

Temperature dependence of metal film growth via low-energy electron diffraction intensity oscillations: Pt/Pd(100)

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A commercial, conventional low-energy electron diffraction apparatus is used to monitor Bragg intensity oscillations during the growth of Pt on Pd(100). The effect of substrate temperature between 80 and 400 K is investigated. Between 80 and 300 K, two to three Bragg oscillations are observed. The oscillation amplitude damps out quickly as film coverage increases at fixed temperature, but damp out less quickly at the higher substrate temperatures. Above ~ 350 K, reconstruction of the Pt overlayer interferes with the oscillations. These data indicate that a kinetic barrier, most probably the barrier to surface diffusion, inhibits the system from achieving macroscopic equilibrium, and that the true equilibrium growth mode for this system is layer-by-layer. A new, analytical procedure is used to determine the coverage distribution within the layers from the Bragg intensities during growth. Bragg oscillations are predicted to occur at low substrate temperatures where surface diffusion is minimal and deposition is essentially random, but restricted to the fourfold hollow adsorption sites.

I. INTRODUCTION

Metal films on metal substrates can exhibit unusual catalytic, chemisorptive, and magnetic properties.¹ To understand these properties, it is important to understand how the film is spatially distributed on the surface, e.g., does the film form two-dimensional layers or three-dimensional clusters? The spatial arrangement as a function of coverage is referred to as the growth mode. In this paper, we present new experimental and theoretical approaches to determining details of the growth mode of Pt films on Pd(100).

In layer-by-layer (Frank-van der Merwe) growth, each layer fills completely before the next layer is populated. One can think of this phenomenon as the formation and annihilation of steps as each layer forms. The expected low-energy electron diffraction (LEED) spot profiles at nonintegral coverages consist of two parts: a broad, Lorentzian-like distribution indicative of short-range order and the presence of steps, summed with a Bragg peak indicative of long-range order.² LEED is most sensitive to surface disorder at the out-of-phase condition, where the diffracted intensities from atoms in consecutive layers interfere destructively. At these energies, for *perfect* layer-by-layer growth, the normalized Bragg intensity oscillates between 1 and 0 for completely filled and half-filled layers, respectively. Both reflection high-energy electron diffraction (RHEED) and LEED have been used to follow growth of overlayers by monitoring the Bragg intensity as a function of coverage.³

Previous Auger electron (AES) and ultraviolet photoemission spectroscopic studies of Pt on Pd(100) at 300–350 K have indicated that Pt grows isomorphically with the substrate in a layer-by-layer fashion up to at least three atomic layers.⁴ Since Pt and Pd have the same bulk structure, with lattice constants agreeing to within 0.8%,⁵ there is little interfacial strain. This promotes layer-by-layer growth.⁶ A subsequent study of this system⁷ showed that LEED could be used to observe oscillations in the Bragg intensity as the Pt film was deposited at 300 K. This confirmed the earlier hypothesis of layer-by-layer growth. However, the oscillation

amplitude decreased as coverage increased, indicating an increasing number of partially occupied layers as thickness increased, i.e., imperfect layer-by-layer growth.

In this work, we analyze deviations from equilibrium growth of the Pt overlayer on Pd(100), by investigating the effect of substrate temperature. We use a commercial LEED apparatus to monitor variations in the Bragg intensity as a function of Pt coverage and substrate temperature between 80 and 400 K. We outline a new, analytical procedure for obtaining the coverage distribution among layers as a function of total coverage from these data.

II. EXPERIMENTAL DETAILS

Experiments are performed in a stainless-steel UHV chamber equipped with a Pt evaporator,⁸ standard Varian four-grid LEED optics, single-pass cylindrical mirror analyzer (CMA), mass spectrometer, and ion gun. LEED spot profiles, taken at normal incidence, are measured with a computer-interfaced, silicon-intensified-target video camera.⁹ The Pd(100) sample is cleaned of bulk contaminants to within the detection limit of Auger analysis.¹⁰

In a typical experiment, Pt is dosed for 10 s while the Pd sample is held at constant temperature. The pressure in the chamber typically rises to $\sim 6 \times 10^{-10}$ during this dose. The Pt 64-eV and Pd 327-eV Auger peaks are measured at three positions to ensure uniformity of the film. The sample is next turned toward the LEED optics and selected spot profiles are measured at given energies. Each Pt dose, followed by AES and LEED measurements, takes a total period of 4–5 min. Repeating the evaporation and subsequent measurements, spot profiles are accumulated as a function of Pt coverage. Alternatively, spot profiles are recorded as a function of energy at a given coverage. We discuss results of both types of experiment.

