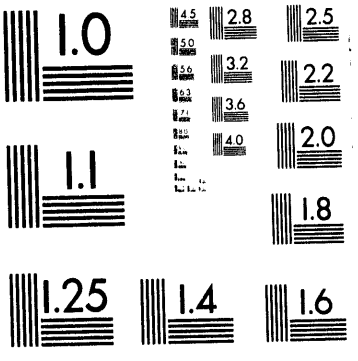
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RHEED Studies of the Nucleation, Growth, and Mobility of Ag Atoms on the SI (111) 7 x 7 Surface

by Kelly Ryan Roos

thesis submitted to Iowa State University

Ames Laboratory, U. S. DOE

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DISCLAIMER

RHEED studies of the nucleation, growth, and mobility of Ag atoms on the Si(111)7x7 surface

Kelly Ryan Roos

In charge of major work: Michael C. Tringides
From the Department of Physics and Astronomy
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The low temperature and flux dependent growth of ultrathin Ag films on the Si(111)7x7 surface is studied with Reflection High-Energy Electron Diffraction (RHEED). The grazing incidence geometry of RHEED allows for an incident molecular beam normal to the surface, and makes it an ideal surface probe for studying ultrathin film growth in real time. Short-lived oscillations in the diffracted intensity are observed during Ag deposition at 150 K, indicating quasi-layer-by-layer growth mediated by adatom mobility. When the 150 K growth is performed over a wide range of deposition rates F, the peak intensity is observed to scale, i.e. I(Ft) depends only on the total amount deposited, which implies thermally activated diffusion is absent at 150 K. Scaling is not obeyed at higher temperatures (T≥473 K) for the growth of the $\sqrt{3}x\sqrt{3}R30°$ ($\sqrt{3}$) superstructure. Testing for scaling of the diffracted intensity constitutes a new experimental method which can be applied generally to determine if thermal diffusion is active at a particular temperature. Scaling is consistent with a constant diffusion length R_0, independent of substrate temperature and deposition rate. The presence of a non-thermal diffusion mechanism (responsible for the constant diffusion length R_0) is confirmed by monitoring the flux dependence of the $\sqrt{3}$ superstructure growth during deposition at T≥473 K. At these temperatures the total diffusion length R is given by $R=R_0+(4Dt)^{1/2}$, where $(4Dt)^{1/2}$ is the thermal component. A non-zero intercept R_0 is found by plotting the peak intensity $I_p^{1/2}$ (a measure of the average domain size) vs. deposition rate $F^{-1/2}$ (F^{-1} is proportional to the

available diffusion time). From the FWHM of a low coverage (0.2 ML) $\sqrt{3}$ spot, an estimation of 50 Å is made for a lower bound of the magnitude of R_0. A likely mechanism responsible for this non-thermal diffusion distance is transient mobility, where an atom's condensation energy is inefficiently transferred to the lattice, and contributes to lateral motion before equilibration.

RHEED studies of the nucleation, growth, and mobility of Ag atoms on the Si(111)7x7 surface

by

Kelly Ryan Roos

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I shall not go into several lines of sentimental mush in acknowledging the patient and tenacious support my wife, Renée, has shown over the past six years simply because several lines of sentimental mush stated in an acknowledgment section of a thesis dealing with adatom mobility could not even begin to properly express the deep love, appreciation, and gratitude I feel for her. So I'll simply say thanks! I know it was tough sometimes, but thanks for hanging in there with me. And thank you too, Rebi, for understanding (yeah, right!) when I didn't have time to read you books.

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GENERAL INTRODUCTION

An Explanation of the Dissertation Organization

This dissertation consists of four papers which have been submitted for publication in scholarly journals. A general introduction including this format explanation and a literature review which sets up the problem precedes, and a general summary which discusses the results follows the four papers. The list of references cited in the general introduction and the general summary appears at the end of the dissertation.

