in a vacuum system equipped with LEED and a manipulator that allowed liquid nitrogen cooling (to 180 K) and direct resistive heating of the samples. Samples were cut from a 1-mm-thick *n*-type Si(111) wafer with a resistivity of $5 \Omega \text{ cm}$. Copper and gold films were deposited from an e-beam source equipped with a biased grid in front of the evaporator to stop charged ions from hitting the surface. The thin films were grown on UHV cleaned Si(111) surfaces with 7×7 LEED patterns. Their deposition rate was calibrated

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with a quartz crystal oscillator. The photoemission experiments were performed at the ASTRID storage ring at Aarhus University, Denmark, using the SGM1 beamline equipped with a spherical grating monochromator and a SCIENTA analyzer with a radius of 20 cm. All experiments were done at normal emission of the emitted electrons. During recordings of some of the valence band spectra, the acceptance angle of the analyzer was reduced from a full angle of 16° down to 2° . The films studied were grown as a wedge on the Si surface extending over 1.5 cm by moving the sample into the shade of a fixed screen during metal deposition at constant rate. Subsequently, the wedge-shaped film can thus be quickly studied for systematic effects of the thickness by translating it through the photon beam. The size of the beam in the direction of the wedge must be small enough to ensure that the measurements are performed on a well-defined thickness. Previous investigations have shown that the width of the beam at the sample is $150\ \mu\text{m}$ for the smallest slits used and four times larger for the slit used for the valence band spectra.¹¹ With a wedge length of 15 mm, the maximum variation in film thickness then should not exceed 25 ML.

The sample used in this work was prepared by depositing seven layers of Cu on a clean Si(111) 7×7 sample kept at 180 K. After Cu deposition, the sample was allowed to anneal at room temperature for several hours and the surface was monitored with LEED and with core and valence band spectra. After cooling to 180 K again, a Au wedge was grown with a thickness of 25 ML at the thick end and leaving some uncovered Cu at the other end.

The growth of copper on Si(111) 7×7 from the submonolayer regime to more than 20 layers has previously been investigated using both core level and valence band spectroscopies.⁸ During deposition of the first five layers of Cu, the surface appears disordered from LEED images and the core level spectra show a strong reacted Si $2p$ component shifted to lower binding energy compared to bulk Si. After five layers of Cu, the growth of this reacted component ceases as the diffusion through the layer decreases, and a pure(111)-oriented Cu layer starts to form on top.

Figure 1 shows valence band spectra from 7 ML Cu at three different photon energies at the bottom of the figure and spectra recorded using 47 eV photons at different positions on the Au wedge, corresponding to varying Au thickness, in the upper part of the figure. The Cu spectra contain the sp band at the lowest binding energy and structures between 2 and 5 eV binding energy related to the d bands. Two structures appear in the bulk band gaps, namely, the Shockley surface state between the top of the sp band and the Fermi level and another surface state below the d band region at 5.3 eV. The Shockley surface state here appears at a binding energy of 0.2 eV, which is considerably lower than the 0.4 eV found for thicker films or bulk Cu samples.¹² Variations in the position of surface states of noble metals on Si(111) with strain in the films have been investigated by Neuhold and Horn.¹³ Also the d bands differ from those of surfaces of bulk Cu(111) where two peaks at 2.5 and 3.8 eV usually dominate the spectrum. Clearly, in the 7 ML film, the

