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The Relationship between the Growth Shape of Three-Dimensional Pb Islands on Cu(100) and the Domain Orientation of the Underlying c(5√2x√2)R45° Structure

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Abstract

We use low energy electron microscopy to identify a correlation between the growth shape of three-dimensional Pb islands on Cu(100) and the domain structure of the underlying Pb overlayer. Deposition of 0.6 monolayer Pb on Cu(100) produces a compressed c(2x2) overlayer, designated c(5√2x√2)R45°, with periodic rows of anti-phase boundaries. We find that heating the surface to temperatures above 100° C coarsens the orientational domains of this structure to sizes that are easily resolved in the low energy electron microscope. Three-dimensional Pb islands, grown on the coarsened domains, are found to be asymmetric with orientations that correlate with the domain structure. Once nucleated with a preferred growth orientation, islands continue to grow with the same preferred orientation, even across domain boundaries.

Keywords: Low Energy Electron Microscopy (LEEM); Low Energy Electron Diffraction (LEED); Surface structure, morphology, roughness, and topography; Epitaxy, Lead, Copper, Low-index single-crystal surfaces

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The self-assembly of individual atoms or molecules into structures of nanometer dimensions is receiving considerable interest as a potential method for producing "engineered" materials with new or vastly different properties. A fundamental understanding of self-assembly at this length scale is a significant challenge because the interactions that lead to nanostructure formation typically involve an interplay between the kinetic behavior of individual atoms and the thermodynamic properties of surfaces and interfaces. The formation of three-dimensional (3-D) islands during heteroepitaxial growth on single-crystal surfaces is recognized as a well-controlled, model process to investigate the fundamental interactions underlying surface self-assembly at the nanometer scale. Extensive research into heteroepitaxial growth on semiconductor surfaces, for example, has provided useful insights into the spontaneous formation of "quantum dots" with potentially interesting device applications. In metal-on-metal epitaxy there are also many systems in which lattice mismatch and/or cohesive energy differences lead to 3-D island growth. Although the metal-on-metal systems that exhibit this behavior can be identified by standard surface techniques, the underlying physics responsible for the observed behavior is not well understood. In this investigation, we explore an important aspect of 3-D island growth on metals; namely, the relationship between the atomic structure of the underlying substrate and the morphology of the islands.

Our investigation is made possible by the unique attributes of the low energy electron microscope (LEEM) [1]. The LEEM is both a direct-space imaging technique with a spatial resolution of 7nm as well as an electron diffraction technique. As such, the LEEM can simultaneously view the shape of 3-D objects and identify the domain structure of the underlying substrate. The instrument is also designed for ultrahigh vacuum surface studies. This combination of capabilities allows us to produce a well-defined, two-dimensional (2-D) metal overlayer on a single-crystal substrate, characterize the domain structure of the overlayer, grow 3-D islands, and determine the relationship between the domain orientation and the 3-D island shape.

The system investigated in this study is Pb on Cu(100). Previous investigations by low energy electron diffraction (LEED) [2-7], He atom scattering [8-11], and scanning tunneling microscopy (STM) [12, 13] have established that Pb grows on Cu(100) in the Stranski-Krastanov mode with three well-defined ordered structures at coverages in the submonolayer range. The three surfaces phases are designated c(4x4), c(2x2), and c(5√2x√2)R45°, which appear at coverages of 3/8, 1/2, and 6/10 monolayer, respectively. At coverages beyond 6/10 monolayer, additional deposition of Pb results in 3-D island growth. It is now generally accepted that the c(4x4) phase is a surface alloy and the two higher-coverage phases are overlayer structures. A LEEM investigation of the time evolution of these structures and transitions between phases is the subject of a separate publication [14].

