A medium energy ion scattering study of metal-on-metal epitaxy and surfactant-mediated growth for the Au on Cu(111) system

T.C.Q. Noakes*, P. Bailey

CLRC Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, UK

Received 5 May 2000; received in revised form 7 March 2001; accepted 22 April 2001

Abstract

The growth of Au on Cu(111) single crystal substrate has been investigated both with and without Sb surfactant. Room temperature deposition of approximately 10 ml of Au onto Cu(111) gave a film with twinned fcc structure, a reasonable degree of crystallinity and clear indications of inter-diffusion at the interface. Annealing this layer to progressively higher temperatures encouraged the diffusion of the Au into the substrate, thus reducing the strain arising from the lattice mismatch between Au and Cu. For a 400°C anneal the Au had almost entirely dissolved into the Cu substrate, such that no apparent twinning could be observed. The use of pre-deposited Sb as a surfactant in the growth of the Au layer was investigated for two levels, 0.2 and 0.5 ml, since above 0.33 ml Sb induces a stacking fault into the top most layer of Cu(111). For the lower coverage, similar results were observed in terms of the degree of crystalline order, but there was some indication that the twinning effect was partially suppressed. This effect was not observed for the higher Sb coverage. The compositional information as a function of depth indicated that for both coverages, the Sb remained at the surface. However, it was also evident that for the lower Sb coverage somewhat greater inter-diffusion between the Au and Cu occurred and it is possible that it is this effect that is actually responsible for the apparent reduction in twinning. These results indicate little benefit in the use of Sb as a surfactant for the epitaxial growth of Au on Cu(111). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Medium energy ion scattering; Epitaxy; Surfactant; Gold; Copper; Antimony

1. Introduction

The growth of well-ordered thin films of one metal on another is of fundamental importance to a number of technological applications including magnetic multilayer materials and corrosion resistant coatings. Many factors can effect the quality of an epitaxially grown film including lattice strain, inter-diffusion and island formation, which may give rise to imperfections such as poor interfacial abruptness, disorder and twin formation. The relative importance of each of these factors is determined by the material combination chosen. Inter-diffusion is a significant factor for a wide range of metallic material combinations including Au/Fe [1,2], although there are other systems such as Cu/Co [3,4] where almost complete immiscibility is seen. In the case of lattice strain, it can arise simply from the difference in lattice parameters between the two materials (e.g. Ni/Cu(100)) [5] or as a result of different crystal structure between the multilayer components and this is certainly common in magnetic multilayer type materials (e.g. Fe/Cu and Co/Cu [3,4,6,7]). This difference may itself lead to additional strain in the grown layers, particularly if one component takes up the structure of the other (e.g. Fe/Cu(111)) [6,7] although conversely there are examples such as Fe(100)/Au(100) [1] where the two components can

* Corresponding author. Tel.: +44-1925-603-424; fax: +44-1925-603-173.
E-mail address: t.c.q.noakes@dl.ac.uk (T.C.Q. Noakes).
grow in their own preferred crystal structure with almost no strain.

Surfactant-mediated epitaxy (SME), where a small amount of the third elemental species is deposited on the surface prior to film growth, is a technique for improving the quality of grown films. SME is particularly established in semiconductor materials, such as Ge/Se/Si(001) [8] where despite a large lattice mismatch, good crystallinity and interfacial abruptness can be achieved using Sb as the surfactant species. In the case of metal-on-metal growth, SME using a Pb surfactant has been used for the growth of Co/Cu where beneficial effects included suppression of twin formation [3].

In addition, Sb surfactant has been used in the homoepitaxial growth of Ag/Ag(111) where a significant reduction in islanding was observed [9].

In the case of the growth of Au on Cu(111), both metals exhibit fcc structure but with very different lattice parameters (4.078 and 3.615, respectively [10]). The expected strain which has a theoretical value of 27% (calculated from the surface mesh of the Cu whilst maintaining the Au atomic density), might give rise to islanding and/or considerable amounts of disorder in the grown layers. In addition, there is complete miscibility between the two components such that inter-diffusion is likely [11]. Sb was chosen as the surfactant and employed at two levels, one above and one below 0.33 ml, which is the critical coverage for the Sb to induce a stacking fault in the Cu(111) surface [12,13].

