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Surface Morphology Changes During Pb Deposition on Cu(100):

Evidence for Surface Alloyed Cu(100)-c(2x2) Pb

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Abstract

Using Low Energy Electron Microscopy (LEEM), we have followed Cu(100) surface morphology changes during Pb deposition at different temperatures. Surface steps advance and 2-D islands nucleate and grow as deposited Pb first alloys, and then dealloys, on a 125°C Cu(100) surface. From LEEM images, we determine how much Cu is being displaced at each stage and find that the amount of material added to the top layer for a complete Pb/Cu(100) $c(4 \times 4)$ reconstruction (a surface alloy) is consistent with the expected $c(4 \times 4)$ Cu content of 0.5 monolayer. However, as the surface changes to the Pb/Cu(100) $c(2 \times 2)$ overlayer, we find that the displaced material from surface dealloying, 0.22ML, is more than a factor of two lower than expected based on a pure Pb $c(2 \times 2)$ overlayer. Further, we find that in the 70 to 130°C range the amount of Cu remaining in $c(2 \times 2)$ increases with increasing substrate temperature during the deposition, showing that surface Cu is alloyed with Pb in the $c(2 \times 2)$ structure at these temperatures. When holding the sample at 125°C, the transformation from the $c(2 \times 2)$ structure to the higher coverage $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ overlayer structure displaces more Cu, confirming the $c(2 \times 2)$ surface alloy model. We also find the $c(2 \times 2)$ surface has characteristically square 2-D islands with step edges parallel to the (100) type crystallographic directions, whereas the $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ structure has line-like features which run parallel to the dislocation double rows of this surface's atomic structure and which expand into 2-D islands upon coarsening.

Keywords: Low Energy Electron Microscopy, Growth, Nucleation, Surface reconstructions and relaxations, Copper, Lead, Low index single crystal surfaces

Introduction

Pb on Cu(100) is a lattice-mismatched system with intriguing physical properties. Previous investigations by low energy electron diffraction (LEED) [1-10], He atom scattering [11-13], scanning tunneling microscopy (STM) [14,15] and Rutherford backscattering [16] have established that Pb grows on Cu(100) in a prototypical Stranski-Krastanov mode with three well-defined ordered structures at submonolayer coverages. Beyond a critical coverage (0.6 monolayers), additional deposition of Pb results in three-dimensional island growth. Despite the fact that Pb is essentially immiscible in bulk Cu, the first ordered structure that appears upon deposition of Pb on Cu(100) is a surface alloy. Additional Pb deposition causes this structure to dealloy and results in the formation of Pb surface overlayers. Although a substantial body of literature has been written on the Pb locations within these surface structures, there is comparatively little characterization of the system's surface morphology, identification of the surface Cu content, examination of the alloying and dealloying process, or determination of temperature effects on the deposition process. To address these issues, we have used the real-time, real-space imaging and variable sample temperature capabilities of the low energy electron microscope (LEEM) to characterize the growth of the different overlayer phases.

Background on the Pb/Cu(100) System

The first comprehensive UHV surface science study of the Pb on Cu(100) overlayer system was reported by Henrion and Rhead in 1972 [1]. Their LEED observations, made during Pb deposition at room temperature, identified three distinct overlayer phases as a function of increasing Pb coverage. From that and several subsequent investigations, atomic structures of the overlayers were identified and are shown in Fig 1. Initially Pb substitutes into Cu surface sites in a one to one ratio [14] leading to a less intense and less sharp 1×1 LEED pattern than that of clean Cu(100). The lowest coverage ordered phase produces a $c(4\times 4)$ LEED pattern and corresponds to a Pb coverage of 0.375 monolayer. Earlier LEED studies [2] interpreted this overlayer as chains of Pb on top of the Cu(100) substrate. A more recent LEED I-V analysis by Gauthier et al. [9], including new information from STM investigations by Nagl et al. [14] and Roberts et al. [15], provides compelling evidence that the $c(4\times 4)$ phase is not an overlayer phase, but a surface alloy consisting of Pb chains within the first layer of Cu (Fig. 1b) and where three Pb atoms have substituted for four of the eight $c(4\times 4)$ Cu atoms. Interestingly, the addition of more Pb to the $c(4\times 4)$ phase at or below room temperature causes the topmost surface layer to de-alloy [15] and produces a $c(2\times 2)$ structure at 0.5 ML of Pb. LEED I-V analysis by Hösler et al. [4,6], low energy ion scattering (LEIS) studies by Platzgrummer et al. [12], and STM analysis by Nagl et al. [14] and Roberts et al. [15] (all conducted at or below room temperature) show that the $c(2\times 2)$ phase is essentially an overlayer structure with Pb atoms residing on top of the Cu(100) surface layer in every other four-fold hollow site (Fig. 1c). In this conversion the addition of one more Pb atom to the $c(4\times 4)$ unit cell,

