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Optimum Cu buffer layer thickness for growth of metal overlayers on Si (111)

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Thin Cu films deposited on Si(111) surfaces may serve as excellent substrates for uniform or epitaxial growth of other metallic layers. The initial deposition of Cu on Si(111) leads to the formation of reacted layers building a chemical phase on the surface that saturates or stabilizes after deposition of the equivalent of 6 ML of unreacted Cu. Photoemission with synchrotron radiation shows that for further Cu deposition a perfect Cu film with a surface state and clear signs of quantum-well states are forming. The growth of thin Ag layers on such a Cu buffer phase leads to well-ordered films with optimally sharp Ag quantum-well levels.

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The initial growth of metal films on semiconductors usually includes some forms of islands preventing the formation of flat films. The most obvious reasons for this are the poor lattice match of most metals to, for instance, Si(111), and differences in the surface energies of the semiconductor and metal. In some cases the growth is further complicated by an interfacial chemical reaction between the metal and the substrate. Buffer layers that can improve the growth conditions are thus an important issue in thin film growth and in the evolving nanotechnology with such systems. Though Cu is known to react chemically with Si, the epitaxy of thicker deposits of Cu on Si(111) 7×7 has been observed using a number of techniques,[1–5] and improved film growth has been observed for several metals on Si(111) on top of a thin Cu buffer layer.[1,2] Improved growth of Ni (Ref. 1) and Fe (Ref. 2) films, aiming at silicon based magnetic systems, has been observed with 30–35 Å intermediate Cu layers deposited at room temperature (RT), and it was found that the Cu layer stabilized growth of epitaxial magnetic layers on top of it. However, no systematic search for an optimum buffer layer thickness has yet been presented.

Structure investigations of the Cu/Si (111) system using low-energy electron diffraction (LEED),[1,2] reflection high-energy electron diffraction (RHEED),[3,4] and x-ray diffraction[5] have demonstrated that for epitaxy the Cu [110] direction aligns with the Si [211] direction, thus leading to a 30° rotation of diffraction patterns. Walker, Specht, and McKee[5] showed that the formation of a reacted layer at the Si/Cu interface plays a key role in overcoming the 15% lattice mismatch between the two materials. Ordered copper-silicide islands with a 7% misfit of the lattice constant at the Si substrate were formed during the growth of the first 6 ML. The islands then coalesce and an epitaxial Cu layer starts to grow. Film growth at RT and at 160 K has been compared in RHEED experiments.[4] Irregular RHEED intensity oscillations observed up to 8 ML were explained by the formation of a silicide layer with the distance between atomic layers smaller than that of bulk Cu(111). Above 8 ML regular RHEED intensity oscillations were observed.

The present work investigates Cu films on Si(111) 7×7, and their properties as buffer layers for further metal growth. Photoemission core-level spectra give information about reactions and an intermixing of substrate and film materials, while valence-band spectra contain information about the highest-lying levels, where the confinement of electrons in the thin film may lead to quantum-well (QW) effects. One of the most extensively deposited metals is Ag for which QW states have been studied for growth on a variety of metallic[6,7] and semiconducting[8–11] substrates. In the present case a thin Ag layer is deposited to test the quality of the Cu-induced buffer layer and determine the thickness where optimum overlayer growth properties are obtained.

The experiments were performed at the ASTRID storage ring at Aarhus University, Denmark, using a beamline equipped with a spherical grating monochromator and a SCIENTA analyzer. All experiments were done at normal emission of the emitted electrons. During recordings of valence-band spectra the acceptance angle of the analyzer was reduced from a full angle of 16° down to 2°. The vacuum system was equipped with low energy electron diffraction and a manipulator that allowed liquid-nitrogen cooling (to 170 K) and a direct resistive heating of the sample. The samples were cut from a 1-mm-thick *n*-type wafer with a resistivity of 5 Ω cm. Copper and silver were evaporated from thermal sources consisting of tungsten coils wrapped around boron nitride crucibles. A quartz crystal oscillator was used to calibrate the deposition rate. To facilitate systematic measurements wedge shaped thin metal films were grown on clean Si(111) 7×7 surfaces by slowly moving the sample into the shadow of a fixed shield during deposition. After this sample preparation, the film thickness was varied by scanning the wedge through the photon beam, as described in a previous work.[11]