From the point of view of medium energy ion scattering (MEIS), this is a good system to examine as the components have a large mass separation allowing them to be completely resolved for independent analysis. MEIS is an ideal technique for investigating thin film growth as it can provide compositional and structural information as a function of depth in the near surface region with almost monolayer depth resolution.

Recently, MEIS has been used to carry out a number of experiments involving metal-on-metal systems that exploit both the high depth resolution and the crystallographic information provided. This work has included the analysis of magnetic multilayer materials [1] and most recently, investigations into metal-on-metal growth, including Co/Cu(111) [4]. Additionally, there is some previously published data on Fe/Cu(001) [14] and Au/Pd(110), which is particularly relevant here since it nicely demonstrates the ability of the technique to detect an improvement in the crystallinity of a 35-Å film of Au on annealing to 300–400°C [15]. Some preliminary work on the use of Pb in the surfactant-mediated epitaxy of Cu/Cu(111) and Cu/Co(0001) has also been conducted but is as yet unpublished.

2. Experimental

The experiments were carried out using the Daresbury MEIS facility (described elsewhere [13]) using 100 keV He⁺ ions. The toroidal electrostatic energy analyser used produces two-dimensional maps of scattered ion intensity that are typically displayed as false colour images (not shown here) [1,13]. These maps can then be processed by integration in either angle or energy to produce more conventional one-dimensional plots. Energy spectra give information on the composition as a function of depth, whereas angular spectra reveal the atomic arrangement of the atoms via the intensity variations caused by blocking of the scattered ions by atoms nearer to the surface. Blocking patterns can be produced for specific elemental components, or for given depth regions in the sample, depending on the area of the two-dimensional spectrum that is gated.

Another type of spectrum, also presented in this paper, is obtained by plotting the integrated counts from some region of the detector (often the whole area), as a function of the azimuthal orientation of the sample. Plots of this type show intensity variations arising from the channelling of the ions into a crystalline sample and these give symmetry information about the surface. By selecting the appropriate analyser energy, element (and potentially depth) specific information can be obtained.

A single crystal Cu sample with (111) surface orientation was prepared by repeated cycles of 1 kV argon ion bombardment and annealing to 700°C until Auger electron spectroscopy (AES) showed no surface contamination and low energy electron diffraction (LEED) gave a sharp (1×1) pattern, indicating low step density. Au deposition onto the sample at room temperature was achieved by passing a current through a W wire filament coated with Au at approximately 1300°C, forming molten droplets. A quartz crystal microbalance was used to monitor deposition and using a calibration derived from previous unpublished work, approximately 10 ml of Au was deposited for all the experiments conducted. Deposition of Sb onto the sample at 100°C was achieved using a Knudsen cell (WA Technology Ltd) at 455°C, having a characterised deposition rate allowing approximately 0.2 and 0.5 ml to be achieved for the relevant experiments. LEED was used to confirm that a $\sqrt{3} \times \sqrt{3}$ R30° reconstruction was absent for the low dose experiment and present in the case of the higher dose sample indicating the presence of a stacking fault [12,13]. AES was used after deposition of both Sb and Au to check that the desired coverages had been achieved and these doses were confirmed during the MEIS experiments.

3. Results

3.1. Room temperature deposited and annealed samples

Azimuthal scans were taken using incidence angles
of 35.3° and 54.7° (consistent with ⟨110⟩ and ⟨100⟩ type channelling) and an analyser angle of 120°, gating both the bulk Cu signal and the overlayer Au signal. Fig. 1 contains a plot of the azimuthal scan data for the 35.3° incidence and the top two panels contain data from the bulk Cu signal and the Au overlayer for an as-deposited sample with no surfactant and no post-annealing. Whilst the substrate displays a pattern with 120° repeat distance (threefold symmetry) the overlayer has a 60° repeat distance (sixfold symmetry). One potential explanation of this effect is that twin formation has occurred in the grown layer with the co-existence of two domains of fcc Au rotated by 60° with respect to each other. The following three panels contain data from deposited films that have been annealed to progressively higher temperatures. For annealing temperatures of 100 and 200°C very little change in the channelling pattern could be observed. However, on annealing to 400°C threefold symmetry could be seen to appear in the overlayer signal along with a considerable reduction in the total number of counts (as evidenced by the increased noise level). Azimuthal data taken with a 54.7° incidence revealed similar behaviour and is therefore not shown.