plus the rearrangement of two of the Pb atoms already there, leads to the removal of the remaining four Cu atoms. Further Pb deposition causes the $c(2 \times 2)$ overlayer to disorder through the introduction of surface dislocation lines [4,7,14], resulting in initial splitting of the 2×2 spots and, eventually, a diffuse (1×1) LEED pattern. Near 0.6 ML a third ordered overlayer structure appears, with a $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ diffraction pattern. LEED I-V analysis by Hösler and Moritz identified this structure as a periodically dislocated $c(2 \times 2)$ overlayer [7]. Pb atoms still reside in the four-fold hollows, but the structure is compressed to allow for the extra coverage of Pb atoms (Fig. 1d). Sanchez and Ferrer deduced a similar structure using thermal-energy atom scattering, except that two Pb atoms of the unit cell protrude higher than the other Pb atoms [11]. Once the $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ structure has been achieved, further deposition of Pb results in the growth of three-dimensional Pb islands.

Our current body of knowledge raises an important question: How do Cu atoms get back into a complete Cu layer during conversion from the $c(4 \times 4)$ to the $c(2 \times 2)$ phase? This is one of the questions we have addressed in this investigation.

Experimental Techniques and Procedures

The low energy electron microscope used in this study is a commercial system based on the design of Bauer [17] and modified to include two additional ultra-high vacuum chambers: one for Auger electron spectroscopy and a second for Ne ion sputtering. The sample was a Cu single crystal with the (100) surface polished to within 0.1° . Producing clean Cu(100) surfaces proved to be problematic. Surfaces prepared using the published procedure of repeated sputtering and annealing cycles appeared to be clean by LEED and

Auger electron spectroscopy standards, but were obviously not clean when viewed in LEEM. We found that clean surfaces could be reproducibly achieved by heating the sample to 800°C (where some sublimation occurs) in a 3% hydrogen/argon mixture outside the vacuum chamber (to remove sulfur from the near-surface region). This was followed by high-temperature Ne ion sputtering in the sample preparation chamber. During sputtering, the Ne pressure was 5×10^{-5} Torr, the bombarding voltage was 1 kV, and the sample temperature was held near 800°C. After sputtering, the sample was slowly cooled to room temperature and transferred to the LEEM main chamber without exposure to air.

Pb was deposited from a heated PBN crucible holding 99.999% pure Pb wire. Typically the deposition rate started off very low but settled at 0.043 ± 0.008 monolayers per minute after five to seven minutes for the region of the sample opposite the objective pole piece. The line-of-sight from the doser to the sample was 80° off normal, which leads to a non-uniform deposition across the sample. This non-uniform deposition did not affect the results significantly because the region examined was quite small (a few microns) and the Pb coverage could be inferred indirectly from the LEED pattern. (We noted that the nonuniform lead coating significantly altered the alignment of the instrument during a long deposition or if one moves from one sample region to another.) The background pressure in the system was typically in the low to mid 10^{-10} Torr range during Pb deposition. When the deposition source was turned off, the background pressure fell into the mid 10^{-11} Torr range.

Several imaging modes of the LEEM were used during the course of the investigation. These included LEED, bright-field imaging, and dark-field imaging. The

procedures for obtaining these imaging modes can be found in papers by Bauer and Tromp [17,18]. LEED was used to identify the overlayer structure (and thus the coverage) as Pb was deposited on the surface. Bright-field imaging (obtained by selecting the (0,0) LEED beam) was used to follow the growth of surface reconstruction domains and islands during deposition. Dark-field imaging (obtained by selecting the appropriate non-integral-order LEED beam) verified the location and type of surface domains and found the orientational relationships between the different surface morphology features and the LEED pattern.

As will be discussed in more detail below, in order to obtain quantitative information about the displacement of surface Cu as the Pb deposition proceeds, the location changes of surface steps and the areas of new 2-D islands were measured. The reproducibility of these measurements among different deposition runs or from one surface region to another ranged between 3% and 8%. Other errors such as uncorrected drift or location inaccuracies from imaging conditions were no more than 5%. The temperatures quoted in this study were measured from a thermocouple mounted near the edge of the quarter inch diameter sample. We estimate that the actual sample surface temperature is typically 10° to 20° higher than this reading.

Results and Discussion

LEED/Auger observations of Pb deposition at room temperature and 125°C.