III. EXPERIMENTAL RESULTS

To follow the formation of layers during growth, the Bragg oscillations are analyzed at an energy where diffrac-

tion is sensitive to the presence of steps, i.e., an energy where the scattering from atoms in different levels is out-of-phase. We determine an out-of-phase condition for the Pt-Pd system by measuring the full width at half-maximum (FWHM) of the $(1, \bar{1})$ beam as a function of energy, for Pt-covered Pd, at room temperature. A maximum occurs at ~ 145 eV. For comparison, we calculate out-of-phase energies for Pt on Pt and Pd on Pd from the equation given by Henzler.¹¹ We assume the fourfold hollow is the adsorption site, and use bulk values for the interlayer spacings. This calculation indicates an out-of-phase condition at 140.5 eV for Pt on Pt and 142.5 eV for Pd on Pd.¹¹ These values agree favorably with our experimental data for Pt on Pd. Thus, both the experimental data and the calculation show that 145 eV represents an energy at, or very nearly at, an exact out-of-phase condition for this system.

It is fortunate that the $(1, \bar{1})$ reflex has appreciable intensity at this energy, enabling clear separation of the diffracted peak from the background. For the $(1, 0)$ beam, out-of-phase conditions coincide with extreme minima in the I - V curves, or at inconvenient energies. We thus confine our discussion to the $(1, \bar{1})$ reflex.

The $(1, \bar{1})$ spot profiles are shown in Fig. 1 as a function of cumulative evaporation time. In experiments of this type, the substrate temperature is held constant except during LEED data acquisition. During this time the heating current is chopped, so as not to distort the diffraction pattern. (The temperature drop during chopping does not exceed 12 K. The average temperature drop for substrate temperatures between 80 and 350 K is 4 K.)

At zero Pt coverage (first profile, Fig. 1) the sharp spot profile reflects the intrinsic order of the substrate and the instrumental response function. As Pt coverage increases, no new LEED spots are observed, but the integral-order spots take on a new shape. These profiles are clearly separable into two parts: a sharp, narrow Bragg peak, summed with a broader, Lorentzian-like distribution. The intensity of the Bragg peak oscillates in a manner similar to that expected for

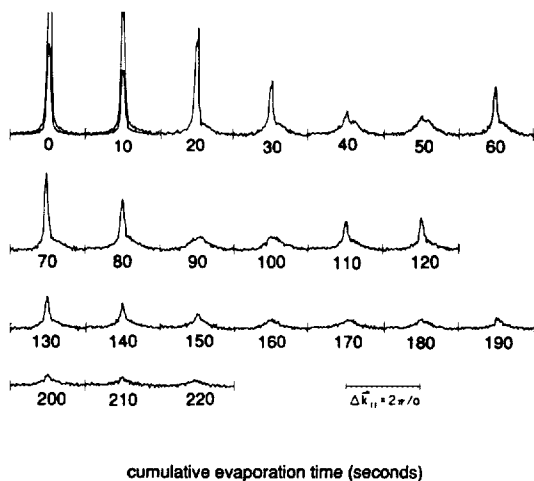


FIG. 1. $(1, \bar{1})$ spot profiles as a function of cumulative evaporation time at 145 eV. The substrate temperature is 250 K. The first profile is that of the clean substrate. The second profile is taken after a 10-s Pt dose. The 10-s dose is repeated before each of the following profiles. The profiles are divided into three rows, each row roughly showing the filling of a Pt layer.

layer-by-layer growth, although it never regains its full initial intensity.

In order to interpret the intensity behavior one must consider the effect of the difference in scattering factors of Pt and Pd. If there is an appreciable difference, the intensity would first be characteristic of the scattering factor of Pd, and then reflect that of Pt as the coverage increases. However, the ratio of atomic scattering amplitudes, calculated on the basis of the partial-wave analysis equation¹² at 145 eV, is 0.987, i.e., essentially unity.

We obtain profiles similar to those of Fig. 1 for substrate temperatures between 80 and 400 K. Bragg intensities, normalized to the Bragg intensity of clean Pd, are shown in Fig. 2 for temperatures between 80 and 350 K. When depositing at 350 K and above, Pt overlayer reconstruction interferes with the oscillations.⁴ The temperature regime above 300 K, and the associated reconstructions, are not discussed further in this paper.

