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Surface unwetting during growth of Ag on Si(001)

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The room-temperature growth mode of Ag on Si(001) was studied using scanning tunneling microscopy. This system grows in a Stranski-Krastanov mode, but the nature of the initial two-dimensional layer has remained controversial. These results show that a two-dimensional Ag layer completely covers the surface at one monolayer. Above one monolayer, three-dimensional Ag islands nucleate and the two-dimensional layer partially unwets the surface. This unwetting phenomenon explains some of the discrepancies between prior studies. [S0163-1829(96)53150-4]

Heteroepitaxial growth is governed by many parameters. In the simplest picture, there are three growth modes.[1] The three parameters that determine growth mode are the free energies per unit area of the overlayer/vacuum interface γ_o, the overlayer/substrate interface γ_i, and the substrate/vacuum interface γ_s. Three-dimensional island, or Volmer-Weber, growth occurs when $\gamma_o+\gamma_i>\gamma_s$. Ideal two-dimensional, layer-by-layer, or Frank-Van der Merwe, growth occurs when $\gamma_o+\gamma_i<\gamma_s$. And when $\gamma_o+\gamma_i\approx\gamma_s$, Stranski-Krastanov growth occurs: one or more two-dimensional layers followed by three-dimensional island growth. The Ag/Si(001) system has been shown to exhibit Stranski-Krastanov growth by Auger electron spectroscopy/scanning Auger microscopy,[2] scanning tunneling microscopy (STM),[3] and high-resolution reflection electron microscopy.[4]

While various techniques have agreed on the Stranski-Krastanov growth mode, the nature of the two-dimensional (2D) layer and the coverage at which 3D island growth commences have remained controversial. STM studies have shown that for low coverages, Ag atoms adsorb in bridge sites between Si dimer rows.[3,5,6] If a complete 2D layer consists of Ag atoms in such bridge sites, then the layer will have a density of 0.5 ML. Here, 1 ML$=6.78\times10^{14}$ cm^{-2}, the atomic density of the Si(001) surface. In addition, studies such as the scanning Auger microscopy mentioned above[2] have measured the density of Ag atoms in between 3D islands to be less than 1 ML, in seeming agreement with the STM bridge site studies. These prior studies have also shown 3D island growth occurring at coverages below 1 ML.[2,3] However, another STM study[7] found that the Ag in bridge sites was a minority effect (possibly associated with defects in the Si substrate), and that most of the Ag agglomerated into a 2D layer that covered the surface at 1 ML. In addition, this study saw no 3D islands for coverages below 1 ML. A more recent STM study[5] showed that after a high (>10 ML) coverage of Ag was deposited onto the surface, there were gaps in the 2D layer between 3D islands. They concluded that this system was ''pseudo-Stranski-Krastanov,'' meaning that 3D growth proceeded without the completion of the 2D layer. In summary, various experiments have failed to agree upon the density of the Ag 2D layer, the coverage at which 3D islands nucleate, and if the 2D layer ever completely covers the surface.

The present study seeks to resolve the controversy surrounding this system by focusing on the room-temperature (RT) growth of Ag on Si(001) in the coverage regime just below and just above 1 ML. The STM measurements presented show that a single 2D Ag layer completely covers the surface at a coverage of 1 ML, 3D islands do not begin to form until the 2D layer completes, and upon nucleation of 3D islands, the 2D Ag layer partially unwets the surface, meaning that some of the Ag leaves the 2D layer and goes into 3D islands, exposing areas of the original clean Si surface. This leads to a surface similar to ''pseudo-Stranski-Krastanov,'' but substantially different in its evolution to this final state.

In general, unwetting can occur in any system where the energy per adatom is lower in 3D islands than in an initially formed 2D layer, but the transition from the metastable 2D layer to 3D islands is inhibited by a barrier. For example, it is surmised that in the case of Ag/Mo(100) (grown at 573 K), 2D islands grow until they reach a critical size, at which point some fraction of the 2D islands are consumed by 3D islands.[8] This study of the Ag/Si(001) system is unique because the specific overlayer coverage at which this transition occurs is directly observed. In addition, most metal on silicon systems are Stranski-Krastanov, with the initially formed 2D layers stable as coverage is increased.

