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Reflection high-energy-electron-diffraction studies of mass transport and low-temperature growth of Ag/Si(111)

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We have studied the growth modes and mass-transport mechanism of the Ag/Si(111) system by using reflection high-energy-electron-diffraction quantitative spot analysis. The growth mode at 150 K is quasi-layer-by-layer, indicating significant adatom mobility. The scaling of the specular beam intensity with time for several deposition rates suggests the absence of thermally activated diffusion. The presence of nonthermal diffusion is further confirmed from the comparison of the initial growth rates and the final full width at half maximum attained at different deposition rates for the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)R30° system.

Reflection high-energy-electron diffraction (RHEED) has become an indispensable technique for studying ultrathin-film growth during molecular-beam epitaxy (MBE) providing *in situ* detailed morphological information about the growing film. The specular spot intensity of a RHEED pattern is found to oscillate in time for layer-by-layer growth.[1] The period of oscillations is equal to the time required for the surface to return to a smooth state after the initial "smoothness" has been destroyed due to the increase of the surface step density caused by the deposited atoms; thus RHEED is a unique surface probe for identifying layer-by-layer growth.

Even though the technique of RHEED oscillations has been used to determine the growth modes in many MBE studies, many fundamental questions concerning the microscopic processes of ultrathin-film growth remain unanswered. One such question is the puzzling observation of RHEED intensity oscillations at low temperatures.[2-4] Layer-by-layer growth and, consequently, RHEED intensity oscillations require mass transport. When oscillations are observed at low temperatures, it is not clear if the diffusion barrier is low enough so thermal diffusion can operate to transport material across the surface. For some systems, the presence of the oscillations at such low temperatures suggests that a different source of translational energy exists. In this paper, we propose a method of analyzing the oscillations to decide if thermal diffusion operates, without the need of complementary transport experiments.

Several competing explanations have been proposed for the driving mechanism behind the mobility of adatoms at low temperatures: the two-barrier model based on an island-size-dependent diffusion barrier,[5] "funneling,"[4] and transient mobility.[2,6] Recent molecular-dynamics calculations[7,8] show that the choice of the interatomic potential is critical in determining the growth mechanism. Despite several specific studies, where the individual mechanisms operate, it is not clear what type of systems support each mechanism.

Ag/Si(111) is a well-studied system whose growth modes have been identified for temperatures ranging from room temperature to the range where the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$)R30° reconstructed overlayer is formed.[9] We have chosen this system to use quantitative RHEED analysis to determine the growth modes in more detail and extend the growth characterization to low temperatures to test if oscillations are present. The experiments were performed in a UHV system with base pressure 5×10^{-11} Torr having a RHEED diffractometer and a Knudsen cell to evaporate Ag. The relative deposition rate was measured with a quartz monitor, and the absolute rate in terms of the oscillation period at 150 K. A video camera was used to collect the pattern images which were stored and analyzed with an IBM-AT computer. Details of the experimental set up will be described elsewhere.[10]

Figure 1 shows typical results for the behavior of the specular intensity during Ag growth for a deposition rate of ~0.01 ML/sec. For $T=483$ and 573 K, temperatures within the $\sqrt{3}$ structure range, the specular intensity decreases monotonically during the formation of the $\sqrt{3}$ layer and then remains constant. The surprising result in Fig. 1 is the presence of short-lived intensity oscillations in the specular intensity at 150 K. This result is remarkable not only because the temperature is so low but also because the growth involves an overlayer which is highly heteroepitaxial with respect to the substrate. Both the type of lattice and the lattice constants are highly mismatched. The presence of only a *few* oscillations is expected since the driving mechanism behind the quasi-layer-by-layer growth should be quickly suppressed by the different energetics of the lattices involved. As the temperature is increased the oscillations disappear gradually. The disappearance of the oscillations implies either columnar growth or step flow (i.e., the surface maintains a steady-state condition as the deposited atoms diffuse to the island edges and no nucleation takes place in the middle of the terraces). In the latter case, thermal diffusion is the driving mechanism behind the growth. As we increase the temperature beyond 373 K, the growth is interrupted by the formation of the $\sqrt{3}$ structure, so we are unable to check for the phenomenon of reentrant[5] oscilla-