A sequence of LEED patterns obtained during deposition of Pb at 125°C is shown in Fig. 2. The same sequence is observed in a room temperature deposition and is consistent with the previous LEED studies of Pb on Cu(100) mentioned above. Upon

initial Pb deposition, the (1x1) diffraction spots of the clean surface become dimmer. The first ordered structure to appear is c(4x4), corresponding to the surface alloy shown in Fig. 1b. With additional Pb deposition, c(2x2) spots appear. These spots briefly coexist with the c(4x4) pattern at 125°C. Eventually, the (4x4) spots disappear and the pattern is entirely c(2x2), corresponding to the overlayer structure shown in Fig. 1c. Additional Pb causes the c(2x2) pattern to disappear leaving a diffuse (1x1) pattern. The final pattern to appear is $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ corresponding to the compressed overlayer structure shown in Fig. 1d.

We checked the cleanliness of the Pb-covered surfaces by interrupting deposition at coverages corresponding to well-defined LEED patterns and examining the surfaces with Auger Electron Spectroscopy (AES). Fig. 3 shows AES spectra from c(4x4) and $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ surfaces. Signals corresponding to common impurities such as oxygen, carbon, and sulfur are below the AES detection limit.

We followed room temperature deposition of Pb on Cu(100) with both mirror microscopy and bright field imaging. The images show that the surface becomes more textured during the deposition, but dramatic changes corresponding to the growth of the different phases are not observed. This is because relevant surface features, typically 10 nm [15], are just at the resolution limit of the instrument. The situation is quite different when the deposition was carried out at higher temperatures (50-150°C). Here, the effects of surface alloying, de-alloying and overlayer compression are clearly evident and will be discussed next.

Initial Deposition of Pb on Clean Cu(100), Random Substitution

A sequence of bright-field LEEM images taken during Pb deposition onto a clean Cu(100) surface is shown in Fig. 4. The sample temperature during deposition is 138°C. The region imaged in Fig. 4 is free of steps, with the exception of the single-atom-high step appearing at the bottom of the image. The cusp-like shape of the step is due to step pinning which occurred during the sublimation stage of cleaning the surface. (During the course of deposition, the image becomes progressively darker. The loss of intensity is compensated for by increasing the gain on the imaging detector and thus is not apparent in the images shown in Fig. 4.) The LEED pattern during the entire growth sequence shown in Fig. 4 remains (1x1). This is ascertained by periodically switching to LEED mode while the islands grow.

It is apparent from Fig. 4 that Pb deposition causes the step to move outward and induces the nucleation and growth of circular features on the terrace. Similar, but much smaller, features were observed in room temperature STM studies by Nagl et al [14], who determined the step height to be one Cu atomic layer high and were interpreted to be predominantly copper islands (presumably with some Pb substitution), an interpretation supported by Roberts et al. [15]. Based on our observations, we also interpret the circular features seen in Fig. 4 as predominantly Cu, and not Pb, islands. In further support, we have found that Pb islands produce entirely differently images in the LEEM. In a separate experiment we grew Pb islands on clean Cu(100) keeping the sample about 30 degrees below room temperature during deposition. In that case, the Pb islands were uniformly dark, whereas in Fig. 4, only the edges of the islands are dark and these edges have the same appearance as the step on the Cu terrace. The generation of Cu atoms from Pb incorporation is also consistent with the motion of the step in Fig. 4. Even

before the Cu islands nucleate, the step moves outward. We conclude that the step motion is due to attachment of Cu adatoms released by Pb incorporation, as is illustrated in Figure 5. As the concentration of Cu increased, Cu islands (presumably with some substituted Pb) nucleate and grow on the terrace. Excess Cu can then become incorporated at the step or the edge of the islands. This competition for adatoms explains the denuded zone (region free of islands) near the step. Through careful measurement of the advance of steps and the area of new islands, we now have a means of tracking Cu displacement as the Pb deposition proceeds.

The c(4x4) phase: Surface alloying

The c(4x4) surface nucleates when the material added to the top layer is between 0.23 and 0.40 monolayer (ML). The added material is the sum of the new 2-D island area and the new area created by the advancing step. The coverage range prior to the onset of the c(4x4) phase reflects dependence on growth temperature and step concentration in the region (more steps and higher temperatures lead to earlier nucleation). We followed the growth of the c(4x4) structure in bright-field LEEM mode by using appropriate conditions of electron energy and objective focus. A sequence of LEEM images from a different growth sequence showing the transformation of the surface to the complete c(4x4) structure is shown in Fig. 6. The dark regions of the image correspond to the c(4x4) structure, as confirmed by dark-field imaging on one of the non-integral c(4x4) LEED spots. The images show that the c(4x4) structure nucleates at the upper side of steps and proceeds to grow away from the steps in both directions. Whether nucleation at the steps is due to an increased concentration of Pb at these locations or a smaller kinetic

barrier for conversion to the ordered structure at the steps could not be determined from these experiments.