Literature Review

The growth of ultrathin films on atomically clean surfaces is a subject of great interest to experimentalists, as well as theoreticians, involved in work ranging from practical device applications to fundamental research in physics and chemistry of surfaces. Problems of particular interest, especially in light of the recent technological shift from micro- to nanoelectronics, are what happens to incoming atoms when they are adsorbed on the surface from the gas phase, and how efficiently can they be manipulated to form optimal atomic structures. Since the quality of a grown film depends greatly on what happens to the individual atoms as they arrive at the surface it is imperative that the various atomic processes involved in crystal growth be fully understood. In the spirit of contributing to this understanding this study has been undertaken.

The main aspect of ultrathin film growth addressed in this work is the mobility of adatoms on the surface. It is traditionally believed [1] that the only source of adatom mobility is the mechanism of thermally activated diffusion which is normally described as a

random walk performed by atoms hopping over a diffusion barrier. From the random walk result [2], the average distance R traveled by a single adatom, from the landing site, is given by $R=(4Dt)^{1/2}$, where D is the temperature dependent diffusion coefficient, and t is the diffusion time. Since the process is thermally activated, D has the form $D = D_0 \exp\left(-\frac{E_d}{kT}\right)$, where E_d is the diffusion barrier, T the substrate temperature, and k the Boltzmann constant. D_0 is the prefactor which, for typical single atom diffusion, is $D_0 = \frac{1}{4}a^2\nu \approx 10^{-4}\ \mathrm{cm}^2/\mathrm{sec}$, where a (≈3 Å) is the lattice constant, and ν (≈10^{13} Hz) is the frequency of vibration of the atom in the potential well. During deposition of atoms onto a surface, the time t is the average time an adatom is allowed to diffuse from its adsorption site to the point where its motion is terminated by its incorporation into growing nuclei. The allowed time t is therefore inversely proportional to the flux F, or the rate at which atoms are deposited onto the surface (i.e., the faster atoms arrive at the surface, the sooner will a diffusing adatom encounter another atom or cluster of atoms).

This simple picture of adatom mobility should lead to the following results for ultrathin film growth. If deposition is performed on a substrate at a temperature which is high enough so that diffusion of adatoms is fast, the growth of the film should then be 2-dimensional; atoms are nucleated to form clusters, and the clusters grow by spreading out laterally over the surface. If the atoms are so mobile that all those which land on top of growing clusters can traverse the distance to the growing cluster edge and hop down to the lower level, then the film will grow perfectly in a layer-by-layer mode, periodically changing from smooth to rough at the growth front. Perfect layer-by-layer growth is practically impossible to achieve since close to completion of the first layer, the clusters are extremely large (growing clusters have coalesced to form very large ones), and it is probable that nucleation will take place on top of the growing layer before it is fully occupied. However, even for imperfect layer-by-layer growth, where more than one level is

simultaneously occupied, at least initially there is a periodic change in the morphology from rough to smooth as the growth proceeds.

If deposition is performed at substrate temperatures which are low enough so that adatoms are unable to overcome the diffusion barrier, then the adatoms will not move from the site at which they are adsorbed. In this case, the growth will be 3-dimensional in nature, characterized by islands growing normal to the surface, and by monotonically increasing roughness at the growth front.

It is clear in this picture that the rate of deposition F should play an important part in deciding the average cluster size, and therefore the cluster density, in a given layer before coalescence, near the completion of the layer, acts to smooth it out. Relatively high deposition rates are expected to effectively shorten the distance adatoms diffuse before aggregation and produce smaller average cluster sizes, while relatively low rates are expected to allow adatoms to diffuse over longer distances so that the number of clusters formed will be smaller and the average cluster size will be larger than for the case of higher deposition rate. It is important to note that the deposition rate should also be crucial in deciding the mode of growth, whether 2-dimensional or 3-dimensional, since, for sufficiently high F, the adatom diffusion length is effectively zero because of immediate aggregation, and the situation is then the same as that for low temperature 3-dimensional growth. However, until recently [3,4] the role of the deposition rate has not been explored experimentally to the same degree as the role of the substrate temperature; typical growth experiments were performed at different temperatures with the same deposition rate. In order to understand whether these intuitive expectations described above are empirically verified, another major theme of this work, along with exploring the role of adatom diffusion, is the flux dependence of the growth of ultrathin films.