Two-dimensional data sets were taken for 110 and 100 incidence angles over scattering angles between 82 and 130° and energies from the primary energy to 77.5 keV. Angular projections from the 110 data sets are shown in Fig. 2. The substrate clearly shows the blocking features that are expected for a ⟨111⟩ surface. However, for the as-deposited surface and those annealed to 100 and 200°C a somewhat different pattern is seen. This result confirms twin formation, with the dips seen being directly attributable to the anti-phase portion of the deposited overlayer. This signal dominates the spectrum since for this part of the overlayer, the incidence angle is not along a large, well-defined, crystallographic orientation and hence complete sub-surface illumination is seen. For the 400°C annealed sample the crystal structure has returned to single domain fcc. Much lower intensity is seen, not only due to the dilute nature of the Au, but also due to the incomplete channelling seen in this more bulk-like sample. The large feature at 90° (⟨001⟩ blocking) can be seen in this data. For the lower temperature samples, the amplitudes of the blocking dips are less than expected for a perfect crystal with equal occupation of the twin domains, revealing some reduction in crystalline quality in the deposited films in comparison to the bulk. Simple inspection of the data suggests that there is no improvement in crystal quality on annealing the films to 200°C (the 400°C sample is more difficult to compare due to the absence of twinning).

The interpretation of the blocking dip amplitudes is complex, since contributions are expected not only for fcc and fcc twin, but also for disorder in the layers. Quantitative analysis is possible by comparing each data set with simulations produced using the VEGAS code [16]. The input to these simulations was simply the atomic positions in an Au fcc crystal structure with ⟨111⟩ orientation and a value for the bulk vibrations of the atoms which can be calculated from the Debye temperature. Simulations were run for incoming ions in two directions to produce blocking curves for fcc and fcc twin. These simulations could then be blended in different ratios with some contribution from the signal expected from amorphous material, which was included to take into account disorder in the grown layers. It should be noted that the use of an amorphous signal is something of a simplification, since disorder may well have more subtle effects on the blocking curves, including reduction in the width of blocking features. The experimental data and simulated blocking curves were then compared using established methodology [13], which involves a χ² measure of the degree of fit. Table 1 shows the results of this fitting for the films annealed to different temperatures. The results of the simulation work confirmed the qualitative assessment that twin formation has occurred in the deposited layers with equal occupation of both domains, which only reverts to a single domain on annealing to 400°C. In addition, all the fits benefited from the addition of an amount of disorder at a level of approximately 28%. These samples therefore exhibited a reasonable degree of crystallinity throughout, although the simulations confirmed the lack of improvement with increased annealing temperature.
In addition, the angular positions of the blocking dips can provide information on rhombohedral strain in the grown layer. Fig. 3 shows the strain measurement derived from the (110) twin blocking dip for the whole of the layer plotted as a function of the anneal temperature. It can be seen that the strain is considerably reduced with increasing temperature, probably as a direct result of the inter-diffusion of the Au and Cu.

It was also possible to section the overlayer signal layer-by-layer and Fig. 4 shows such a plot for the room temperature-deposited sample. It should be noted, however, that due to the energy resolution (particularly the contribution of energy loss straggling) the numbers generated represent a rolling average of three layers near the surface degrading to four to five layers by 10 layers down. For the deepest values, there is no strain as this signal comes from the low level of Au that has diffused into the Cu substrate. As the depth decreases and the Au content goes up, a peak in the strain is seen at over 8%. Taking into account that this represents an average over three to four layers the real strain could be as much as twice as high as this and is probably localised in one to two layers. Closer to the surface the strain is reduced, probably via formation of lattice defects or islanding and the blocking dips return to bulk positions. The data are consistent with a Stranski–Krstanov type growth mechanism.

Energy projections from the same two-dimensional data sets were extracted at a scattering angle of 97° and converted into a depth scale for each elemental component shown in Fig. 5, using the path length to depth ratio (2.87) and the stopping power (30 eV/Å [17]). The room temperature data show that whilst the surface is entirely composed of Au there is a considerable amount of Cu present over the depth range of the deposited film. This effect could arise due to a number of phenomena including variation in the thickness of the deposited layer, interfacial roughness or inter-diffusion of the Cu and Au. However, roughening effects, including those arising from film thickness variation, are not consistent with the MEIS data which show pronounced surface peaks not typically observed from samples with rough surfaces (e.g. [18]). Also, the long
tail on the low energy Au signal could only arise due to features having high perpendicular to parallel aspect ratio forming ‘sharp spikes’ of Au protruding into the Cu matrix. Whilst this is not entirely impossible, it is less likely than inter-diffusion as an explanation of this data. In addition, previous studies of evaporated Au/Cu multilayers using X-ray diffraction (XRD) and scanning tunnelling microscopy (STM) have indicated low levels of roughness and film thickness fluctuation [19]. Whilst some islanding cannot be ruled out and probably does occur, contributing in a minor way to the energy spectra observed, the mixing of Au and Cu signal seen here is thought to arise predominantly from inter-diffusion of the two components.