The changes in 2-D island coverage from clean Cu(100) to a surface completely covered with c(4x4) range between 0.50 and 0.56 ML, in good agreement with the LEED I-V model obtained by Gauthier, Moritz, and Hösler [9]. That is, we expect half of an initially flat Cu(100) surface to be displaced upward by one Cu(100) step height because of the Cu displacement caused by Pb. The island coverage beyond 0.5 ML could be attributed to measurement errors or perhaps to extra copper displaced from the numerous surface domain boundaries seen by STM [14].

The c(2x2) phase: Partial Surface De-alloying

As noted above, the addition of more Pb to the alloyed c(4x4) surface causes it to transform to the c(2x2) structure. To follow the time evolution of this process, we first produced a c(4x4) surface in the manner described in the previous section. We then coarsened away most of the 2-D island structure by heating to a temperature of 245°C for about 15 minutes, similar to the approach of Ref. 15. An example of such a surface is shown in Fig. 7a. (Initially we proceeded without coarsening away the original islands, but subsequent Pb deposition produced more complex, island on island morphologies whose interpretations were more uncertain.) The micrographs shown in Fig. 7 are bright-field LEEM images with the electron energy adjusted to maximize intensity from c(2x2) regions (1.0 eV). In Fig. 7a there are two islands remaining from the coarsening near the center and steps near the top and bottom of the image. Figs. 7b through d show the same surface during Pb deposition with the sample at a temperature of 123°C. Like the c(4x4)

phase, the brighter $c(2 \times 2)$ phase nucleates at step edges and grows across the terraces. In Figures 4 and 6 the steps and islands have rounded features, but in Figure 7 the majority of surface step edges align with the $[100]$ type bulk crystallographic directions leading to more or less square shaped islands as the $c(2 \times 2)$ domains nucleate and grow. The $[100]$ type directions are the directions of close packing of the Pb and adjacent Cu atoms along the step. A more typical surface, prepared by growing Pb onto flat $c(4 \times 4)$ at 57°C and then coarsening briefly at 100°C , is shown in Fig 7f to highlight the square nature of the step edges.

From Fig. 7 it is obvious that the original islands increase in size and that the steps advance as the Pb deposition proceeds. A plausible mechanism for this gradual conversion is presented in Figure 8. The process involves taking Cu atoms, which are displaced by deposited Pb, and moving them to the step edges. The Pb atoms at the step edge move onto the upper and lower terraces to form the $c(2 \times 2)$ overlayer structure. As more Cu is transported to the steps, the $c(2 \times 2)$ structure expands outward while the step also advances. This mechanism is consistent with the observation that there is no apparent step contrast at $c(4 \times 4)$ / $c(2 \times 2)$ phase boundaries.

Measurements of the coverage of the top layer added material in going from a surface completely covered with $c(4 \times 4)$ and held at 125° to a surface completely covered with $c(2 \times 2)$ yields 0.22 ML, as is listed in Table 1. This coverage change initially seems quite at odds with the LEED I-V model of $c(2 \times 2)$ surface obtained by Moritz, and Hösler [4,6] and the room temperature dealloying study of Roberts et al. [15] who respectively predicted and measured an island coverage change of 0.50 ML (illustrated in Figure 7e). Even more perplexing, Figure 9 shows that the amount of material expelled from the

original surface decreases (roughly linearly) with increasing substrate temperature during the deposition. We can explain both of these observations by proposing that, for Pb depositions between 70 and 130°C, c(2x2) remains a Pb / Cu surface alloy with between 0.15 ML and 0.30 ML Cu in the structure, respectively. The most likely sites for this Cu would be randomly distributed in surface four-fold hollow sites between Pb atoms, thermally substituted into Pb c(2x2) sites, or both. The measured c(2x2) order to disorder transition begins near 100°C and is completed at about 240°C [19]. Hence the thermal substitution possibility arises from the fact that c(2x2) is partially disordered at 125°C. If one considers a simple model with Cu only in the sites between Pb atoms (illustrated in Fig 10a and 10b), then Fig 9's temperature dependence can be interpreted as a solubility effect: the higher the temperature, the more Cu stays in the surface layer. In terms of the atom substitutions and removals discussed in the literature background section above, our result means that (at these temperatures) the fourth Pb atom per c(4x4) unit cell deposited in this transition leads to roughly two of the four remaining surface alloy Cu atoms being removed from the cell, versus all four as the literature suggests.

Another interpretation of Fig 9 is that, since at higher temperatures surface copper is more mobile, it can move more quickly to step bunches (microns away) where it cannot be readily measured. While we cannot completely rule out this possibility, preliminary Ostwald ripening measurements [19] show that in the 70 to 130°C temperature range, surface diffusion requires at least 30 to 40 minutes to transport the "missing" amount copper over c(4x4) or c(2x2) while the deposition times were 10 minutes or less.

