Origins of Nanoscale Heterogeneity in Ultrathin Films

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A key challenge in thin-film growth is controlling structure and composition at the atomic scale. We have used spatially resolved electron scattering to measure how the three-dimensional composition profile of an alloy film evolves with time at the nanometer length scale. We show that heterogeneity during the growth of Pd on Cu(001) arises naturally from a generic step-overgrowth mechanism relevant in many growth systems.

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Thin films play a key role in many technologies. Applications range from promoting chemical reactions at surfaces, preventing interdiffusion, and electrical isolation to more exotic ones in nanotechnology, where reduced dimensionality gives rise to unique electronic or magnetic properties. One particularly important issue in the growth of ultrathin films is controlling compositional heterogeneity. It is well known that films can be inhomogeneous, but determining exactly how and why heterogeneity develops is extremely difficult. In general, understanding how the three-dimensional composition profile of the film evolves with time is required. Detailed information of this type has proven difficult to obtain because high spatial resolution must be combined with subsurface chemical sensitivity. Here we describe spatially resolved electron diffraction measurements that overcome these limitations and allow us to unambiguously determine how nanometer-scale compositional inhomogeneity develops during growth. By measuring the evolution of the three-dimensional composition of a growing film in real time, we show that a simple step-overgrowth mechanism, potentially relevant in many systems, is responsible for the heterogeneity we measure.

We have measured the development of compositional heterogeneity during the growth of ultrathin Pd films on Cu(001) using low-energy electron microscopy (LEEM) [1]. In LEEM, an image is formed from the low-energy electrons reflected from a surface. An image of the Cu(001) surface recorded during Pd deposition at 200 °C is shown in Fig. 1(a). The surface contains a number of single-atomic layer steps, identified by sharp changes in image contrast. In these regions, one sees dendritic-type growth outward from the advancing step and a continuous decrease in image intensity away from the step on the upper terrace. The image intensity is determined by the local electron reflectivity. While the spatial variation of the intensity shows directly that the surface is heterogeneous, the exact nature of the inhomogeneity is unclear. One would like to understand precisely how the surface is inhomogeneous and to identify the atomic-scale kinetic processes that are responsible. These are difficult issues because of the inherent complexity of the growth environment.

Here we show how spatially resolved measurements of the alloy composition can be used to understand the heterogeneous growth. As we describe in detail below, we determine the alloy concentration point by point on the surface by quantitatively analyzing the image intensity as a
function of electron kinetic energy. The results of this analysis are shown in Fig. 1(b) for an area of the surface near an atomic step. The images show the concentration of Pd in each of the first three layers of the surface after the deposition of 0.45 ML of Pd at 200 °C. The analysis shows that the top layer is almost entirely Cu, while most of the deposited Pd is located in the second layer. Near the step, there are significant variations in the Pd concentration. Most importantly, there is a substantial amount of Pd in the first layer, while most of the Pd transferred to the third layer is virtually immobile at 200 °C. In the simplest scenario, the amount of Pd buried by the step is equal to the instantaneous concentration in the second layer, leading to a characteristic profile for c₃ in the overgrown region.

Before evaluating the step-overgrowth model in more detail, we first describe how the layer-resolved Pd concentrations shown in Fig. 1(b) are derived from the image intensities. Our analysis is based on comparing the measured electron reflectivity to that calculated for a trial structure and is essentially identical to the approach used to analyze low-energy electron diffraction (LEED) [4]. The method is similar in spirit to the “fingerprinting” approach used by Schmid et al. to determine overlayer coverages during a chemical reaction [5]. In our experiments, the incident electron beam is normal to the surface. We place an aperture in the optical path so that only electrons reflected specularly—i.e., into the (00) LEED diffraction beam—contribute to the image. Thus, the LEEM image intensity measures the spatial variation of the (00) diffraction beam at a particular energy. By recording images at different electron beam energies, the dependence of the reflected electron intensity on electron kinetic energy is recorded for any point in the field of view. In the LEED literature, these data are called intensity-versus-voltage curves (or simply “IV curves”). The IV curves are computed for a trial structure and compared with experiment. The parameters of the trial structure (which include the Pd concentrations in the first three surface layers) are varied to give the best agreement with the measured IV curve. In this way, we determine the values of c₁, c₂, and c₃ point by point at the surface. Examples of measured and computed IV curves are shown in Fig. 3.