Si $2p$ spectra have been recorded at regular intervals along the wedge-shaped Cu film, starting with the 7×7 surface at one end and ending with 15 ML at the other end. The spectra have been decomposed into spin-orbit split components using the program FITXPS.[12] Figure 1 shows the evolution with coverage of the spectral components. The insets show the raw spectra. Other metal Si systems (e.g., Ag and Al on Si) show improved properties for films deposited at low temperature and subsequently annealed at RT compared to direct RT growth. This growth procedure is also investigated for the present system. Figure 1(a) shows data recorded

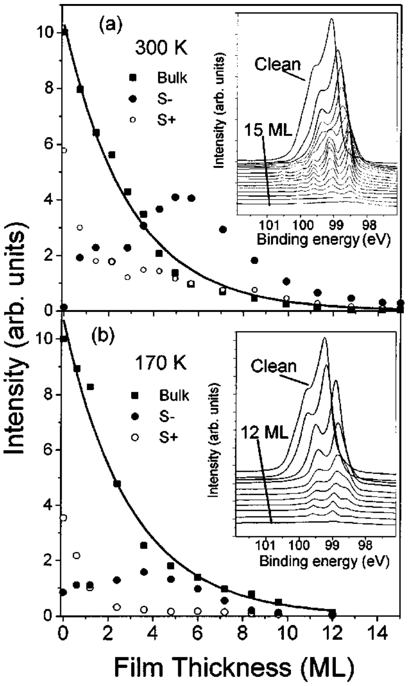

FIG. 1. The components of the Si $2p$ core-level spectra as a function of film thickness obtained from data recorded at room temperature (a) and at 170 K (b) using a photon energy of 130 eV. The recorded spectra are shown as insets.

at RT from a film deposited at RT, while the data in Fig. 1(b) were obtained from a film grown and kept at 170 K. The spectra of the clean 7×7 surface have been fitted with a bulk component and two surface components shifted respectively 0.3 eV up (designated S_+) and 0.7 eV down (designated S_-) in binding energy relative to the bulk component. This together with a spin-orbit splitting of 0.60 eV and a branching ratio of 0.54 is consistent with results in the literature.[13] On the 7×7 surface, S_+ is due to adatoms and atoms binding to adatoms, and S_- is due to restatoms.[13]

Deposition of Cu leads to decay of the bulk peak and quenching of the surface states of the clean 7×7 surface, while new surface components are induced due to the reaction between Cu and Si. As for the clean surface, the fits accommodate two surface components, one above (S'_+) and one below (S'_-) the bulk peak. Along with the decay of the surface states the bulk peak shifts ~0.2 eV toward lower binding energy due to band bending. The surface component S'_+ decays quickly during the growth of the first 2 ML, and then at a slower rate at higher coverages. The energetic position of S'_+ largely follows that of the bulk contribution. The other new component S'_- is quite small in the beginning but grows during Cu deposition to a maximum at 5–6 ML. The position of S'_- shifts from 0.7 eV (S_-) below the bulk peak to 0.5 eV (S'_-) during the deposition of the first two Cu monolayers. No further shifts of induced surface components take place during growth above 2 ML. These core-level shifts are in agreement with the results of Ref. 14. Also the variations of the widths of the two reacted components with thickness follow the trends described in Ref. 14. According to that work the S'_+ component is due to silicide formation while the S'_- component comes from a solid solution of Si in Cu. Thus, at saturation of the surface contributions to the Si $2p$ spectra at 6 ML, the surface seems to consist of a solid solution of Si in Cu. The decay length of the bulk peak, both at RT and 170 K is equivalent to the thickness of three Cu monolayers or 6 Å, in good agreement with the expected mean free path of electrons in Cu.[15]