One may be asked if the surface site between c(2x2) Pb atoms is large enough to accommodate a Cu atom. The interatomic distance between top layer, nearest neighbor

Cu and Pb atoms is $2.84\text{\AA}$ in $c(4\times 4)$ [9]. From the model of Hösler and Moritz [6] we calculate the comparable spacing would be $2.61\text{\AA}$ in an unrelaxed $c(2\times 2)$ alloyed surface. But given the rather large relaxations of Pb from four fold hollow sites seen in $c(4\times 4)$ [9] we expect relaxation to play a large role in an alloyed $c(2\times 2)$ surface.

Another question one could raise about the surface alloy $c(2\times 2)$ model is that no evidence of surface Cu atoms exists in the very careful LEED I-V analyses carried out by Hösler and Moritz [6]. If the Cu is distributed in a truly random manner, we would only expect a stronger LEED background signal, or if only partially ordered, then perhaps faint streaks. We have often seen faint LEED streaks if $c(2\times 2)$ covered, as-deposited samples are allowed to cool below 50°C . A more important consideration is that the surface analyzed in the LEED I-V study was prepared by depositing excess Pb and flashing the surface repeatedly to 425°C until the $c(2\times 2)$ pattern was its strongest. In trying to reproduce this sample preparation procedure, we found that LEED patterns taken at room temperature of 425°C flashed $c(2\times 2)$ consistently had two faint, elongated spots with about equal spacing between each other and the (0,0) and $c(2\times 2)$ type beams. These faint spots could be due to Cu in the $c(2\times 2)$ overlayer or to a variety of surface morphology features such as step bunches. We should also note that STM images showed no evidence for Cu in $c(2\times 2)$ [14] but then published images of $c(4\times 4)$ do not clearly show the presumably more visible copper rows of $c(4\times 4)$ [14, 15]. Roberts and coworkers [15] saw complete surface dealloying in an STM study where 0.175ML Pb was deposited at -73°C on coarsened $c(4\times 4)$, followed by very slow heating to room temperature. This result turns out to be consistent with the data in Fig. 9 which, if extrapolated, crosses 0.5ML (full dealloying) between -73°C and room temperature.

The $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ Phase: Continued Surface De-alloying

The growth of the $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ surface at 125°C from a 2-D island coarsened $c(2 \times 2)$ surface is shown in Fig. 11. From Figs. 11a and 11b we see that, as Pb is deposited and the surface proceeds through the disordered structure between 0.5 and 0.6 ML, the large island gradually increases in size and three new 2-D islands nucleate, together corresponding to 0.13 ML growth (for this experiment) when the $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ surface is completed. This further supports the partially alloyed $c(2 \times 2)$ model since one would not expect an island coverage change from the literature models for $c(2 \times 2)$ and $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ since neither model has surface Cu. But if one extends an alloyed $c(2 \times 2)$ model to $c(5\sqrt{2} \times \sqrt{2})R45^\circ$, one would expect at least 0.05 ML of copper to dealloy in the $c(2 \times 2)$ to $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ transition since the dislocation lines put Pb into one tenth of the sites originally available for the surface alloyed Cu in $c(2 \times 2)$.

In Figure 11c we see the bright $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ domains nucleating at steps and growing outward on the upper and lower terrace surfaces. Figure 11d shows the conucleation of line like features along with new $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ domains in the flat regions as well as at the corners of the square 2-D islands. To the best of our knowledge this is the first report of these features. At this temperature the line features grow linearly at an average rate of 19.6 ± 13.6 nm per sec. (much quicker than the 2D islands grow) until they either run into a $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ domain or until the surface is completely covered with $c(5\sqrt{2} \times \sqrt{2})R45^\circ$. Preliminary experiments varying the temperature at which growth from $c(2 \times 2)$ to $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ occurs suggest an Arrhenius type relationship between the line feature growth rate and temperature, but this is the