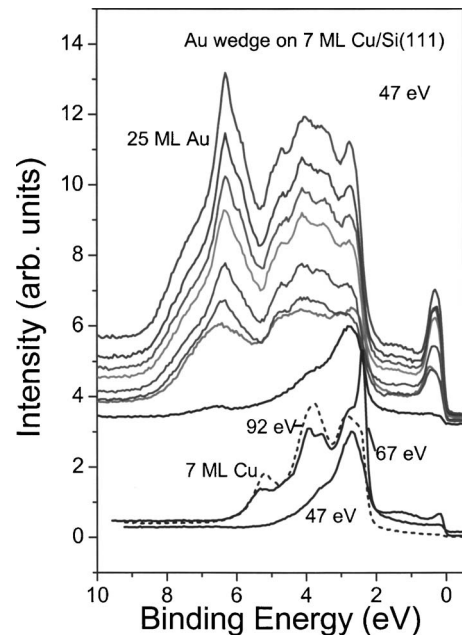


FIG. 1. Valence band spectra of the Cu–Au system. At the bottom, spectra from seven layers of Cu on Si(111) are shown at three different photon energies. The upper part of the figure shows spectra recorded at 47 eV photon energy for films with increasing Au thickness in steps of 3.5 ML.

band structure has not yet developed fully to the bulk level. All the structures show a strong energy dispersion as found for the bulk Cu(111) surface in the work by Louie *et al.*¹⁴ At 2.2 eV a sharp peak appears for 67 eV light, and two contributions can be identified at 3.5 and 3.8 eV binding energies. In the work by Louie *et al.*¹⁴ oxygen exposure was used to quench surface contributions in the d band region. In this way the 2.2 eV peak was identified as a surface feature.

The upper part of Fig. 1 shows how the Au sp bands and d bands form with growing film thickness. The Shockley surface state starts to form about 0.5 eV below the Fermi level already from the first layer the Au. Only a small shift toward lower binding energy is seen as this state grows in intensity with increasing thickness. Courths *et al.*¹⁵ have investigated the d band spectra of Au(111) in detail using angle resolved spectroscopy. All the structures of the bulk spectra can be identified in the spectra in Fig. 1. Going from 3.5 to 7 ML, the d band structures sharpen and shift to lower binding energy. From 7 ML the main effect of the growing film thickness is an increase in intensity of the peaks.

We will now turn to a more detailed investigation of the sp part of the Au spectra through the scans shown in Fig. 2. In order to increase the angular resolution, the acceptance angle of the spectrometer was reduced to 2° . Spectra recorded with different photon energies from a 20-layer-thick film show two broad peaks at 1.4 and 2.0 eV independent of photon energy. The variation of these peaks with film thickness has been investigated using 47 eV photons, since this energy gives a flat sp band and thus the best observation of the peaks. Figure 2 shows that the structures in the sp band shift to lower binding energy with growing film thickness. The position of the bulk band edge at the L point is marked

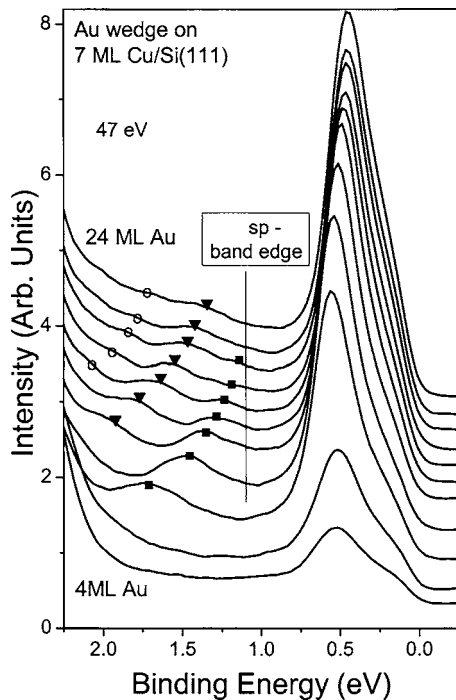


FIG. 2. Valence band spectra from a Au wedge grown on seven layers of Cu on Si(111) using 47 eV photons. During recording of the spectra, the acceptance angle of the analyzer was reduced to 2° . The Au *sp* band edge and structures attributed to quantum well effects are marked.

at a binding energy of 1.1 eV. The shifts of peaks toward the band edge with increasing film thickness as well as the absence of shifts with photon energy are typical signatures of confinement effects.¹⁶