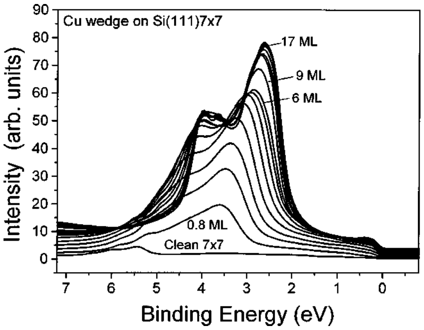

FIG. 2. Cu valence-band spectra recorded with 47-eV photons on a room-temperature-grown Cu wedge.

Growth of Cu on Si at low temperature leads to a reduction of the reacted components in the Si $2p$ spectra as seen in Fig. 1(b). This is consistent with the RHEED results of Ref. 4. However, annealing of the present wedge grown at low temperature leads to a growth of the surface contributions to levels comparable with those of the film grown at RT.

Valence-band spectra recorded using 47-eV photon energy on a RT-grown film are shown in Fig. 2. As the coverage grows, the Fermi edge sharpens and the d band develops toward the bulk shape and position about 2 eV below the Fermi edge. The double-peak structure appearing ~5 eV down at the lowest coverage is an artifact caused by third-order diffraction in the input grating leading to a weak Si $2p$ spectrum. The spectra for the thickest film develop transitions in the range from 2.6 to 3.9 eV below the Fermi edge, in agreement with data for bulk crystals.[16] The dominant peak in the d-band spectra shifts upward from a binding energy of 3.5 eV at 0.8 ML to about 2.5 eV at 17 ML. The major part of the shift takes place during growth of the first 6 ML, and after 12 ML very little development of the spectrum takes place.

More details of the *sp*-part of the valence bands are displayed in Fig. 3 where the dominating structure is the surface state. This wedge was grown at 170 K, and subsequently allowed to anneal at RT. The surface state starts to develop above 6-ML coverage and shifts up to 0.35 eV below the Fermi level at 17 ML close to the position found for bulk Cu(111).[17] Below the surface state weaker structures can be seen that shifts upward with the film thickness. This is taken as a sign of QW states in the film. Details of the structure of the valence-band spectra are obtained by calculating the second derivative of the spectra. The inset in Fig. 3 shows the peak positions derived in this way. A simple model of the expected QW energies E is obtained by requiring constructive interference of an electron wave multiply reflected in the barriers of the thin film.[18] This gives the well-known condition

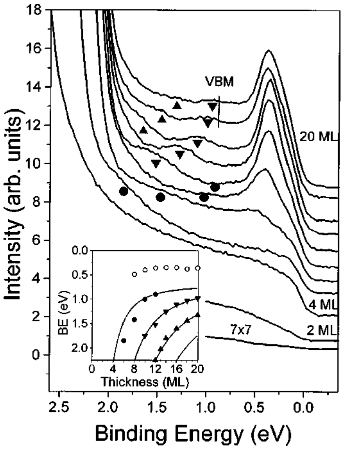

FIG. 3. Cu valence-band spectra recorded with 47-eV photons from a Cu wedge grown at 170 K and annealed to room temperature. The inset shows the thickness dependence of the quantum-well levels along with fits of Eq. (1) to the data. The open symbols show the position of the surface state.

$$2dk(E)+\Phi_v(E)+\Phi_b(E)=2n\pi,$$

where k is the Bloch wave vector, d is the film thickness, n is an integer, and Φ_v and Φ_b are the phase shifts upon reflections at the vacuum and Si boundaries, respectively. A two-band model for $k(E)$ with half the band gap equal to 2.55 eV is used.[18] The phase shift at the free surface (Φ_v) has been represented by the WKB result as described by Smith.[18] Within the small energy range where QW levels are observed it has not been possible to extract an energy dependence of Φ_b. The solid curves on the inset on Fig. 3 are thus obtained with constant Φ_b and an effective mass of 1.4. It should be noted that the thickness of the well is taken as the total thickness of the deposited layer (reacted plus pure Cu). The wavefunctions thus extend through a film that has a gradual change in lattice constant, at least for the part closest to the substrate.