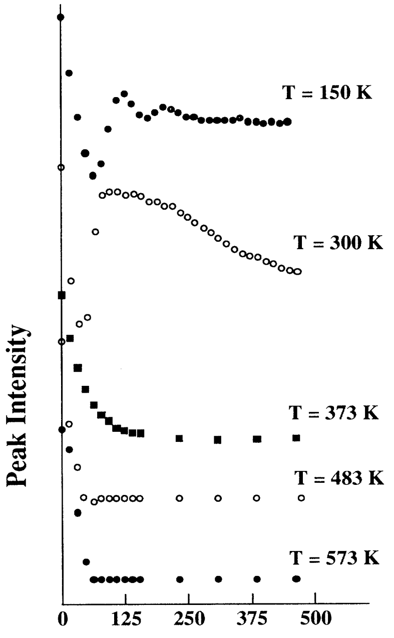

FIG. 1. The normalized peak intensity of the specular beam vs deposition time for different substrate temperatures at a deposition rate of ~0.01 ML/sec.

tions with this system.

The short-lived oscillations in the specular intensity imply the existence of significant adatom mobility at 150 K; however, negligible thermal diffusion has been observed[11] for the Ag/Si(111) system when μm-sized islands of Ag are deposited with a masking technique at room temperature. It is not clear, though, how these measurements apply to our experiment which involves smaller Ag islands. So instead of merely making the assumption, based on Ref. 11, that thermally activated diffusion is not present for $T \leq 300$ K, we check it experimentally.

As a confirmation of the absence of thermal diffusion, we have examined the time dependence of the specular beam intensity for different deposition rates. If thermal diffusion operates in the system we should expect the number of oscillations to depend on deposition. At high deposition rates, the probability of island nucleation is higher so a large number of small islands is formed, and the surface is "rougher." At low deposition rates, the atoms have enough time to join the growing nuclei so a small number of large islands is expected. More oscillations should be present in the low flux growth, and more importantly the amplitude of the oscillations should be higher. The intensity at time $t, I(t)$, can be plotted in the form $I(t)/I(0)$ vs t/τ, where τ is the time of the first oscillation, to test if the data collapse into a universal curve (i.e., scaling holds) for different deposition rates. For systems driven by thermal diffusion, this should not be true. This method can be used generally to decide the presence of thermal diffusion from experiments performed at different deposition rates.

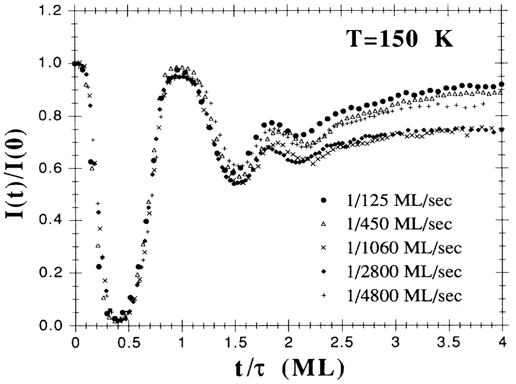

FIG. 2. The normalized peak intensity of the specular beam $I(t)/I(0)$ vs t/τ for different deposition rates at a substrate temperature of 150 K. τ is the time of the first oscillation. The number and amplitude of oscillations [since $I(0)$ is the same] are flux independent.

The results of the analysis to test for scaling are shown in Fig. 2. Plotting the specular intensity for the various deposition rates this way allows us to accurately compare the number and shape of the oscillations. With the rescaling of the data, the curves are essentially identical. The quasi-layer-by-layer growth is independent of the deposition rate. We have the same number of oscillations, with unchanged amplitude (within 5% variation), since $I(0)$ is essentially identical for the clean surface, for all deposition rates. The first minimum is zero because a constant, flux independent background of less than 10% of the initial intensity was subtracted from all profiles. It is remarkable that the whole first oscillation results in the same rescaled curve, independent of the deposition rate; the small deviations observed at later times can be attributed to statistical differences in the grown film after 2–3 layers have been deposited, because of twin boundaries[12] between the Ag crystallites. We can thus rule out the presence of thermally activated diffusion at 150 K. If thermal diffusion is not responsible for the quasi-layer-by-layer growth, then what are other alternative mechanisms? One possible scenario, but not the only one, involves the excess energy of the deposited atom with respect to the substrate that can be transformed into lateral motion. Such effects have been observed[6] in the dissociation of O_2 absorbed on Al(110) by measuring with scanning tunneling microscopy the size of oxygen islands formed and during Xe deposition[12] on Pt(111) by measuring the accommodation of the incoming Xe atoms to the steps.