Reproducibly clean Cu(100) surfaces are obtained by heating the sample to 800° C in a 3%hydrogen/argon mixture outside the vacuum chamber (to remove sulfur from the near-surface region), followed by high-temperature Ne ion sputtering in the LEEM sample preparation chamber. During sputtering, the Ne pressure is $5x10^{-5}$ Torr, the bombarding voltage is 1 kV, and the sample temperature is held at 800° C. After sputtering, the sample is slowly cooled to room temperature and transferred to the LEEM main chamber. Pb, with a purity of 99.999%, is deposited on the Cu(100) surface in the main chamber from a heated PBN crucible. The background pressure in the system is typically in the low to mid 10^{-10} Torr range during Pb deposition. When the deposition source is turned off, the background pressure falls into the 10^{-11}

Torr range. We verify the sample cleanliness after Pb deposition with Auger electron spectroscopy. Common impurities such as S, O, and C are all below the Auger detection limit.

A LEED pattern from a Cu(100) surface with Pb coverage corresponding to the $c(5\sqrt{2}x\sqrt{2})R45°$ phase is shown in Fig. 1(a). The overlayer is grown with the sample at room temperature. A top view of the accepted atomic model for this structure is shown in Fig. 1(b). This is the overlayer structure upon which 3-D island growth takes place. The $c(5\sqrt{2}x\sqrt{2})R45°$ structure consists of Pb atoms residing in four-fold hollows of the Cu(100) substrate. It is the same structure as the c(2x2) structure, except there is an extra anti-phase boundary along the <100> direction every 5^{th} Cu lattice spacing. Note that this structure gives rise to two rotationally inequivalent domains oriented perpendicular to each other. If a LEED pattern were recorded with only one of the domains present, it would be two-fold symmetric. The LEED pattern shown in Fig. 1 is four-fold symmetric because the total areas of the two domains within the probed region are approximately the same.

We find that the small $c(5\sqrt{2}x\sqrt{2})R45°$ domains grown at room temperature can be coarsened in to larger domains by heating the surface to temperatures of 120° C and above. The LEED pattern show in Fig. 2(a) is from a Pb/Cu(100) surface in which the overlayer structure was grown at room temperature and subsequently annealed for a few minutes at 300° C. The diffraction spots are clearly more intense in one direction indicating that at elevated temperatures one of the two domains became larger in area than the other. The predominance of one domain is confirmed using a contrast mode in the LEEM known as dark-field imaging. The imaging mode is analogous to that used in the transmission electron microscope (TEM). An aperture is placed in the beam path allowing a single, non-integral LEED beam to pass through to the detector. A direct space image is formed using the selected beam. An example of a dark-field image from the same surface used for the diffraction pattern in Fig. 2(a) is shown in Fig. 2(b). The beam that was used to form the image in Fig 2(b) is circled in Fig. 2(a). This beam receives intensity only from regions on the surface with one particular domain orientation. Thus, the bright/dark contrast of Fig. 2(b) shows the domain structure of the overlayer. A dark-field image from the LEED beams oriented 90° to the circled one gives the same image, but with the contrast reversed (not shown). The domain size in this example is several microns, compared to the <10 nm size domains grown at room temperature.

We examine the time evolution of the domain structure during coarsening by obtaining a dark field image of a $c(5\sqrt{2}x\sqrt{2})R45°$ surface grown at room temperature and observing changes in the image while heating the sample. Figure 3 shows selected images from a videotape recorded during the domain coarsening process. The coarsening appears to take place by a gradual separation into two domains. If there is domain nucleation and growth, it is taking place at a length scale smaller than our spatial resolution. Although this type of coarsening behavior prevents us from studying domain boundary motion, we can still define the temperature conditions required to produce domains sufficiently large to be imaged in the LEEM.

Deposition of Pb on the $c(5\sqrt{2}x\sqrt{2})R45°$ surface overlayer phase results in the growth of 3-D Pb islands. Figure 4 shows a mirror image (sample bias 1 V less than the beam energy) of a Cu(100) surface with enough deposited Pb to produce 3-D islands. Similar images are obtained using the bright-field imaging mode. The dark regions are 3-D Pb islands, and the curved lines are step bunches on the substrate surface. The sample temperature is held at room temperature for the entire deposition sequence. As mentioned above, overlayers grown under these conditions have a domain size less than the spatial resolution of our microscope. The size distribution of the 3-D islands is fairly uniform with an average size of ~100 nm. The most interesting feature in Fig. 4 is that the 3-D Pb islands are asymmetric -- nearly rectangular in shape. There are two primary orientations of the islands in directions perpendicular to each other. The shapes of these islands are quite different from Pb islands grown on Cu(100) at low temperatures, where fractal-like islands grow from square sub-units [15].