Figure 1 shows a pair of STM images from the same surface. Panel (a) was taken after 0.95 ML of Ag had been deposited. Almost all of the surface is covered by a 2D layer of Ag atoms, with the remaining surface being clean Si. Onto this surface additional Ag was deposited, so that the total coverage was 1.10 ML. Panel (b) shows an image taken after this second deposition. Now, a smaller fraction of the surface is covered by the 2D Ag layer and there is more Si visible. This illustrates how the 2D layer unwets the surface after 3D island nucleation. The unwetting, previously observed, can explain much of the controversy surrounding this system.

All experiments were done in an ultrahigh vacuum chamber with a base pressure of less than 7×10^{-11} Torr. The system includes facilities for sample cleaning and metal deposition, a low-energy electron diffraction (LEED) optics, and a STM. The Si(001) samples were cut from commercial wafer stock. Prior to introduction into the chamber, the wafers were degreased with solvents. Once in vacuum, the samples were outgassed with a filament heater to approximately 500 °C. To prepare clean surfaces, the samples were heated by passing a direct current through them. The samples were first flashed to above 1150 °C and held for 30 sec; then rapidly cooled to 1000 °C. They were held at this temperature for about 10 min, then slowly cooled to room tempera-

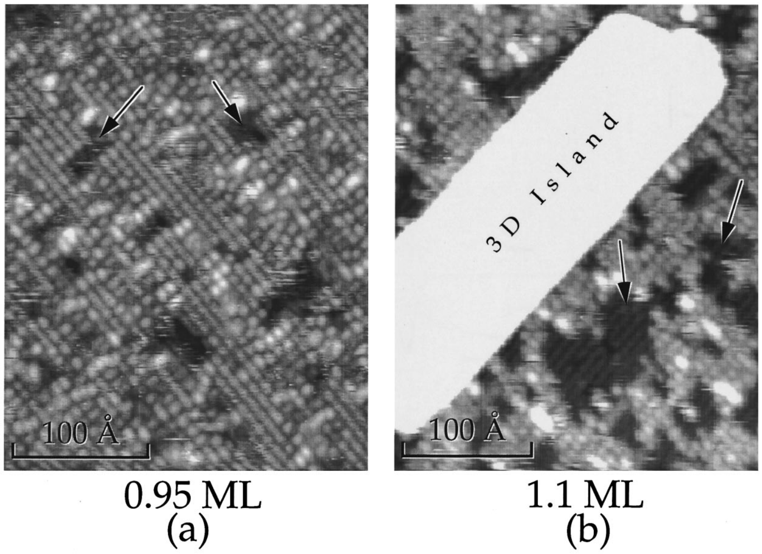

FIG. 1. A pair of STM images with (a) 0.95 and (b) 1.1 ML Ag deposited at RT. Both images were taken from the same surface, with an additional Ag deposition occurring after the image in panel (a) was taken. Arrows point out some areas of bare Si in both panels. There is a 3D island in panel (b) which is shown as a white outline.

ture. During dc heating, temperatures were monitored by an infrared pyrometer, and the pressure was constrained to below 1×10^{-9} Torr. The order of the surface was determined by LEED and STM. All measurements were done at room temperature.

The Ag source was an Ag bead on a resistively heated tungsten filament. The sample was at room temperature during deposition. The evaporation rate was calibrated by a quartz crystal microbalance. The Ag coverages were determined by timed exposure to the source. Typically, Ag was deposited at rates near 0.2 ML/min. For coverages below 1 ML, the calibration was checked by measuring the area of the surface covered by the 2D layer, and was consistent with our prior work.[7]

As was previously mentioned, these experiments were carried out in a sequence of coverage steps. For coverages below 1 ML of Ag, no 3D islands were observed. Figure 2(a) shows a large-scale STM image of a surface covered by 0.95 ML of Ag. Single atomic height steps due to the underlying Si can be seen running through the image. Each terrace in the image is covered by a nearly complete 2D Ag layer. No 3D islands are observed. By measuring the area covered by the 2D layer in many images such as the one in Fig. 1(a), we have determined that 95% of the surface is covered by the layer, in fortuitous agreement with our coverage calibration. Areas of the surface not covered by the 2D layer are clean Si.