To summarize: 2-dimensional layer-by-layer, or quasi(imperfect)-layer-by-layer, growth should occur for high substrate temperatures where adatoms are mobile, and deposition rates which are not too high, with varying rates of deposition leading to varying cluster densities within a forming layer, and 3-dimensional island growth should occur for low temperatures where adatoms are immobile, and for temperatures where adatoms are potentially mobile but where they are deposited at a rate which is sufficiently high to effectively quench out their mobility.

However, recent experimental results have clearly violated this traditional picture of ultrathin film growth. A 2-dimensional growth mode has been observed during growth in several different epitaxial systems [5-7] at substrate temperatures (77-150 K) where adatoms should not be thermally mobile under the influence of thermally activated diffusion. These results suggest that another mechanism, different from thermal diffusion, operates to drive adatom mobility in these experiments.

Two mechanisms have been proposed to explain the observation of adatom mobility in the absence of thermal diffusion. One, so called "funneling" [8], suggests that due to binding site constraints, atoms cannot adsorb to the steep faces of islands which have formed as a result of inactive thermal diffusion, and are required to "funnel" down to fill in lower levels. The result would be a certain degree of mobility and quasi-layer-by-layer growth characterized by very small 3-dimensional islands at the growth front. The other explanation proposed [5] to explain low temperature growth involves the condensation energy, and has come to be known as transient mobility. If an atom is to be adsorbed onto the surface it must dissipate a small amount of thermal energy kT_s (~0.1 eV), where T_s is the temperature of the source, and also a substantially larger (2-3 eV) condensation energy. It has been proposed [5] that this large excess energy is dissipated by the lattice over a finite time of several picoseconds, and converted into translational kinetic energy which can carry

the atom across the surface. The distance traveled would thus depend on how fast equilibration occurs. There exists a good deal of other experimental evidence supporting the existence of transient mobility [9-11]. Because the condensation energy is so large, this mechanism can account for the experimental results; however, there is also evidence against it. In Molecular Dynamics simulations [12] of low temperature single metallic atom depositions on fcc(001) metallic surfaces, it was found that transient mobility does not operate, while similar simulations [13] of a Si on Si(111) system reveal a large degree of lateral motion because of prolonged equilibration and inefficient energy transfer. Also, in a recent low temperature Field Ion Microscope study [14] of metallic atom condensation on Ir(111) showed no evidence for transient mobility-the metallic atoms remained at the site at which they were adsorbed. It is clear from these results that the existence of transient mobility is still a controversial subject, and whether transient mobility is present may depend on the specific system.

Because the bulk of low temperature epitaxial growth studies [3,5-7] has involved metallic fcc/fcc systems, we have chosen to perform growth studies on a metal/semiconductor system, Ag/Si(111), to study low temperature and flux dependent growth, to see if thermal diffusion operates in this system at low temperature (150 K), and, if not, to identify alternate mobility mechanisms. These results will be compared with those of other studies to identify the factors controlling low temperature growth on specific systems. Ag/Si(111) has been studied extensively in the literature [15], but no work on the flux dependence and low temperature mobility has been performed quantitatively for this system. It is well suited for ultrathin film growth studies as no interdiffusion of Ag into the bulk Si occurs, and there is no alloying of the Ag and Si atoms at the interface. The Si(111) surface reconstructs during sample cleaning to form the 7x7 surface geometry which is characterized

by large terraces (>1000 Å). This distance is large compared to the average diffusion length of Ag adatoms at low temperatures (T≤300 K), so steps do not play a role.

In order to study the low temperature and flux dependence of the growth, an experimental technique must be employed which can effectively determine the growth mode. Reflection High-Energy Electron Diffraction (RHEED) [16] is such an experimental tool and a RHEED diffractometer has been designed and built for these studies. In RHEED, a high energy electron beam is incident at grazing angles toward the surface. The low grazing angle ensures that the beam penetration is minimized so that only the top 2-3 layers are probed. The grazing angle geometry allows the installation of a molecular beam source normal to the surface so that the evolution of a growing film can be monitored in *real time* during growth.