subject of another paper [19]. Not shown in Figure 11 are “secondary” nucleation events that occur between Figures 11e and 11f as the Pb coverage approaches 0.6 ML. These secondary nucleations are needed to fill in the $c(5\sqrt{2}\times\sqrt{2})R45^\circ$ surface since there seems to be a limited extent to which the $c(5\sqrt{2}\times\sqrt{2})R45^\circ$ domains can grow perpendicular to the line features at a given temperature. The secondary nucleations yield shorter line features, as is apparent in the length distribution histograms shown in Figure 11g. The average length of the line features in Figure 11f is 0.19 ± 0.02 microns and their density is 50.1 ± 3.3 per micron squared (when away from the “denuded” zones associated with steps). The line feature density varies from 160 per micron squared at a deposition substrate temperature of 67°C to 17.4 per micron squared at a substrate temperature of 150°C . (The features are smaller than the resolution of the instrument when the substrate temperature is below 60°C .) Figure 11h is a bright field image taken with slightly misaligned illumination, which reveals the two different $c(5\sqrt{2}\times\sqrt{2})R45^\circ$ domain orientations as different gray levels. Note that the vertical lines are always associated with one domain orientation while horizontal lines are always associated with the other. Subsequent examination of these relationships in dark field images found that the line features are always perpendicular to the primitive $c(5\sqrt{2}\times\sqrt{2})R45^\circ$ diffraction spot used to image that line features’ associated $c(5\sqrt{2}\times\sqrt{2})R45^\circ$ domains. This means the surface dislocation double rows of Pb in $c(5\sqrt{2}\times\sqrt{2})R45^\circ$ (Fig 1c) run parallel to the adjacent line features and the anisotropically faster $c(5\sqrt{2}\times\sqrt{2})R45^\circ$ growth direction also runs parallel to the line features. Indeed, careful comparison of Figures 11d, e, and f shows that the bright $c(5\sqrt{2}\times\sqrt{2})R45^\circ$ domains tend to grow faster when following the line features than when they grow outward away from the lines.

Upon mild heating (150°C) the line features coarsen as shown in Fig. 12. All of the lines which had nucleated at corners of the square islands coarsened into the square islands (arrowed in Fig. 12). This fact, plus the similar coarsening behavior and coarsening temperatures (125°C to 175°C) of the line features and the $c(2 \times 2)$ square islands [19], lead us to postulate that the line features are essentially long, narrow versions of the square 2-D islands associated with the $c(2 \times 2)$ surface. That is, the line features are very likely single step high regions of copper covered with the prevailing $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction, copper likely expelled from the $c(2 \times 2)$ surface alloy. From this assumption and measurements of Figure 12b we conclude that the line features had a surface coverage of about 0.11 monolayers before coarsening. This leads to an estimation of the average line feature width of between 8 and 12 nm depending on the initial line feature density. Taking this 0.11 ML into consideration, plus the 0.10 ML average growth of the 2D islands in the $c(2 \times 2)$ to $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ transition, we arrive at total cumulative displacement of Cu from clean Cu(100) to complete $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ of 0.97 ± 0.04 ML.

Conclusion

The technique of measuring surface step motion and 2D island growth over micron sized areas in LEEM allowed us to track the substrate species in the Pb on Cu(100) surface reconstructions and find major inconsistencies in the surface dealloying of Cu over a broad temperature range. As mentioned above and listed in Table 1, the interpretation of the $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ line features as copper islands covered with $c(5\sqrt{2} \times \sqrt{2})R45^\circ$, when combined with the other Pb induced Cu displacements, leads to an

average cumulative Cu displacement of 0.97 ± 0.04 ML in going from the clean Cu(100) surface to a complete $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ surface at 125°C . This total cumulative displacement occurs in the following stages: 0.53 ML upon completion of $c(4 \times 4)$, 0.76 ML upon completion of $c(2 \times 2)$, and 0.97 ML upon completion of $c(5\sqrt{2} \times \sqrt{2})R45^\circ$. The literature based models of this system would predict 0.50 ML upon completion of $c(4 \times 4)$, 1.0 ML upon completion of $c(2 \times 2)$, and 1.0 ML upon completion of $c(5\sqrt{2} \times \sqrt{2})R45^\circ$. Our simple surface alloyed $c(2 \times 2)$ model predicts 0.50 ML upon completion of $c(4 \times 4)$, 0.75 ML upon completion of $c(2 \times 2)$, and 0.80 ML upon completion of $c(5\sqrt{2} \times \sqrt{2})R45^\circ$. This simple model is based on random occupancy of about half of the “between Pb” Cu surface sites and ignores thermal $c(2 \times 2)$ Pb / Cu site substitution. It correctly predicts some dealloying in the transition from $c(2 \times 2)$ to $c(5\sqrt{2} \times \sqrt{2})R45^\circ$, but clearly not enough. In addition to ignoring thermal site substitution this model doesn’t compensate for the extra compression on the surface Cu sites from the Pb in the $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ dislocation rows. That is, while the nearest neighbor Pb to surface Cu spacing is $2.84\text{\AA}$ in $c(4 \times 4)$ and would be $2.61\text{\AA}$ in unrelaxed, alloyed $c(2 \times 2)$, it would be $2.48\text{\AA}$ in unrelaxed alloyed $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ [7]. Clearly more work is required, both experimentally and through simulations, to determine the thermal behavior of $c(2 \times 2)$ and the dynamics of the $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ domain and line feature interactions and interdependencies. By studying the amount of Cu which dealloys in the $c(4 \times 4)$ to $c(2 \times 2)$ transition as a function of temperature, we have found solubility like behavior of Cu in the $c(2 \times 2)$ surface alloy.