The fact that the 2D layer nearly covers the entire surface at a coverage of 0.95 ML is strong evidence that the layer does completely cover the surface at 1.0 ML, and thus the layer has a density of 1 ML. This is in agreement with a previous study published by Lin, Wan, and Nogami,[7] which proposed a model for the structure of the 2D Ag layer (based on STM images), repeated here. Figure 3(a) shows a filled-states STM image of a Si(001) surface with 0.2 ML Ag on the surface. Most of the surface consists of bare Si dimer rows. Several 2D Ag islands have also nucleated. The features in the Ag islands display both 2×1 and 2×2 periodicities. An outline of one unit cell of each of these structures has been placed on the image. In both cases each unit cell has two maxima paired along the Si dimerization direction. For the 2×2 structure the spacing of these maxima in the direction along the Si dimer rows is double that of the 2×1. The atomic arrangement is not as clear in empty-states images. Figure 3(b) shows our model for these structures. This model features 1 ML of Ag atoms dimerized on the surface. The position of the dimers corresponds to the position of the

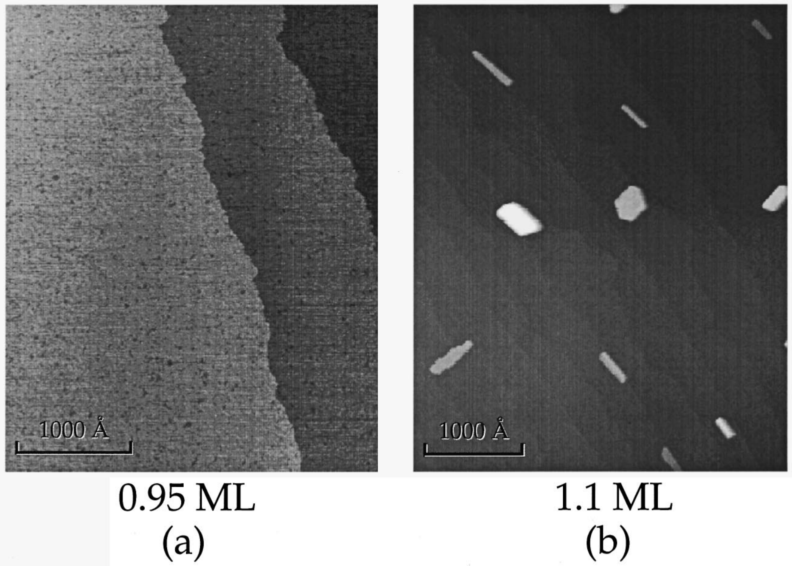

FIG. 2. A pair of large scale STM images of a surface with (a) 0.95 and (b) 1.1 ML Ag deposited at RT. These images are taken from the same surface as shown in Fig. 1. As the coverage approaches 1.0 ML, a 2D Ag layer nearly covers the entire surface, as shown in panel (a). It is not until the coverage exceeds 1.0 ML that 3D islands nucleate.

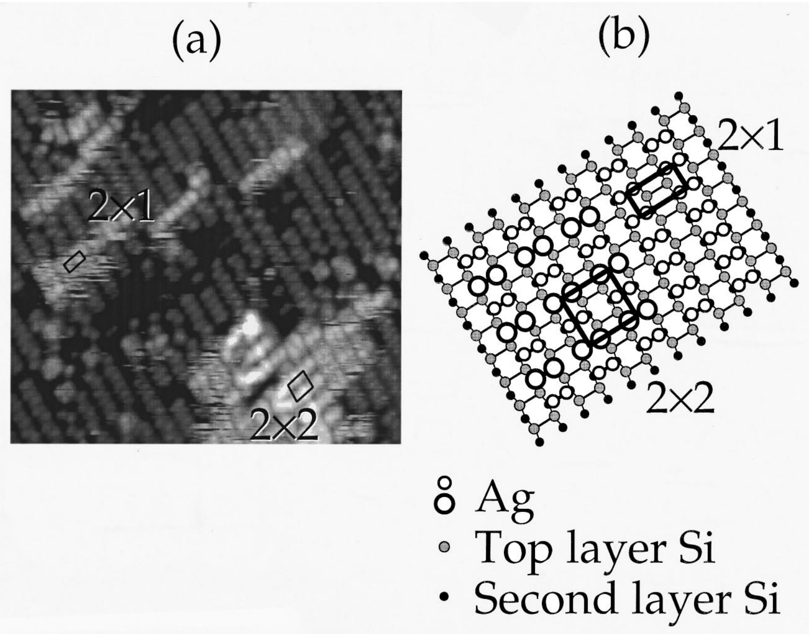

FIG. 3. Model proposed for the atomic structure of the 2D Ag layer. Panel (a) shows a filled-states STM image of a surface covered by 0.2 ML Ag. The 2D Ag islands exhibit local areas of both 2×1 and 2×2 order, as indicated by the unit cell outlines. Panel (b) shows the corresponding atomic model. The unfilled circles (both large and small) represent Ag atoms, which are dimerized. The shaded and filled circles represent surface and second-layer Si atoms, respectively.

maxima in our STM images: in the trenches between Si dimer rows, and in line with the minima between neighboring Si dimers within a row. The density of Ag atoms is the same in both the 2×1 and 2×2 structures. In the 2×2 model, half of the Ag dimers are drawn with larger circles; these represent the maxima that appear higher in the STM images. One possible explanation for why half of the dimers are seen by the STM tip as higher is that the surface is corrugated in these areas in order to relieve strain.