IV. DISCUSSION

We observe distinct oscillations in the Bragg intensity at substrate temperatures between 80 and 300 K. For perfect layer-by-layer growth, the maxima should occur at full-layer coverages with unit amplitude. The reduction of the measured Bragg intensity at each maximum, relative to zero Pt coverage, indicates incomplete filling of one layer before the next layer begins to grow. Figure 2 shows that the amplitude at a given oscillation increases with increasing substrate temperature, up to 300 K. This is more clearly shown in Fig. 3,

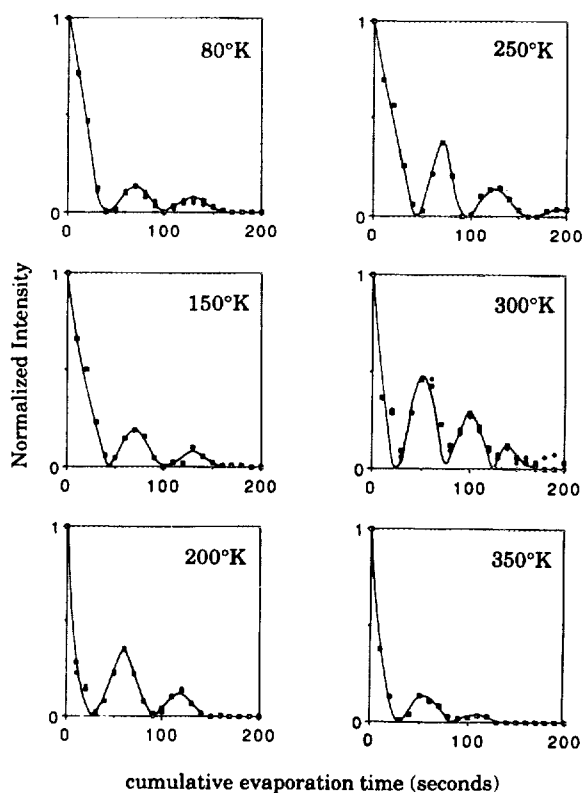


FIG. 2. Normalized Bragg intensity as a function of cumulative evaporation time t , for the temperatures indicated. The beam energy is 145 eV. Curves between data points are drawn in to guide the eye.

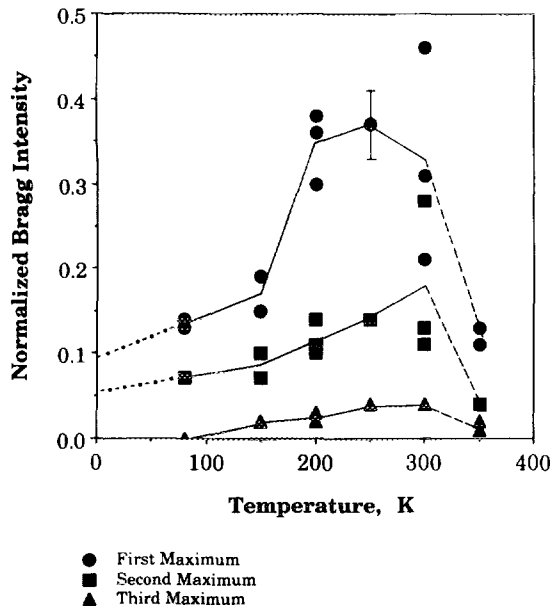


FIG. 3. Normalized Bragg intensity for the first, second and third maxima as function of substrate temperature. Straight lines, which connect the average value of intensity at each coverage, are shown for clarity. Dashed lines indicate temperatures at which Pt reconstruction interferes with the oscillations. Dot-dash lines show the extrapolation to 0 K.

where the Bragg intensities at the first, second, and third maxima are plotted as functions of substrate temperature. This demonstrates the trend toward more perfect layer-by-layer growth with increasing substrate temperature.

The data of Figs. 2 and 3 indicate that at substrate temperatures exceeding ~ 150 K, diffusion plays an important role in smoothing the film. The top curve of Fig. 3, which represents the intensity at the first maximum, demonstrates this most clearly. The sharp increase at ~ 150 K indicates that at this temperature the Pt adatoms have sufficient thermal energy to overcome the barrier to surface diffusion, leading to a more perfect (smoother) film. The temperature at which diffusion begins to play a role suggests that the surface diffusion barrier is on the order of 10 kcal/mol. These data indicate that Pt adatoms are kinetically trapped in upper layers as the film grows at low temperatures ($T < 150$ K), and the true equilibrium growth mode for this system is layer-by-layer.

V. BRAGG INTENSITY ANALYSIS

We are interested in the relationship between the coverage distribution among the layers and the Bragg intensity during growth. Only in perfect layer-by-layer growth is this relationship well understood: the maxima in the Bragg intensity correspond to coverages of completed layers. Here, we explore the more complicated case of imperfect growth.