Why are the 3-D islands grown at room temperature asymmetric with two preferred orientations in orthogonal directions? The fact that the islands grow on an overlayer structure having two domains with atomic chains perpendicular to each other suggest that there may be a correlation between the island shapes and the domain orientation of the $c(5\sqrt{2}x\sqrt{2})R45°$ structure. This correlation cannot be discerned from the images in Fig. 4 because the domain size is too small to be imaged in the LEEM. To further investigate the possibility of a such a correlation, we first grow a $c(5\sqrt{2}x\sqrt{2})R45°$ overlayer at room temperature and subsequently coarsen the structure until the domains can be resolved in the LEEM. We then grow 3-D islands on top of the coarsened domains. A typical result of from this type of experiment is shown in Fig. 5. The photograph is a bright-field LEEM image, which allows us to view the shape of the 3-D islands. In order to observe the domain structure of the overlayer in the same image, the incoming electron beam is tilted along the direction of the dislocation rows. We confirm that the contrast difference in the bright-field image reflects the domain structure by obtaining dark field images of the same region. It is clear from the image in Fig. 5 that the shape of the 3-D islands is correlated with the domain structure of the $c(5\sqrt{2}x\sqrt{2})R45°$ Pb overlayer. All of the islands in the bright area (one domain) are aligned parallel to each other, and, likewise, all of the islands in the dark area (other domain) are aligned parallel to each other in the direction orthogonal to the islands in the bright area. From the orientation of the LEED pattern and dark field images, we find that the long axis of the 3-D islands is parallel to the dislocation rows (see Fig. 1).

Having established a correlation between the 3-D island shape and the domain orientation of the 2-D overlayer, it is interesting to re-examine the island growth shown in Fig. 4. In this case the 3-D islands are grown on overlayers where the domain size is very small (<10 nm) in comparison to the island size (~100 nm), and yet the islands still grow asymmetrically. This suggests that once the islands are nucleated with a preferred growth direction, they continue to grow with that preferred direction, even when they reach a domain boundary. We find further evidence for this preservation of island orientation across domain boundaries in the experiments with large domains as well. Several examples of 3-D islands crossing domain boundaries are seen in Fig. 5 (indicated by arrows). By viewing videotapes of the growth sequences, we observe that most islands stop growing when they encounter a domain boundary, but a few continue to grow as if the boundary were not present. We currently have no explanation for this effect, but suspect that it may be possible for the growing island to locally change the underlying domain orientation as it grows.

In summary, we have used various imaging modes of the LEEM to identify an important correlation between the growth shape of 3-D Pb islands on Cu(100) and the domain orientation of the underlying Pb overlayer structure. The results have interesting implications for the formation of self-assembled, nano-structures on surfaces where the ability to manipulate properties of the nano-particles is often desired. The discovery that the atomic structure of submonolayer films can influence the morphology of 3-D nanostructures of the same material adds another means by which such manipulation can be achieved.

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Figure Captions

Fig. 1 (a) LEED pattern (130 eV) from a Cu surface covered with 6/10 monolayer of Pb. The periodicity is c(5√2x√2)R45^0. (b) Model of the accepted atomic structure.