One clearly observable feature of Fig. 3(a) is the streakiness near the edges of the Ag islands. These streaks occur at all coverages and occur mostly at the edges of the 2D Ag islands. They are associated with Ag atoms moving as the tip scans over them. Ag seems to be bound quite weakly to the Si underneath it, and thus is quite mobile at the edges of 2D islands. Note that if this were some sort of tip instability, the streaks would also occur over areas of clean Si.

Once the coverage is increased to above 1.0 ML, 3D islands nucleate on the surface. Figure 2(b) shows a large-scale view of the same surface as Fig. 2(a). Additional Ag has been deposited so that the total coverage is 1.1 ML. 3D islands have nucleated over the entire area. This confirms the growth mode as Stranski-Krastanov, with the transition to 3D growth starting at 1.0 ML.

However, Fig. 1 illustrates that the growth mode does not conform to the simplest picture of Stranski-Krastanov behavior. Many images similar to the one in Fig. 1(b) were analyzed to determine that after the additional deposition of Ag, 78% of the surface was covered with a 2D layer, down from 95% before the deposition. Upon nucleation of 3D islands, some of the Ag in the 2D layer must have been removed and incorporated into the 3D islands. Thus, the 2D layer partially unwets the surface after the onset of 3D island growth.

Figure 1(b) shows that unwetting occurs near 3D Ag islands. Figure 2(b) (an image of the same surface) shows that the islands are spaced thousands of Å apart. Does unwetting occur in areas far from 3D Ag islands? Many images taken at varying distances from the nearest 3D island were analyzed, and there was no statistically significant correlation between proximity to a 3D island and fraction of the 2D film that unwets. The unwetting seems to proceed more or less uniformly over the entire surface.

The unwetting of the 2D Ag layer in the presence of 3D islands can resolve much of the controversy surrounding the Ag/Si(001) surface. It allows for the formation of a complete 2D Ag layer at 1 ML,[7] and at the same time, an average of less than 1 ML of Ag between 3D islands. This explains results such as those seen by scanning Auger[2] as well as the STM observations of pseudo-Stranski-Krastanov growth.[5]

The unwetting displayed by this system suggests some interesting energetics. The fact that Ag grows in a strictly 2D manner for coverages below 1 ML means that the free energy associated with the 2D Ag layer is less than the free energy of the Si/vacuum interface. The observed unwetting means that it is energetically favorable for Ag to be in a 3D island rather than in the 2D layer. However, if the most energetically favorable site for an Ag atom to occupy is in a 3D island, why does the 2D layer form initially in the absence of 3D growth, and why does most of the 2D layer remain in place after the formation of 3D islands?

A partial explanation for this behavior lies in the fact that the structure of the Ag in the 2D layer is completely different than that of bulk Ag, and thus the bonding arrangement for an isolated Ag atom on top of the 2D layer would also differ from bulk Ag. It is then possible that an atom on top of the 2D layer is energetically unfavorable in comparison to an atom in the 2D layer, and in turn that Ag in the 2D layer is energetically unfavorable to Ag in a bulk Ag island. These energetics explain the formation of a complete 2D layer at up to 1 ML, and the unwetting once the 3D islands of Ag are present, respectively. The transition to 3D growth is blocked by the absence of bulk Ag until the coverage reaches 1 ML, a point at which Ag can no longer be accommodated in the 2D structure shown in Fig. 3(b).