Additional confirmation that another type of diffusional mechanism is present in this system can be obtained by studying the formation of the $\sqrt{3}$ structure, which is known to form at $T > 473$ K, as a function of deposition rate. One expects thermal diffusion to be present at these high temperatures. If, however, only thermal diffusion was operating then the full width at half maximum (FWHM) of the $\sqrt{3}$ spots, measured after 1 ML of Ag has been deposited on the clean substrate at $T > 473$ K, would be flux dependent, with narrower FWHM's observed at lower deposition rates because the atoms would have more time to join the growing domains. As Fig. 3 shows, for Ag deposited at a sub-

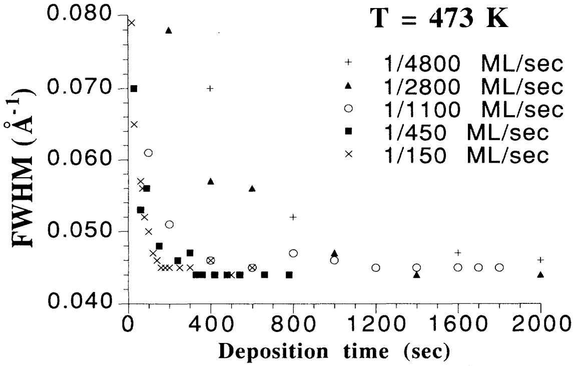

FIG. 3. The FWHM of the $(\frac{1}{3},\frac{1}{3})$ order spot of the $\sqrt{3}$ superstructure RHEED pattern vs time for different deposition rates at a substrate temperature of 473 K. The FWHM's are flux independent.

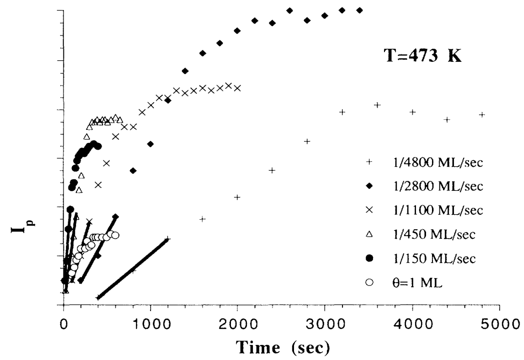

FIG. 4. The peak intensity of the $(\frac{1}{3},\frac{1}{3})$ order spot of the $\sqrt{3}$ superstructure RHEED pattern vs deposition time for different deposition rates at a substrate temperature of 473 K. The set of data labeled $\theta = 1$ ML is the peak intensity of the $(\frac{1}{3},\frac{1}{3})$ spot vs time after deposition of 1 ML at $T = 150$ K, followed by upquenching to $T = 473$ K. Heavy lines indicate that the comparison is restricted to early times when blocking effects are minimal.

strate temperature of 473 K with rates varying from $\frac{1}{150}$ to $\frac{1}{4800}$ ML/sec, the final FWHM is flux independent and well above the instrumental width. There must be another mechanism driving the system towards the $\sqrt{3}$ phase which produces a diffusion length almost independent of the growth conditions, i.e., the extra time available to diffuse at lower fluxes. The adatom condensation energy, if not efficiently transferred to the substrate, offers this type of mobility, independent of the additional time to diffuse at lower deposition rates, because the transfer process is completed at a much faster time scale of 10^{-12} sec. The deposition rate was varied by only a factor of ~ 50 because of experimental difficulties of going to higher effusion cell temperatures. One might question whether this variation includes low enough deposition rates so that the constant FWHM is not simply limited by the supply of atoms: atoms join the growing domains at a constant rate (the atom arrival rate) because diffusion is much faster than the deposition rate. If this is the case then the island area should grow at a constant rate and the peak intensity (i.e., area) which scales with the square of the number of scatterers, would increase like t^2, where t is the time. As will be seen shortly in Fig. 4, this is not the case.

If we deposit a constant amount of Ag onto the clean Si(111)-(7×7) surface at a low temperature and then upquench the substrate to a temperature within the $\sqrt{3}$ superstructure range, thermal diffusion alone will cause the $\sqrt{3}$ overlayer to form out of the initial random configuration. If we form the $\sqrt{3}$ structure in a different way, by first depositing Ag atoms from the source onto a clean substrate, held at the same temperature the upquench experiment was performed at, then, we would expect the nonthermal contribution to diffusion to be present only in the deposition experiments. It would be interesting to test if evidence for this additional contribution can be identified by comparing the deposition with the annealing experiment.