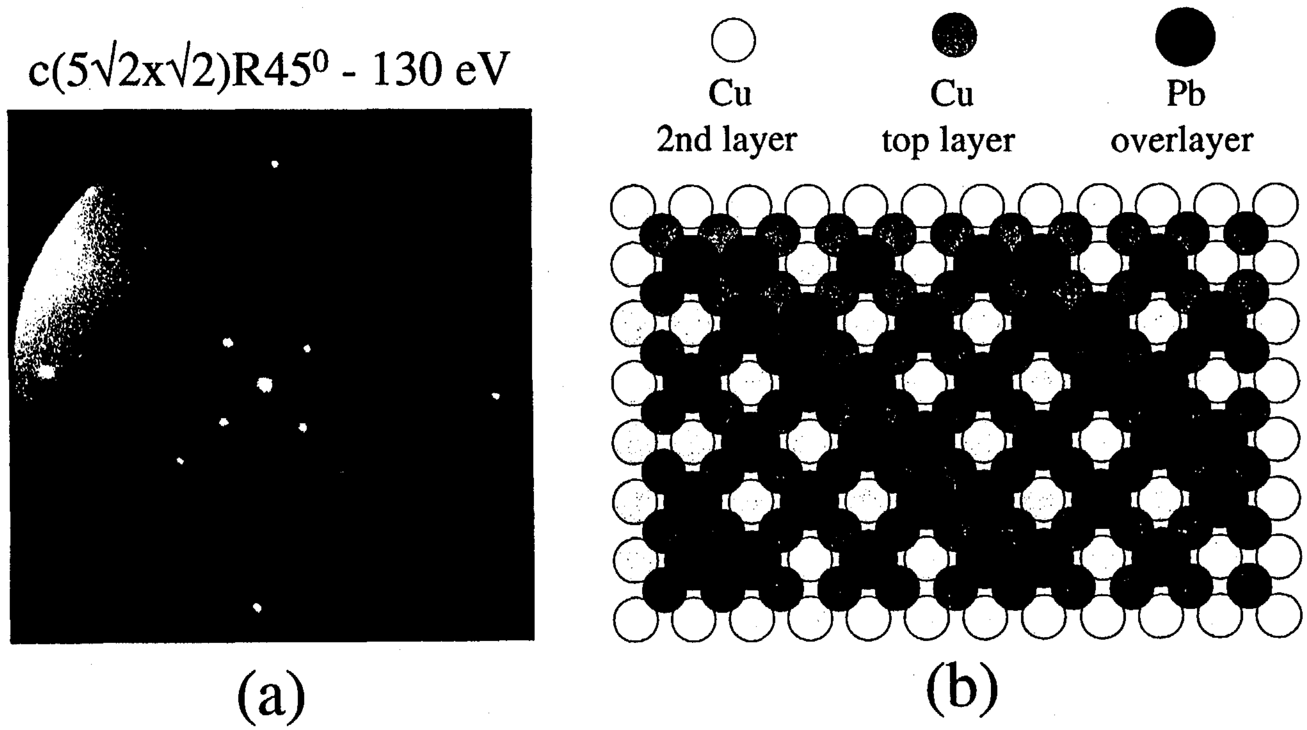
Fig. 2 (a) LEED pattern (130 eV) from a c(5√2x√2)R45^0 overlayer in which the domain structure has been coarsened by heating the sample to 300° C. The pattern has two-fold symmetry. (b) Dark-field LEEM image from the LEED spot indicated in (a) showing the domain structure.

Fig. 3 Sequence of dark-field LEEM images showing the gradual coarsening of the c(5√2x√2)R45^0 domain structure. The sample was warmed from 25 to 160° C during a time interval of approximately 30 min. The bright region corresponds to one of the two rotationally inequivalent domains.