Inspection of the room temperature data shows that considerable inter-diffusion has occurred even before any subsequent annealing is carried out, with mixing extending over a depth of some 35–40 Å (much greater than the depth resolution for these data). As the anneal temperature is raised, further inter-diffusion can be clearly seen with some increase in the penetration depth of the Au, but more noticeably, an increased amount of Cu in the near surface region. By 400°C the Au signal has been almost totally dissipated, although there is still an Au-rich region at the surface itself, possibly due to the formation of a surface alloy. For this anneal temperature, the majority of the gold has dissolved into the Cu substrate to form a dilute solid solution which is consistent with both the azimuthal scans and blocking patterns obtained.

3.2. Surfactant-treated samples

Azimuthal scans at incidence angles of 35.3 and 54.7° were taken at a 120° analyser angle for layers deposited with differing levels of surfactant and the 35.3° data are compared with the room temperature non-surfactant sample and bulk signal in Fig. 6. The film grown with 0.5 ml of pre-deposited Sb gave very similar behaviour to that grown without surfactant, showing clear 60° periodicity. However, the film grown with 0.2 ml of surfactant did exhibit some indications of 120° periodicity. In particular, the fact that the dip at 120° is slightly bigger than those at 60° and 180°, together with the presence of two satellite features at 48° and 72° may demonstrate some reduction in the amount of fcc twin present. Data for 54.7° incidence (not shown) gave similar marginal evidence of a reduction in twinning for the 0.2-ml Sb grown layer.

Two-dimensional data sets were taken as before for the surfactant grown samples in 〈100〉 and 〈110〉 incidence geometries and angular projections from the 〈110〉 data for the Au overlayer signal are shown in Fig. 7 with the bulk signal and non-surfactant grown sample. The higher level Sb grown sample again looks very similar to the non-surfactant sample. However, for the 0.2-ml Sb grown sample, although there are still clearly blocking dips arising from twinned material, the number of counts are lower and the amplitude of the main (011) type blocking dip is reduced. Both these factors imply some reduction in the amount of twinned fcc present in this layer. Quantitative interpretation of the data was also carried out as before to determine the amount of fcc twin present and these data are presented in Table 2. The difference of 16 ± 14% seen in the twin content between the non-surfactant and low

![Fig. 4. Layer-by-layer strain profile of the room temperature-deposited Au overlayer. A measured maximum strain of approximately 8% can be seen although the actual strain could be as much as twice this since the effect of straggling on the energy resolution means that each point represents a rolling average of one to two points either side.](image-url)
Sb grown films indicates the marginal nature of the reduction in twinning seen. As with the annealed samples, the amount of disorder required to fit these data was virtually identical, showing no significant difference in the degree of crystallinity. In addition, the angular positions of the blocking dips are very similar for all samples indicating little difference in the amount of strain present.

Depth profile information derived from the energy spectra obtained from the same two-dimensional data as the blocking curves is shown in Fig. 8. The Sb signal for both low and high dose samples can be seen to reside exclusively at the surface, confirming that the surfactant effectively ‘floats’ during Au deposition. The Au and Cu signal in the 0.5-ml dosed sample show similar behaviour to the non-dosed sample. However, for the 0.2-ml dosed sample there is clearly evidence of increased diffusion of Cu upwards into the deposited Au layer. In this sense, there are similarities between this sample and those produced by annealing the non-treated sample. For this reason it is likely that the apparent reduction in twinning seen for a low dose of Sb is probably just an artefact of the increased inter-diffusion of Au and Cu.