The formation of the Au surface as a function of film thickness can also be followed through the Au *4f* core lines. Citrin *et al.*¹⁷ showed that the core lines of Au(111) surfaces of bulk crystals have a surface contribution shifted by 0.4 eV to lower binding energy. Figure 3(a) shows spectra recorded using 190 eV photons on the Au wedge at 1, 6, 8, and 12 layers along with a decomposition into bulk and surface contributions. Figure 3(b) shows the areas and binding energies of the peaks as a function of film thickness. The surface contribution forms during the initial growth and shifts to lower binding energy as the layer thickness grows. After six layers the surface contribution still dominates. After eight layers the energy positions of both contributions have reached stable levels, and after 12 layers no further changes in the core level spectra are found. The appearance of the surface contribution in the core level spectra is a sign of a clean Au(111) surface and in contrast to spectra from Au films grown directly on Si.⁶ Direct growth of Au on Si also leads to two components in the spectra, but in that case the additional peak originates from reacted Au shifted to higher binding energy. The core levels in Fig. 3 have a strong resemblance to spectra reported by Hsieh *et al.*¹⁸ for thin Au layers on Ag(111). Similar ratios between surface and bulk contributions are found, and the surface shift of 0.33 eV found in Ref. 18 is comparable to the 0.37 eV found here. Based on their data, Hsieh *et al.* found the escape depth of

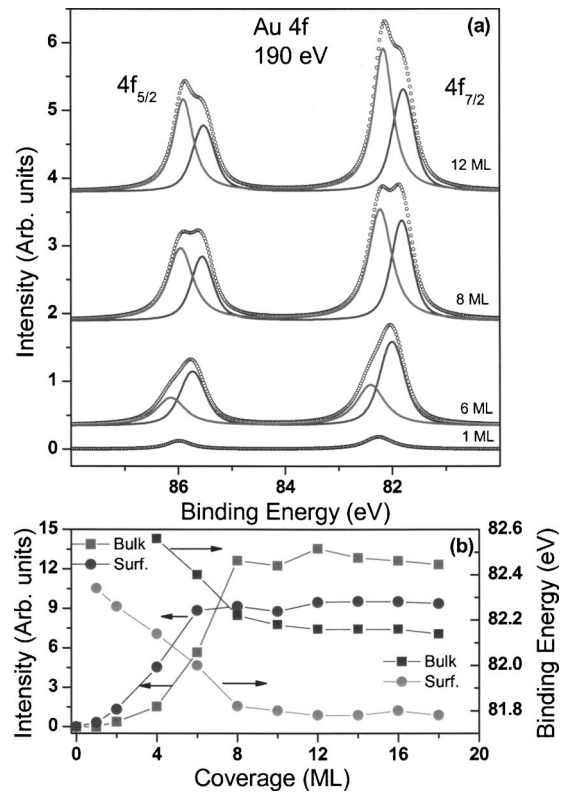


FIG. 3. Au *4f* core level spectra (a) at four different thicknesses shown along with decomposition into bulk and surface contributions. The experimental data are shown with open symbols, and the bulk and surface contributions as fully drawn curves. In (b) the areas of surface and bulk parts as well as the peak position are shown as functions of film thickness.

the electrons to be 5 Å. Since this only corresponds to about two layers of Au, the saturation in the development of Au *4f* spectra around 8 ML is an effect of the development of the Au(111) structure rather than just an effect of the escape depth.

In order to investigate the crystalline order of the thin film, LEED images were recorded at regular intervals along the Au wedge corresponding to about 1 ML steps in film thickness. The 7 ML Cu film forms a sharp (111) pattern that is rotated 30° relative to the underlying Si(111) structure. Previous investigations have shown that thinner Cu layers are disordered and contain substantial amounts of Si.⁷ They are thus not suitable for epitaxial growth. The initial deposition of the first few monolayer of Au on the seven-layer Cu film leads to weak LEED patterns. As the Au coverage increases, the LEED patterns sharpen and no further change is seen above 8 ML. The ratio between the lattice constants of the Au and Cu films is found to be 1.10, in good agreement with bulk lattice constants. The image from 4 ML Au shows a more diffuse pattern with 4% larger distance between spots compared to the 20 ML pattern. Clearly the crystal structure of very thin Au films is not fully developed due to the mismatch in lattice constants of Cu and Au and thus strain in the Au layer.