Kinetics may also play a role in why the 2D layer forms in the absence of 3D island growth and why the 2D layer does not completely unwet the surface. If the deposition rate is low enough, there will never be a high enough density of Ag atoms on the 2D layer for a 3D island to nucleate. The Ag atoms can diffuse to the edge of the 2D layer before encountering another diffusing Ag atom. Thus, 3D island growth will be deferred until the 2D layer completely covers the surface. In addition, the surfaces imaged with coexisting Ag 3D islands and 2D layer may not be in their equilibrium states. It is then possible for some of the Ag to remain in the 2D layer even though it is energetically favorable for it to be incorporated into the 3D islands. Annealing the surface should then drive it closer to its equilibrium state. These kinetic effects can be studied with further experiments varying the deposition rate and temperature. Experimentally, annealing is limited to about 150 °C before the 2D layer undergoes a phase transition. Our initial experiments at very low annealing temperatures were unable to show any further unwetting.

It should also be noted that a partially occupied 2D layer may coexist in equilibrium with the 3D islands. Any Si(001) substrate has a certain number of defects in the surface and near-surface regions. These defects could add to the free energy of the regions of 2D layer nearest the defects. This seems plausible, since the 2D layer is clearly repelled by missing dimer defects. Now suppose that the energy associated with a 3D island site is between the energies of the 2D layer away from and near substrate defects. Then, upon nucleation of 3D islands, it is energetically favorable for the Ag in 2D layers near defects to be incorporated into the islands, but the remainder of the 2D layer would be stable. Thus, the (remaining) 2D layer and 3D islands may coexist in equilibrium. In this scenario, the fraction of the surface that unwets is determined by the initial condition of the substrate rather than the kinetics of the process. In any event, the effect of defects could be clarified by varying the coverage on the same substrate or by studying the behavior of substrates with different defect densities. A high defect density seems to decrease the coverage at which 3D islands nucleate, which might explain why 3D growth was seen below 1 ML in some prior works.[3,9]

Also of interest is the nature of the unwetting process. How does the Ag get from the 2D layer to a 3D island? Perhaps the most obvious method is for an Ag atom to leave the 2D layer and diffuse over the top of it, until it reaches a 3D island and becomes incorporated or until it reaches an edge of the 2D layer and drops off. However, as was previously mentioned, the area of the surface that unwets near islands is about the same as for areas thousands of Å from any island. For shorter Ag diffusion lengths than this, we would expect to see more areas unwet near 3D islands than far from 3D islands. If Ag on Ag diffusion is to be the unwetting mechanism, the Ag diffusion length must be thousands of Å long. A schematic of the Ag diffusion process is shown in Fig. 4(a).

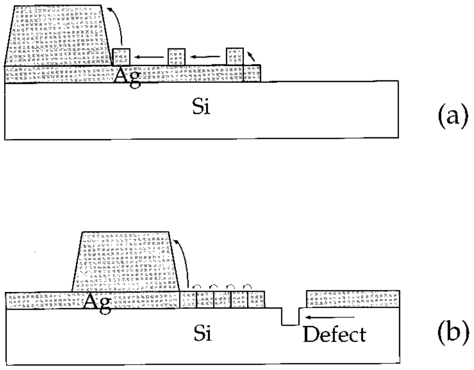

FIG. 4. Schematic models for the unwetting of the 2D layer. (a) Unwetting by diffusion. An Ag atom from the 2D layer is activated and hops up onto the layer. It then diffuses around until it reaches a 3D island and is incorporated into the island. (b) Unwetting by collective motion of the Ag layer. An Ag atom from the 2D layer is incorporated into the 3D island. The perimeter of the Ag layer moves in due to the collective motion of the Ag atoms. The layer may be pinned at defects in the underlying Si, causing gaps to open up.

An alternative method for the Ag movement involves cooperative motion of the 2D layer. In this model, when Ag is drawn out of the 2D layer by a 3D island, the 2D layer contracts around it, due to an effect like surface tension pulling in the atoms at the edges of the 2D layer. This kind of cooperative motion requires that the Ag atoms interact with each other more strongly than with the underlying Si. This may be a reasonable assumption, given the readiness of the Ag at the edges of 2D islands to move under the influence of the tip. What then determines where gaps in the film are situated? Defects in the Si substrate may pin the 2D layer, causing holes to open up. This process is shown schematically in Fig. 4(b).

In summary, this study has shown that the room-temperature growth of Ag on Si(001) proceeds in a Stranski-Krastanov-like manner. These results reaffirm that that a complete 2D Ag layer forms at 1 ML, and that 3D growth starts above this coverage. In the presence of 3D islands, the 2D layer partially unwets the surface. There is no statistically significant difference in the amount of unwetting near 3D islands and far from 3D islands. The results of this study explain apparent discrepancies between prior experiments regarding the nature of the 2D Ag layer.

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