4. Discussion

The observation of significant inter-diffusion even at room temperature is perhaps not surprising since previous studies of non-epitaxial (granular) films of Au on Cu have also demonstrated considerable diffusivity in this temperature range [11]. In addition, that work indicated greater diffusion of Cu in Au than vice versa, which although not strictly comparable (since it measured grain boundary diffusion) is in line with the behaviour seen here. In this present study diffusion probably occurs by a vacancy type mechanism, since enhanced diffusion at domain boundaries would lead to
It is interesting to note that two systems, since it removes the thermodynamic desirability of inter-diffusion. It is interesting to note that two systems, since it removes the thermodynamic desirability of inter-diffusion. The use of Sb as a surfactant shows no real benefit. Previous studies of Au/Cu multilayers using XRD and STM demonstrated the presence of large islands of Au when grown on Cu deposited on oxidised silicon substrates [19]. In that work the roughness of the surface comprising both interfacial roughness and variation in layer thickness was found to be low. In this present study, even less roughness is expected since a single crystal substrate has been used. It is interesting to note that the previous XRD work did not take into account inter-diffusion and strain, both of which are clearly important for this material combination.

This work highlights the importance of diffusion in metal-on-metal growth. In contrast to semiconductor-layered systems, the activation energy for diffusion in metal multilayer systems is typically 1–2 eV lower [10], leading to much greater room temperature diffusivity. For systems such as Au on Cu(111), the large lattice mismatch also provides a driving force for inter-diffusion which can be viewed as an energetically favourable way of reducing strain. Of course, as with semiconductor materials, lattice defects and the formation of islanded structures can also occur as evidenced by the low strain seen near the surface in Fig. 4. The presence of the additional stress relieving mechanism of inter-diffusion may make the growth of well-defined multilayers more difficult to achieve for metallic materials than for their semiconductor equivalents. One approach popular for producing well-ordered semiconductor hetero-structures is to ensure a high level of lattice matching between the substrate and grown layers and this may be even more important for metallic systems, since it removes the thermodynamic desirability of inter-diffusion. It is interesting to note that two systems that have exhibited good multilayer growth properties are: (a) Au/Fe using the (100) surface where very low lattice mismatch is seen; and (b) Co/Cu where inter-diffusion is limited by the low miscibility of these metals. From the data obtained, it is apparent that the observed reduction in twinning using a 0.2-ml Sb dose was simply an artefact of increased inter-diffusion. The only real effect of the Sb appears to be an increase in the perpendicular mobility of the Au and Cu. This effect is perhaps unexpected since part of the surfactant effect claimed for Sb in the homoepitaxial growth of Ag(111) is its ability to reduce the parallel mobility, thereby restricting island formation [9]. A definitive explanation of this phenomenon is not possible, but it may be that the surface-to-incoming atom exchange processes required to allow the Sb atoms to remain at the surface contribute to this effect, perhaps by initiating perpendicular movement of atoms. Clearly, whatever the mechanism is, it has been disrupted in the 0.5-ml Sb grown film and it is likely that this is caused by the presence of the stacking fault, since this represents the only major difference between the samples.

In addition, the use of Sb at either of the coverages employed gave no obvious improvement in the crystallinity of the surfactant grown films. Since the apparent reduction in twinning arises simply as a result of increased inter-diffusion, Sb has no beneficial effects on the growth of Au on Cu(111). Of course there may well be significant differences between this system and those where a surfactant has proved to be beneficial (e.g. Ag on Ag(111) [9] and Co on Cu(111) [3]). Investigation of a system where the benefits of a surfactant are well established using the MEIS technique would clearly be desirable.

5. Conclusions

MEIS has been used to analyse the composition and structure of Au-thin films grown on Cu(111). At room temperature significant inter-diffusion is seen and the grown layers exhibit twin fcc structure with a reasonable degree of crystallinity. Annealing to progressively higher temperatures encourages diffusion but leads to no apparent improvement in crystallinity. At the highest temperature (400°C) the Au dissolves into the Cu matrix with only a small enrichment left at the surface. The use of 0.5 ml of Sb gives no improvement in growth, with similar behaviour to a non-surfactant grown sample. The use of 0.2 ml of Sb does give an apparent reduction in fcc twin formation, but the composition data indicate that this may be an artefact of increased inter-diffusion. For Au layers grown on Cu(111) the use of Sb as a surfactant shows no real benefit.
Acknowledgements

EPSRC are thanked for providing access to the MEIS facility. The FOM institute (Amsterdam) and Paul Quinn (University of Warwick) are thanked for providing the VEGAS code and a user-friendly PC interface, respectively.

References