III. DISCUSSION AND CONCLUSIONS

The appearance of QW levels in the *sp* bands indicates a fairly smooth film on the atomic monolayer scale within the probing area of the photon beam. In the valence band scans, the beam is 600 μm high (in the direction along the wedge) and a few millimeters wide. A large number of domains thus contribute to the signal. Height variations among the domains as well as roughness of the domain surfaces will broaden the QW peaks and, if the variations are many layers, smear them out completely. Another factor affecting the sharpness of QW peaks is the reflection of electrons at the interface to the substrate. Since the band edge of the *sp* band of Cu(111) is 0.85 eV below the Fermi level, the *sp* electrons of the Au overlayer will only experience a relative energy gap at the interface. Experiments by Mueller *et al.*¹⁹ on Ag (which has the same lattice constant as Au) films on Cu(111) show a pronounced broadening of QW peaks at binding energies below the Cu band edge compared to sharp peaks in the direct gap. The relatively broad QW peaks of the Au film are thus primarily an effect of the poor confinement at the interface rather than film roughness.

The thickness of the Cu buffer layer was chosen on the basis of previous experience with Ag metal layers on Si using Cu buffer layers.⁷ Here it was found that seven layers of Cu gave the optimal sharpness of QW peaks in the *sp* bands. Thinner layers led to a disordered surface, and thicker Cu layers led to the formation of Cu QW levels that would couple to the Ag QW levels of the top layer and thus reduce the sharpness of the QW peaks. Though this has not been tested here, the same type of effect is expected for Au layers. This does not mean that thicker Cu layers would not be useful in order to grow Au(111) surfaces on Si. It may very well be possible to obtain more smooth Au films with thicker buffer layers. The seven-layer film was chosen here in order to demonstrate that QW effects can be observed in the Au valence band spectra, which is a sign of smooth film growth.

From the data we can discuss how thick the Au layer has to be before the Au(111) surface character has developed. From Fig. 3, it is seen that the surface component has formed after six layers and the bulk component is fully developed after eight layers. Furthermore, after eight layers, the peaks have also reached stable positions in binding energy. This agrees with the LEED observations where the sharp Au(111) pattern has developed after eight layers.

The morphology of the grown films was investigated using an atomic force microscope, "Ntegra" from NT-MDT. This was done *ex situ* under ambient conditions. We observe that the domain size increases with increasing Au coverage. At low Au coverage, the domains are approximately 150 nm in diameter increasing to approximately 500 nm in the high Au-coverage regime (20 ML). The increase in domain size agrees very well with the observed increase in sharpness of the LEED pattern for thicker Au films.

In conclusion, photoemission studies supported by LEED and AFM experiments demonstrate that thin Au films with surface properties characteristic of Au(111) can be produced on a Si(111) wafer by using a thin Cu layer to separate the Au layer from the Si substrate. The seven-layer Cu film used in the present experiments should be considered as the minimum thickness that can be used. Thinner layers create a disordered film. Though it has not been studied explicitly here, experience from other studies⁷ suggests that thicker Cu films will be useful. From Au core level spectra and LEED, it is concluded that the Au(111) character is reached after eight layers. The QW effects in the valence bands are fairly weak due to the absence of a direct gap at the Cu–Au interface, and they are not observable at all for thick Au layers. With domain sizes of the order of 500 nm, as it was obtained for the 20-layer-thick film, the surface should be well suited as substrate for studies of the interaction between Au(111) and various adsorbates.

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