Both core-level and valence-band data show a transition in film growth at 6 ML: The Si $2p$ surface component S'_- has reached a maximum (Fig. 1), most of the shift of the d bands has now taken place, and QW states are forming in the *sp* band. The formation of the Si $2p$ surface components seem to cease, indicating that the reacted layer becomes an increasingly efficient barrier for diffusion of Cu and Si atoms and that it covers the substrate uniformly. Continued Cu deposition buries the reacted layer under a pure Cu film, and the Shockley surface state becomes visible after two additional layers of Cu. The decay of the S'_- signal from 7 to 10 ML corresponds to a ~6-Å mean free path, as expected for low-energy electrons in Cu.[15] A series of LEED images taken at small intervals along the Cu wedge shows that the 7×7 pattern disappears during the deposition of the first few Cu layers, and the surface appears disordered at ~3 ML, but as the Cu thickness increases a 1×1 pattern rotated 30° relative to the Si pattern is formed. After 6 ML this pattern is fully developed and no further changes are observed as the thickness grows.

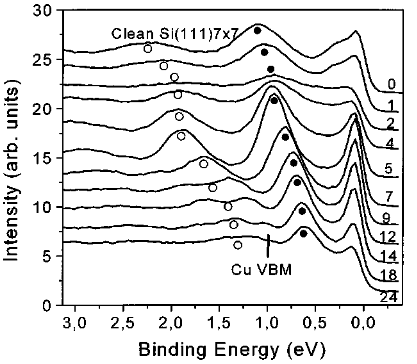

FIG. 4. Valence-band spectra recorded with 47-eV photons from a 10-ML Ag film grown on a Cu wedge (the thickness, given by the numbers on the curves). The symbols in the figure are meant to guide the eye to the shift of peaks with the Cu layer thickness.

The fully developed reacted film reached above 6 ML serves as a good substrate for growth of a pure Cu film with an improved film/substrate registry as demonstrated in Ref. 5. In the present study the appearance of the surface state close to the binding energy found for bulk Cu signals growth of a well-ordered Cu layer. Furthermore, the development of QW levels shows that height variations along the surface are limited to a few atomic layers. The QW levels are not as sharp as those found for Ag (Refs. 9–11) and Al (Ref. 19) overlayers grown on Si(111) under the same conditions, which seems to indicate a rougher film. However, compared to Ag, the energy window for observation of quantization of the *sp* band is much narrower for Cu, and the influence of the intense d bands, which are less susceptible to quantization by the boundary potentials, is stronger. It should be noticed, that even though the composition of the RT grown film and the annealed low-temperature (LT) grown film are the same seen from core level spectra, it is still advantageous to use LT growth combined with RT annealing in order to obtain smooth domains in the film. This is deduced from the enhanced QW effects obtained by this process compared to RT growth. The annealed LT grown film thus forms a better substrate for further film growth.