In addition to elucidating the copper content of the higher coverage Pb induced Cu(100) surface reconstructions, we have determined the $[100]$ type surface step orientations of $c(2 \times 2)$ associated square 2-D islands and for the first time imaged and

determined the orientation and likely nature of long, narrow 2-D islands associated with the $c(5\sqrt{2}\times\sqrt{2})R45^\circ$ reconstruction.

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References

- [1] J. Henrion, and G.E. Rhead, Surf. Sci. 29 (1972) 20.
- [2] A. Sepulveda, and G.E. Rhead, Surf. Sci. 66 (1977) 436.
- [3] M.-G. Barthés, and G.E. Rhead, Surf. Sci. 80 (1979) 421.
- [4] W. Höslér and W. Moritz, Surf. Sci. 117 (1982) 196.
- [5] C. Argile, M.-G. Barthés-Labrousse, and G.E. Rhead, Surf. Sci. 138 (1984) 181.
- [6] W. Höslér, W. Moritz, E. Tamura, and R. Feder, Surf. Sci. 171 (1986) 55.
- [7] W. Höslér and W. Moritz, Surf. Sci. 175 (1986) 63.
- [8] W. Li and G. Vidali, Surf. Sci. 287 (1993) 955.
- [9] Y. Gauthier, W. Moritz, and W. Höslér, Surf. Sci. 345 (1996) 53.
- [10] F. Bocquet and S. Gauthier, Surf. Sci. 416 (1998) 1.
- [11] A. Sánchez and S. Ferrer, Phys. Rev. B 39 (1989) 5778.
- [12] S. Robert, C. Cohen, A.L. L'Hoir, J. Moulin, D. Schmaus, and M.G. Barthes-Labrousse, Surf. Sci. 365 (1996) 285.
- [13] E. Platzgummer, M. Borrell, C. Nagl, M. Schmid, and P. Varga, Surf. Sci. 412

(1998) 202.

[14] C. Nagl, E. Platzgummer, O. Haller, M. Schmid, and P. Varga, Surf. Sci. 331 (1995) 831.

[15] S. Robert, S. Gauthier, F. Bocquet, S. Rousset, J.L. Duvault, and J. Klein, Surf. Sci. 350 (1996) 136.

[16] C. Cohen, Y. Girard, P. Leroux-Hugon, A.L. L'Hoir, J. Moulin, and D. Schmaus, Europhys. Lett. 24 (1993) 767.

[17] E. Bauer, Rep. Prog. Phys. 57 (1994) 895.

[18] R.M. Tromp and M.C. Reuter, Ultramic. 36 (1991) 99.

[19] R. Plass and G. L. Kellogg, in preparation.

Figure Captions

Figure 1a- Top view schematic of a clean Cu(100). First and second layer copper atoms are shown as darker and lighter circles, respectively. A surface step (dashed line) is shown running vertically near the center. 1b- Top view schematic of the c(4x4) structure [9]. Pb atoms are the darkest circles. 1c- Literature model top view schematic of the c(2x2) surface [6] with an antiphase boundary running horizontally through the center. 1d- Top view schematic of the literature model for the $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ surface [7].

Figure 2. Low Energy Electron Diffraction (LEED) patterns showing the different phases of Pb deposited on Cu(100) held at 125°C. 2a- (1x1) clean Cu(100), 2b- c(4x4) at 0.375 ML Pb coverage, 2c- c(2x2) at 0.50 ML Pb coverage, and 2d- $c(5\sqrt{2} \times \sqrt{2})R45^\circ$ at 0.60 ML Pb coverage.

Figure 3. Auger spectra of Cu(100) with 0.375 (dashed) and 0.60 ML (solid) nominal Pb coverages

Figure 4. Low Energy Electron Microscopy (LEEM) bright field images of the nucleation (4a) and growth (4b through d) of single atom high copper islands (with some random Pb substitution) at 4a- 0.05ML Pb coverage, 4b- 0.15ML Pb coverage, 4c- 0.23ML Pb coverage, and 4d- 0.28ML Pb coverage. A monoatomic high step is seen at the bottom of the image. The sample temperature was 138°C

Figure 5. Side view schematics illustrating how step motion can be associated with Pb incorporation into a clean Cu(100) surface.