1 ML of Ag was deposited at 150 K on the clean surface to perform the constant coverage experiment. We then raised the temperature to the desired value, $T = 473$ K, within the $\sqrt{3}$ range in less than 5 sec which is negligible compared to the time of several hundred seconds that it takes the $\sqrt{3}$ spots to saturate. The peak intensity of the $(\frac{1}{3},\frac{1}{3})$ order spot of the $\sqrt{3}$ diffraction pattern is plotted in Fig. 4 as a function of time. With heavy lines we denote the initial regime where the comparison is made, and the domain sizes involved are small. (Since the observed dependence is linear, the slope is constant throughout the growth. This technique can also be applied for nonlinear time dependence if the comparison is restricted to early times.) Also shown is the time evolution of the $\sqrt{3}$ structure growth for five different deposition rates with the substrate at the same temperature, 473 K. Similar results were obtained at other temperatures within the $\sqrt{3}$ range of formation. We see that, for the higher deposition rates, the rate of increase of the $\sqrt{3}$ intensity during Ag deposition is greater than the rate of increase at constant coverage. For the deposition experiments at the slowest rates, the limiting step is the time between the arrival of atoms at the surface, so that the initial slope of the $\sqrt{3}$ spot intensity is less than the slope of the constant coverage intensity. As the deposition rate is increased, the atoms are more efficient in forming a given domain size. Different microscopic processes are involved in the two experiments and it is not clear if, by measuring a faster growth rate during deposition, we can safely assume the existence of non-thermal mobility. Although the experiment is not conclusive about the additional diffusion mechanism, it at least does not contradict the conclusion reached from the scaling of the oscillations at 150 K. We would like to briefly discuss some of the different microscopic processes involved in the two experiments. Although their relative contribution is not known, it would be clear that, for certain conditions, the annealing experiment should grow faster than the deposition experiment. In this case, the nonthermal diffusion can be safely deduced from the comparison. Blocking effects are expected to be present during annealing, where atomic motion is inhibited by the presence of other

atoms. Since the comparison is based on the initial slope of the growth, when the domains are only a few atoms wide, such blocking effects should play a minimum role. During constant deposition experiments the atoms need to travel longer distances to initiate domain nucleation. In addition, repulsive interactions lower the diffusion barrier for the annealing experiment. Since all these effects favor the annealing experiment, and we observe the opposite at high enough deposition rates, it is safe to conclude that, under these conditions, another source of mobility must be present in the deposition experiment. Furthermore if the intensity is plotted vs coverage (instead of time) then a family of different curves is obtained (no scaling is obeyed) with the curve corresponding to the lowest deposition rate highest in intensity, thus confirming that when thermal diffusion is present no scaling holds.

The three experiments we have presented previously point (with unequal deductive strength) to a strong nonthermal mechanism that is partially responsible for the Ag mobility on Si(111). Most likely, it is the only mechanism present at the lower temperatures where oscillations are observed. Although it is not possible to uniquely identify the nature of the mechanism based only on the experimental evidence presented, we can further specify it if we use theoretical studies on Si growth. Molecular-dynamics simulations[8] of the growth of Si on Si(111) with the use of realistic Si-Si potentials have shown that the energy transfer between a deposited Si atom and the substrate is inefficient because of the strong Si-Si covalent bond. Oscillations in the kinetic energy of the incoming atom have been observed, which imply that the atom retains enough of its energy for significant time, and allows for lateral jumps to be performed.

In summary, we have studied the growth modes and mass-transport mechanisms of the Ag/Si(111) system by using RHEED quantitative spot analysis. We have extended the temperature range for growth mode characterization to 150 K and have found that, at this temperature, short-lived oscillations suggest the growth mode is quasi-layer-by-layer indicating significant adatom mobility. We have experimentally ruled out thermally activated diffusion as the mechanism responsible for this low-temperature mobility. This is based on a new method of data analysis, which searches for scaling in the oscillations for different fluxes, that can be used in general to evaluate the role of thermal diffusion, especially on systems that no information is available from other transport experiments. By comparing the final domain sizes of the $\sqrt{3}$ formed at several deposition rates, and the initial growth of deposition vs annealing experiments, we can identify further evidence for this nonthermal diffusion. One possible mechanism involves the inefficient energy transfer between a deposited atom and the substrate which can be transformed into lateral motion. It is clear, by considering systems[2-5] which have displayed low-temperature oscillations, that the detailed microscopic growth mechanism is system dependent and one cannot invoke a simple universal picture to explain low-temperature growth.

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