In our calculations, the alloy composition in the three outermost layers is optimized using the average t-matrix approximation method [6]. We find the best agreement between the measured and computed IV curves when the...
Pd in each layer is located primarily in one $2 \times 2$ sublattice, in agreement with previous LEED analysis [7]. One significant difference between conventional LEED and LEEM is that the electron energy in LEEM is typically much lower. At very low energies, inelastic damping is difficult to treat with the standard LEED-IV formalism because the electron mean free path depends strongly on the energy. Therefore, we use an energy-dependent optical potential (i.e., the imaginary part of inner potential) of the form $V_{\text{im}} = V_{\text{damp}} E^{1/3}$ [8], where $E$ is the beam energy in eV and $V_{\text{damp}}$ is a parameter to be optimized. The real part of inner potential is assumed constant at $-13.4$ eV below 36 eV and has an $E^{-1/2}$ dependence above 36 eV, as proposed by Rundgren [9]. The latter is particularly relevant for Cu(100), where the correct treatment of the low-energy electrons resolved a controversial claim of an in-plane contraction [10,11]. We find the best agreement between the calculated and measured IV curves with $V_{\text{damp}} = 0.86$ eV$^{2/3}$ and the real part of the inner potential fixed at $-13.4$ eV for $E < 36$ eV. Details of the LEED optimization process are described elsewhere [12].

We now describe how the alloy compositions measured near a step validate the step-overgrowth model. Three key signatures of the overgrowth model are (1) the asymmetry in the third-layer Pd concentration near a step, (2) the characteristic profile of the third-layer Pd in the overgrown region, and (3) the correlation between third-layer Pd behind the step and the second-layer Pd in front of the step. Each of these predictions can be rigorously tested by analyzing the Pd concentration near the step. IV curves from four points along a line crossing a step are shown in Fig. 3. The most significant differences between the curves occur for energies below 30 eV. In the overgrown region, the intensity of the peak near 20 eV is lower, and a low-energy shoulder is present at about 13 eV. We find very good agreement between the calculated and measured IV curves at all points on the surface.

The variation in $c_1$, $c_2$, and $c_3$ along a line crossing a step is shown in Fig. 4(a). The analysis shows that most of the Pd is located in the second layer, in agreement with previous LEED studies [7]. Away from the step, the concentrations are spatially uniform, with $c_2 \approx 0.4$ and $c_1$ and $c_3$ about zero. Near the step, $c_3$ is large on the upper side of the step but drops dramatically to zero at the step position. The value of $c_3$ at the upper side of the step is equal to that of $c_2$ on the lower side of the step. This correlation strongly suggests that Pd in the third layer arrives there via the step-overgrowth process.

The time evolution of $c_3$ further confirms this picture. The variation in $c_3$ near the step is shown in Fig. 4(b) for three different times during Pd deposition. It is clear that the amount of Pd buried by the step increases monotonically with time as the step moves. If the buried Pd is immobile, the profile of $c_3$ in the overgrown region should not change with time. For example, the three curves shown in Fig. 4(b) should agree for $x < 500$ nm, which they do. This suggests that diffusion into or out of the third layer is slow at 200 °C. The data in Fig. 4(a) suggest that the Pd instantaneously buried by the step is equal to the value of $c_2$ on the terrace. That is, the spatial profile of the buried Pd is related to the time profile of the Pd in the second layer. In other words, $c_3(x(t)) = c_2(t)$, where $x(t)$ is the step position. We have measured both $x(t)$ and $c_3(t)$ (far from the steps), which allows us to test this prediction. The black line in Fig. 4(b) shows the profile predicted by the step-overgrowth model. The agreement is quite good, showing that the spatial profile of the buried Pd $c_3(x)$ is directly related to the distribution of mobile Pd on the terrace $c_2(t)$. The direct comparison of the measured and predicted alloy composition profiles confirms the basic picture of compositional heterogeneity driven by step overgrowth.