Figure 6. Nucleation and growth of 2-D copper islands up to complete c(4x4). 4a- LEEM bright field image after 0.04 ML of deposited Pb, a double height step is seen running near the center of the image (arrowed). 4b- image taken after 0.17 ML Pb coverage. Note that from shapes caused by the pinning sites of the double step we can determine that the left portion of the image is lower than the rest. 4c- After 0.28 ML Pb coverage and the nucleation of darker c(4x4) domains at the step and island edges, note that the islands have roughened and continued to grow. 4d- The completed c(4x4) surface. The sample temperature was 125°C

Figure 7a- LEEM bright field image of a $c(4 \times 4)$ surface where 2-D islands have been almost entirely coarsened away. 7b and 7c- growth of $c(2 \times 2)$ domains (bright regions) and 2-D islands at 0.02 and 0.09 ML Pb deposited, respectively. 7d- Surface covered completely with $c(2 \times 2)$. 7e- Illustration of the likely step and island locations of 7d if the $c(2 \times 2)$ surface had fully dealloyed. 7f- “Typical” $c(2 \times 2)$ surface 2-D islands from a sample where $c(2 \times 2)$ was grown at 57°C and coarsened briefly at 100°C showing typical square 2-D islands (this image has a field of view of $1.5\ \mu\text{m}$, the others are $2.5\ \mu\text{m}$).

Figure 8a- Side view cut away schematic (looking down a (110) type direction parallel to the alternating $c(4 \times 4)$ Pb and Cu surface rows) of a step region covered with $c(4 \times 4)$. 8b and 8c- illustration of the growth of $c(2 \times 2)$ domains on the upper (8b) and lower (8c) surfaces of the step showing how the step might move under the growing $c(2 \times 2)$ domains in agreement with Figure 7.

Figure 9. Change of 2-D island feature coverage versus substrate temperature in going from 2-D island coarsened, complete $c(4 \times 4)$ to complete $c(2 \times 2)$. Change of 2-D island features includes growth of preexisting 2-D islands, advancement of steps, and nucleation and growth of new 2-D islands.

Figure 10. Top view schematics of the Pb on Cu(100) surface reconstructions shown in Figure 1c and 1d, but illustrating the a simple random site copper alloy version of $c(2 \times 2)$ where roughly half of the “between Pb” four fold hollow sites are randomly occupied with copper (medium gray circles). (This model does not include thermally induced Cu

substitution of Pb that is also likely to be occurring to a small extent.) The dark lines in 10a show the orientations of the steps bounding the square 2-D islands seen in Figure 7b through 7f. The dark line in 10b shows the direction of the long axis of the line features of $c(5\sqrt{2}\times\sqrt{2})R45^\circ$ seen in Figure 11.

Figure 11a- LEEM bright field image of a $c(2\times 2)$ surface after square 2-D island coarsening. Figures 11b, 11c, 11d, 11e, and 11f are images taken after 0.050, 0.057, 0.065, 0.072 and 0.10 ML Pb deposition respectively. The brighter regions nucleating in 11c are $c(5\sqrt{2}\times\sqrt{2})R45^\circ$ domains. 11d shows the nucleation of the line like features discussed in the text. Figure 11g is a histogram of line feature lengths of 11e (dashed) and 11f (solid) which shows a marked increase in the number of shorter line features near the completion of a full $c(5\sqrt{2}\times\sqrt{2})R45^\circ$ surface. Figure 11h is a bright field image of the surface after Pb deposition with slightly misaligned illumination. This reveals which regions have orientationally different $c(5\sqrt{2}\times\sqrt{2})R45^\circ$ domain structures. Note the marked correlation between feature orientation and the underlying domain contrast level, including the steps at the edge of the central terrace. Substrate temperature during the deposition was 125°C

Figure 12 Coarsening of the $c(5\sqrt{2}\times\sqrt{2})R45^\circ$ line features at $T=150^\circ\text{C}$. 12a is a LEEM bright field image of the as deposited surface using slightly off axis illumination to reveal the $c(5\sqrt{2}\times\sqrt{2})R45^\circ$ domain structure. 12b, 12c, and 12d are taken after 30, 100 and 320 seconds, respectively using the same, slightly misaligned imaging conditions.

Table 1 Average and cumulative growth of 2-D islands and advancement of steps upon completion of the various Pb induced Cu(100) surface reconstructions at a substrate temperature of 125°C. The “#M” column lists the number of measurements, the sum column lists the cumulative island and step growth and the comparable theoretical column values are based on our simple model (discussed in the text) and the literature models. S.D. is the standard deviation of multiple measurements, sum S.D.s were added in quadrature.

	# M	Average	S.D.	Sum	S.D.	New Model	Lit. Model
Clean copper to comp. of 4x4	3	0.528	0.025			0.50	0.50
From 4x4 to completion of 2x2	3	0.231	0.014	0.759	0.029	0.75	1.00
From 2x2 to completion of 5x2	4	0.094	0.024	0.853	0.038	0.80	1.00
Additional coverage from lines	2	0.113	0.020	0.966	0.040

(a)

(b)

(c)

(d)

Fig. 3
page

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