The key assumptions of the analysis are the following:

(i) *The fourfold hollow is the adsorption site.* Adsorption into this site maintains the fcc structure, resulting in isomorphic growth. Besides being the physically intuitive site for fcc(100) growth, this site is supported the symmetry of the LEED pattern,^{4,7} and the agreement between the measured out-of-phase energy and the calculation using the fourfold site.

(ii) *The Bragg intensity is given by the kinematic approximation.* Kinematic theory has been used frequently to analyze disorder in epitaxial growth.^{13,14} In kinematic scattering, the intensity at an out-of-phase condition is given by

$$I = (N_0 - N_1 + N_2 \dots)^2 / (\sum_i N_i)^2.$$

In this equation, N_i is the effective number of exposed atoms in layer i , and $i = 0$ corresponds to the surface substrate layer. We assume that each adatom effectively blocks scattering from a net of one atom in the layer below,¹⁵ so N_i is calculated as the difference in coverage between layers i and $i + 1$.

The kinematic approximation has recently been used to analyze the occupations of each layer based on the energy dependence of the intensity.¹⁶ Multiple scattering presumably has less influence on the coverage dependence (which we are concerned with here) than on the energy dependence. Certainly, a full dynamical calculation would lead to a better understanding of the behavior of the Bragg intensity. Ideally this would provide the effective scattering factors for exposed atoms with different local environments, i.e., isolated atoms, atoms at the edge or interior of islands, and those that are partially covered by the next layer. One could then check the above assumptions and modify the kinematic calculation as necessary. However, such large dynamic calculations are not within the scope of this project.

First, we consider the microscopic model for film growth at $T = 0$ K, as developed in Ref. 15. We assume adsorption occurs at a constant impingement rate with an equal probability of filling any fourfold hollow site. In this model, adsorption occurs every time an atom impinges within an area determined by the centers of four neighboring atoms comprising the fourfold hollow site. If an atom strikes an area not so defined (i.e., an incomplete fourfold hollow site), it does not adsorb. The $T = 0$ K assumption implies that there is no diffusion. One can set up and analytically solve the master equations for this model, when they are expressed as a set of coupled kinetic rate equations. The mathematical details are presented elsewhere.¹⁵ From these equations, the partial occupation of each layer and the Bragg intensity is exactly calculated as a function of total coverage or time. Figure 4

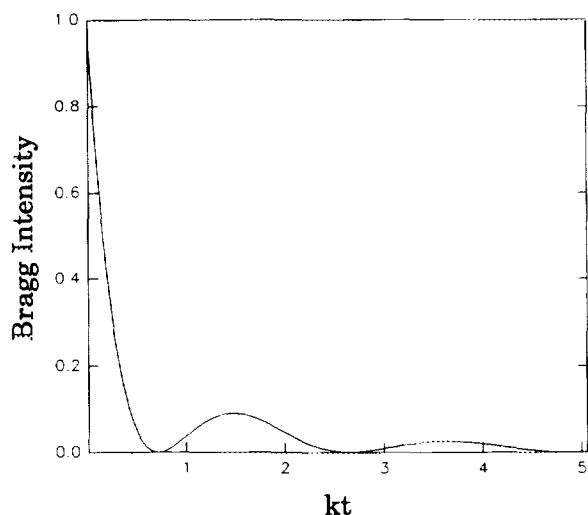


FIG. 4. Calculated Bragg intensity as a function of kt , where k is the impingement rate and t is time. The calculation assumes random adsorption into fourfold hollow sites at $T = 0$ K.

shows the Bragg intensity as a function of time, calculated from the above assumptions. Distinct oscillations are evident. For contrast, random deposition onto atop sites leads to *no* oscillations. In this case, the Bragg intensity simply decays monotonically with coverage.¹⁵ The difference between these two cases is easily explained in terms of the number of atoms required for the adsorption of an adatom. For adsorption into atop sites, *every* exposed atom may serve as the starting point for the growth of an upper layer. Columns of atoms grow independently and diffraction quickly becomes out-of-phase. However, in the case of the fourfold adsorption site, it is necessary to have a square arrangement of four neighboring atoms in the lower layer, thus *creating* the adsorption site for an atom in the next layer. This imposes a severe restriction on the filling of upper layers, which enhances layer-by-layer growth.

To assess the applicability of this model, we compare the intensities at the maxima of the calculated oscillations (at $T = 0$ K) with our experimental data at low temperatures, as shown in Table I. The calculated intensities, at 0 K, agree well with the low-temperature, experimental intensities *extrapolated to 0 K*. (See Fig. 3.) This convergence supports the validity of our assumptions.