We have shown that step overgrowth converts mobile, second-layer Pd into immobile Pd in the third layer. We now show how correlations between the amount of Pd in neighboring layers gives insight into the bonding and stability of the alloy film. As discussed above, the profile for $c_3$ in Fig. 4(a) is determined by the step-overgrowth
mechanism. Contrary to the assumptions of the simplified step-overgrowth model (Fig. 2), $c_2$ is not spatially uniform. Far from the step, $c_2$ is constant at 0.40 ML, but near the step it decreases to half that value. One possibility is that surface diffusion is inhibited (e.g., when $c_3$ is large) and that $c_2$ is not equilibrated laterally. An alternative scenario is that the $c_2$ is equilibrated and that the variation in $c_2$ with $c_3$ is due to a repulsive Pd-Pd interaction. In this case, the correlation between $c_2$ and $c_3$ can be used to infer the strength of this interaction. For example, if there were no interaction between Pd atoms, then $c_2$ would be spatially uniform, and there would be no correlation with $c_3$. Alternatively, if Pd atoms strongly repel, then $c_2$ will be small when $c_3$ is large, and vice versa. Consider a highly simplified model in which the internal energy of the film is proportional to the number of Cu-Pd nearest-neighbor (NN) bonds. This model is motivated by the stability of the $c(2 \times 2)$ structure, in which all of the Pd NNs are Cu, and is supported by first-principles calculations [13] as well as empirical modeling [14]. The theoretical analysis of the bonding shows that Cu-Pd NN bonds are favored over both Cu-Cu and Pd-Pd bonds.

We performed Monte Carlo simulations on the model outlined above to determine if the measured correlation between $c_2$ and $c_3$ is consistent with a fully equilibrated second layer. We do this by computing the equilibrium alloy concentrations for a given value of the Cu-Pd NN bond energy $\epsilon$ and comparing to the measured concentration profiles shown in Fig. 4(a) (taking all other bond energies to be zero). In the simulations, we used the Metropolis algorithm [15] to compute $c_1$ and $c_2$ given a fixed distribution of Pd in the third layer [16]. The two free parameters of the model are $\epsilon$ and the Pd chemical potential $\mu$ [17]. Details of the simulations are given elsewhere [12]. We fix the two model parameters to match the experimental result far from the step: $c_1 = 0.05$ and $c_2 = 0.40$. We then compute $c_1$ and $c_2$ as a function of $c_3$, which is taken from the measured profile. The black curves in Fig. 4(a) show the simulation results for $\epsilon = -25$ meV. The agreement is remarkable given the simplicity of the model. The ability to quantitatively reproduce the measured composition profile strongly suggests that the first two layers are, in fact, laterally equilibrated. That is, the decrease in $c_2$ in the overgrown region near the step reflects an effective Pd-Pd repulsion rather than slow Pd diffusion at the surface. These results also explain how inhomogeneity in the third layer is propagated into the second layer: $c_2$ and $c_3$ are highly correlated. The correlation is driven by the effective repulsion between Pd atoms.

Understanding compositional heterogeneity is a key challenge in the engineering of thin films. By carefully measuring how heterogeneity develops near steps, we have identified the exact process—step overgrowth coupled with inhibited bulk diffusion—that gives rise to heterogeneity. This mechanism is a direct consequence of the energetics of vacancy diffusion and is expected to be relevant in a wide range of growth systems. Proving that the step-overgrowth mechanism is operative in the absence of direct measurements of the concentration profiles is essentially impossible. However, our analysis shows that spatially resolved LEED analysis is a powerful method for determining three-dimensional alloy concentrations locally at surfaces with nanometer-scale resolution. Knowledge of how composition evolves in space and time places strict constraints on models of film equilibration, structure, stability, and growth.

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[16] A trial move in the simulation involves swapping the identities of two atoms in the top two layers of the film.
[17] To be precise, the chemical potential in the model is the energy to replace a Cu atom in one of the first two layers with a Pd atom. The value simply sets the total Pd concentration of the film.