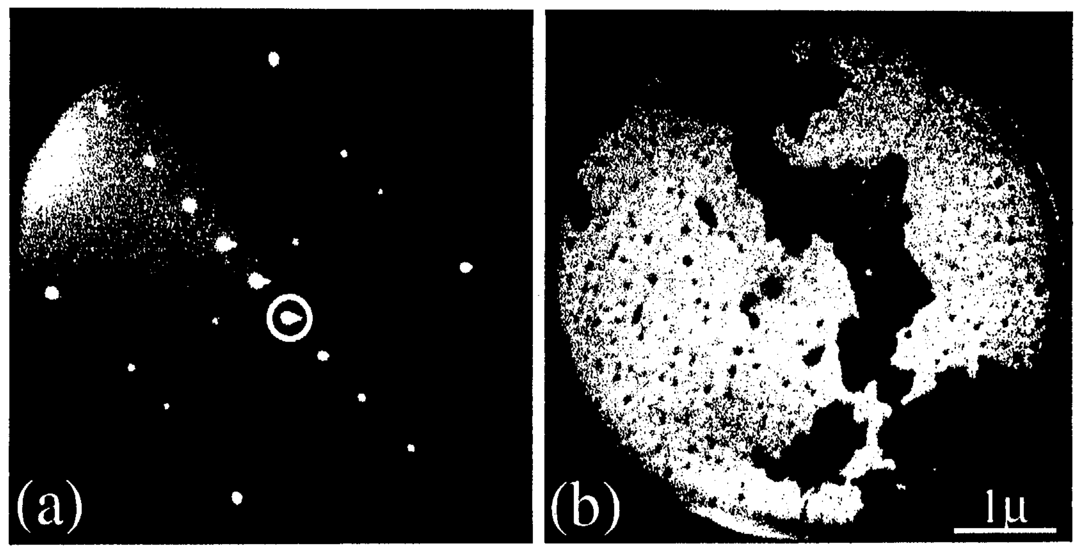
Fig. 4 LEEM image (mirror mode) showing 3-D Pb islands on a Cu(100) surface covered with the c(5√2x√2)R45^0 overlayer. The islands are asymmetric and have two preferred orientations. The overlayer and islands are grown by deposition of Pb with the sample at room temperature.

Fig. 5 Bright-field LEEM image showing the domain structure of a coarsened c(5√2x√2)R45^0 overlayer and subsequently deposited 3-D Pb islands. The island orientation correlates directly with the domain structure. Arrows indicate examples where the 3-D islands extend across domain boundaries.

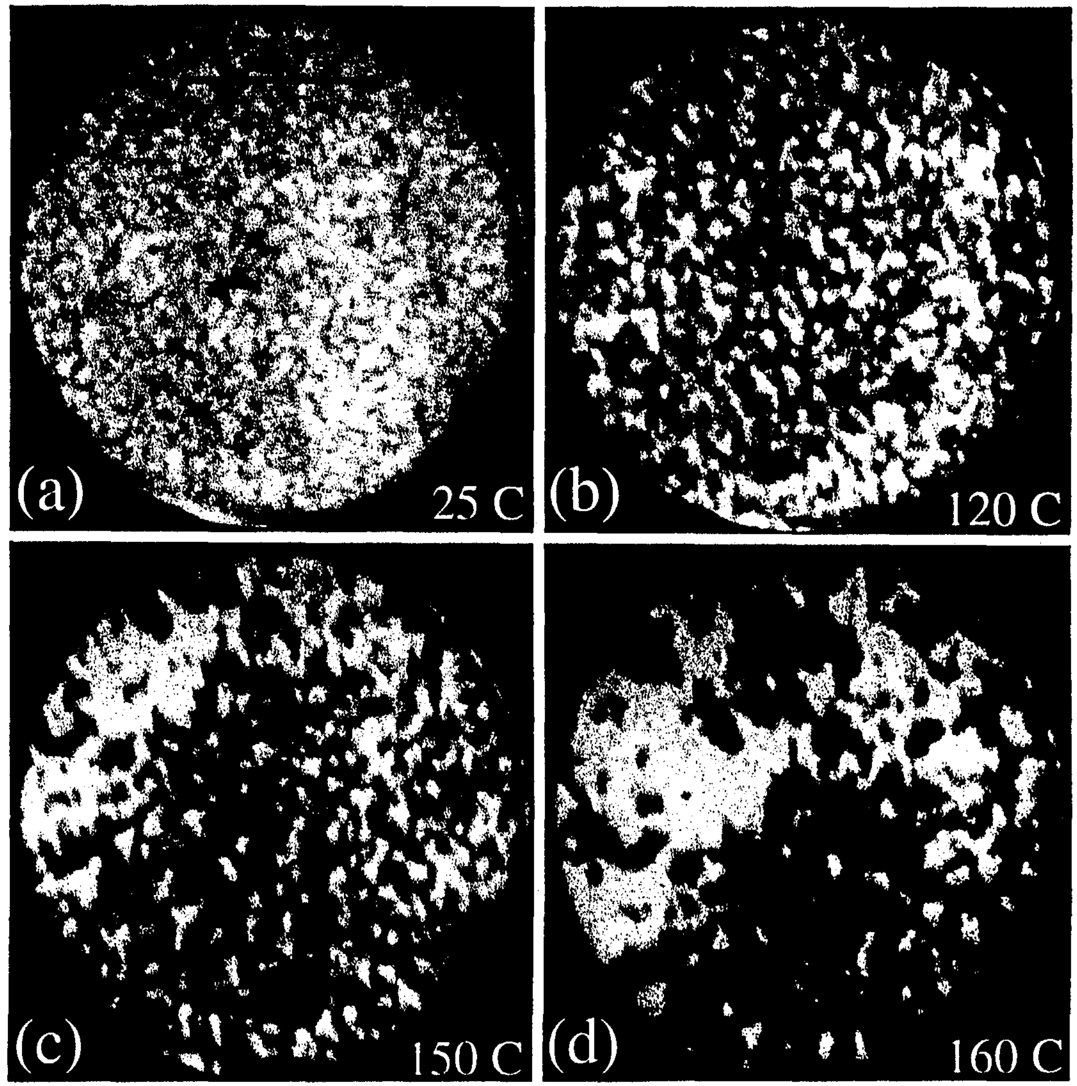
$c(5\sqrt{2} \times \sqrt{2})R45^0$ - 130 eV