For growth at 0 K, the model predicts 0.89 monolayer (ML) coverage at the first maximum of the Bragg intensity. [We define 1 ML, $\Theta = 1$, as one adatom per Pd(100) surface atom.] Here, the coverage distribution is 0.77 ML in the first layer (Θ_1), 0.12 ML in the second layer (Θ_2), and all upper layers are essentially empty. This is quite far from perfect layer-by-layer growth, in which the first maximum corresponds to $\Theta_1 = 1$ and $\Theta = 0$ for all upper layers. Yet, the model predicts oscillations in the Bragg intensity. Thus, oscillations will occur for isomorphic fcc(100) growth, even in the absence of diffusion (i.e., $T = 0$ K), by virtue of the requirement of a fourfold hollow adsorption site.

There is a discrepancy in the time dependence of the calculated and experimental oscillations. The time required to reach the first maximum, relative to that for the second maximum, is substantially smaller for the model than it is for the experiment. (See Figs. 2 and 4.) In the model, we assume an atom adsorbs only if it strikes a fourfold hollow adsorption site (as defined above). Since the number of these sites decrease with time, so does the sticking coefficient. In reality, it is likely that atoms which do not strike a fourfold site are accommodated through local equilibration, rather than reflected from the surface. This would lead to a sticking coefficient that is more constant with time. We will address this issue in future work.

In a separate paper,¹⁰ we develop a generic procedure to approximately, but simply, extract the coverage distribution

TABLE I. Calculated (0 K) and measured (80 and 150 K) Bragg intensities at the first and second maxima.

Temperature	First maximum	Second maximum
0	0.09	0.03
80	0.14	0.07
150	0.17	0.09

from the Bragg intensity for arbitrary temperatures. This procedure focuses on the dependence of Θ_2 on Θ_1 , i.e., $\Theta_2 = f_1(\Theta_1)$. For a given choice of the function f_1 and by using a scaling hypothesis to calculate the analogous functions f_i , which determine the coverages of higher layers, one can calculate the Bragg intensity as a function of total coverage.¹⁵ We vary f_1 to fit the first and second maxima of the experimental data at each temperature, between the limits of $T = 0$ K (which is *exactly* solvable for the random deposition model) and perfect layer-by-layer growth ($\Theta_2 = 0$ for all $\Theta_1 \neq 1$).

The resultant values of Θ_1 and Θ_2 at the first maximum of the Bragg intensity are given in Table II for selected temperatures. In these cases, we find third-layer occupation is negligible. As temperature increases, the coverage in the first layer increases, and the coverage in the second layer decreases. In general, the coverages at the maxima do not correspond to the ideal full-layer values, and the absolute deviation from the ideal values increases with each successive maxima. We find that as temperature increases, the total coverage approaches the ideal layer-by-layer value of unity at the first maximum. This analysis supports the postulate that diffusion does not play a significant role in smoothing the film until the substrate temperature exceeds 150 K.

VI. CONCLUSIONS

We use a conventional LEED apparatus to measure Bragg oscillations during growth of Pt films on Pd(100). At 350 K and above, intensity associated with Pt reconstruction interferes with the oscillations. Between 80 and 300 K, Pt adatoms simply continue the (1×1) fcc structure set by the Pd(100) template. The oscillations are severely damped at all temperatures, but higher substrate temperatures lead to oscillations of increased amplitude. These data indicate the true equilibrium growth mode is layer-by-layer. Damping occurs because the Pt adatoms are kinetically trapped during growth. The barrier to surface diffusion, which is on the order of 10 kcal/mol, inhibits the system from achieving macroscopic equilibrium in these experiments.

In general, Bragg oscillations for isomorphic fcc(100) growth are predicted to exist, even in the absence of diffusion, mainly due to the site requirement for the growth of additional layers. Experimental Bragg oscillation amplitudes for Pt on Pd(100) are analyzed to yield the partial occupation in each layer throughout growth. This analysis clearly demonstrates the trend toward perfect layer-by-layer growth as the temperature increases in this system.

TABLE II. Calculated coverage distribution at the first Bragg oscillation maximum. The temperatures are given in degrees Kelvin, and the coverages are given in monolayers, as defined in the text. The estimated error in the calculations at nonzero temperatures is ± 0.04 ML.

Temperature	First layer	Second layer	Total
0	0.77	0.12	0.89
80	0.78	0.09	0.87
150	0.79	0.08	0.87
200	0.90	0.10	1.00
250	0.90	0.10	1.00

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