In search of an optimum deposited thickness of Cu as a buffer layer for further metal growth 10 ML of Ag was deposited on a Cu wedge with clean 7×7 Si at one end and 24-ML Cu at the other end. Mueller *et al.*[6] found that Ag forms a film of high quality on Cu(111) with QW states appearing sharpest in the absolute gap above the *sp* band edge of Cu, but also visible below the band edge due to the lattice mismatch between Cu and Ag. The valence-band spectra in Fig. 4 show peaks corresponding to QW levels in the Ag film, as previously discussed for Ag on Si(111) 7×7 (Refs. 10 and 11) (notice that the spectra were not taken at equidistant steps along the wedge). However, the position and sharpness of the peaks vary considerably with the amount of Cu below. The spectrum for Ag on the clean substrate is similar to previous spectra.[11] The sharpness of the peaks is reduced at the position with 2–3 ML deposited Cu below, coinciding with the Cu thickness where no LEED pattern could be observed. Moving to a position of a larger amount of Cu below leads to QW peaks even sharper than for the clean 7×7 surface. The sharpest spectra are seen at 7-ML Cu deposition. As the amount of deposited Cu increases further toward a pure Cu layer the sharpness of the Ag QW levels decrease, in particular at energies below the Cu *sp* band maximum. It should be noticed that the leading peak just below the Fermi level falls in the region where the Shockley surface state is found for bulk Ag(111) and also for Ag/Cu(111).[6] For Ag films grown on Si(111) 7×7 it has been shown that strain in the Ag islands shift the *sp* band edge toward or even above the Fermi level.[10] The broad peak just below the Fermi level for Ag on Si(111) 7×7 is thus a QW state.[10,11] In the case of Ag on top of the position of 7-ML-deposited Cu additional experiments probing the dispersion of peak positions with Ag film thickness indicate that the first peak is the surface state. The reacted layer of Cu and Si thus reduces the strain in the Ag overlayer compared to growth directly on the Si(111) 7×7 surface.

In addition to the variation in sharpness, the positions of the QW peaks also vary with the reacted layer thickness. A shift is seen during the first formation of the reacted layer after which the positions are fixed up to 7 ML of deposited Cu. As the reacted layer saturates and is covered by a pure Cu film the peaks again shift to lower binding energy with the major part of the shift taking place from 7 to 12 ML of Cu. The shifts, from the fully developed reacted layer at 7–24-ML Cu, for the second and third peaks, are 0.3 and 0.6 eV, respectively. In the phase accumulation model such shifts correspond to a phase change in the interface reflection of about 180°.

The data in Fig. 4 show that the fully developed reacted layer at 6-ML Cu that is the key to growth of the well-ordered Cu film also serves as an excellent substrate for growth of Ag overlayers. While the core level data show that the reacted layer is completed after deposition of 6-ML Cu the QW levels in Fig. 4 appear sharpest at 7 ML. The data in Fig. 4 may thus indicate that the optimum substrate for Ag growth appears at 7 ML, when the first Cu layer has formed on top of the reacted phase. However, this point has to be investigated in more detail. Compared to growth on the clean 7×7 surface this gives strongly enhanced sharpness of the QW peaks. The quantization of levels extends through the whole Ag *sp* band showing that the coupling between overlayer and substrate states is weak. Thicker reacted layers with properties in the top layers approaching those of pure Cu(111) lead to reduced sharpness of the Ag QW peaks. Above the Cu valence-band maximum a stronger coupling of overlayer and substrate states reduces the quantization effects. However, the sharpness of Ag QW peaks also decreases with the growing Cu film thickness in the band gap above the Cu *sp* band. This is taken as a sign of formation of islands of pure Cu that, though they are crystalline and form QW states, disturb the growth of the Ag overlayer. The Ag film is thus not free to form islands of the size that gives the lowest roughness.

To summarize, it is found that deposition of Cu on Si(111) 7×7 leads to the growth of a reacted layer that saturates at 6 ML of deposited Cu. This stabilized layer is well ordered and acts as a buffer layer for growth of a pure crystalline Cu(111) layer with a quantization of the electronic levels. It is demonstrated that this reacted layer, possibly with the addition of a single layer of pure Cu, also forms the optimum buffer layer for growth of Ag overlayers. Below that thickness the reacted layer is not fully stabilized, and above this thickness the formation of islands of pure Cu disturbs the growth of an Ag film on top. With the optimum buffer layer thickness the sharpness of Ag QW levels is significantly enhanced compared to growth on the bare 7×7 surface.

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