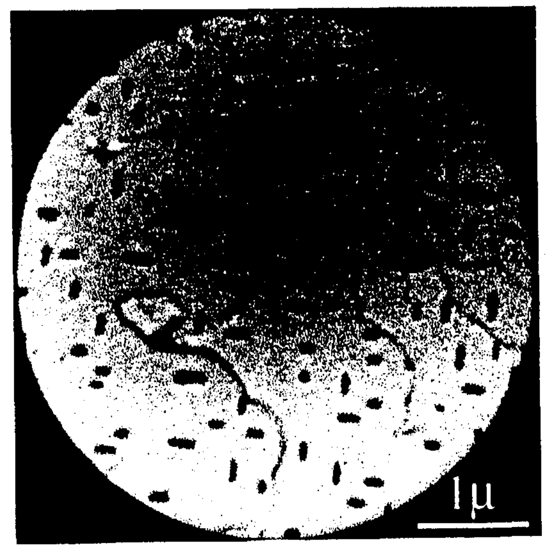
Kellogg and Plass - Fig. 1



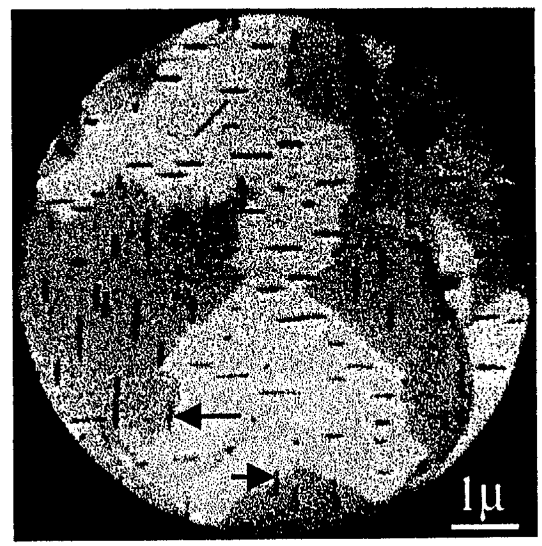
Kellogg and Plass - Fig. 2



Kellogg and Plass - Fig. 3



Kellogg and Plass - Fig. 4



Kellogg and Plass - Fig. 5