The intensity of the specularly reflected beam of the RHEED pattern has been found [17] to oscillate in time during the growth of a film which grows in the layer-by-layer mode with a period which is equal to the time required to deposit one ML on the surface. It is not yet clear what exactly microstructurally causes the RHEED oscillations [18], whether they are due to diffuse scattering because of an oscillating step density during layer-by-layer (or quasi-layer-by-layer) growth, or to interference between different layers which oscillates as the layer occupation oscillates. Regardless of their cause, it is generally accepted that the presence of RHEED intensity oscillations during growth implies a 2-dimensional growth mode and significant adatom mobility. It has been also shown [19] that for 3-dimensional island growth the RHEED specular intensity decays monotonically without oscillations so that the time dependence of the RHEED intensity can effectively distinguish between 2-dimensional and 3-dimensional growth.

In addition to distinguishing whether 2-dimensional and 3-dimensional growth is present, it is important to develop methods to address the puzzling question of why there is

quasi-2-dimensional growth at temperatures where no significant thermal mobility is present. If in the Ag/Si(111) system under study many intensity oscillations are observed, we can clearly conclude that the growth is 2-dimensional, and that adatoms are mobile. However, if the temperature is low enough so that thermal mobility is ruled out, then we need an additional test to determine whether "funneling," transient mobility, or some other yet unknown mechanism operates. For this additional test, the FWHM of the diffraction spots, which is inversely proportional to the average island size on the surface, can be used. As mentioned above, the funneling mechanism is expected to lead to the growth of several successive layers, and high degree of lateral roughness, so that if sharp diffraction spot FWHM's (<25% of the Brillouin zone) are observed, funneling can be ruled out.

At this point a further test is required to determine if transient mobility operates. As described below the best way to test for transient mobility is to perform the low temperature growth experiments at different deposition rates, and compare the amplitude of the observed oscillations. We expect that under transient mobility, the adatoms will be mobile during the equilibration time, and will stop when the condensation energy has been entirely dissipated. Since the equilibration (even slow equilibration due to inefficient transfer of energy to the lattice) takes place on the order of picoseconds, transient mobility should be characterized by a constant adatom diffusion length. There should therefore be no change in the shape and amplitude of the intensity oscillations for growth at different deposition rates since, for deposition rates that can be attained experimentally, the average time between the arrival of two consecutive atoms in a small vicinity on the surface is large compared to picoseconds, and the different deposition rates will not be able to force the formation of varying sized islands within a given layer. The implication then is that the diffracted intensity should scale with coverage (i.e., the intensity is dependent only on the total amount deposited) if transient mobility operates, while for growth under thermally activated diffusion, changes in

the shape and amplitude of intensity oscillations should be observed when comparing growth at different deposition rates.

As will be seen in the papers, this scaling result has been observed in this work, and it is concluded that testing for scaling of the diffracted intensity constitutes a new experimental method which can be applied generally to determine if thermal diffusion is active at a particular temperature. It is also concluded that transient mobility is the likely mechanism present in this system at low temperatures. In the papers, other experiments are also described which further support the presence of transient mobility.

PAPER I

RHEED STUDIES OF MASS TRANSPORT AND LOW TEMPERATURE GROWTH OF Ag/Si(111)

RHEED Studies of Mass Transport and Low Temperature Growth of Ag/Si(111)

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ABSTRACT

We have studied the growth modes and mass transport mechanism of the Ag/Si(111) system by using RHEED 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 non-thermal diffusion is further confirmed from the comparison of the initial growth rates and the final FWHMs attained at different deposition rates for the Ag/Si(111)-($\sqrt{3}$ x $\sqrt{3}$)R30° system.

INTRODUCTION

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 2-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)-($\sqrt{3}$ x $\sqrt{3}$)R30° (hereafter $\sqrt{3}$) 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 $5x10^{-11}$ Torr having a RHEED diffractometer and a Knudsen cell to evaporate Ag. The relative deposition rate was measured with a quartz crystal monitor, and the absolute rate in terms of oscillations observed at low temperatures. 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].

RESULTS AND DISCUSSION

Figure 1 shows typical results for the behavior of the specular intensity during Ag growth for a deposition rate of ~1/125 ML/sec. For T = 483 K and T = 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 figure 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 either 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 that we are unable to check for the phenomenon of reentrant [5] oscillations 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

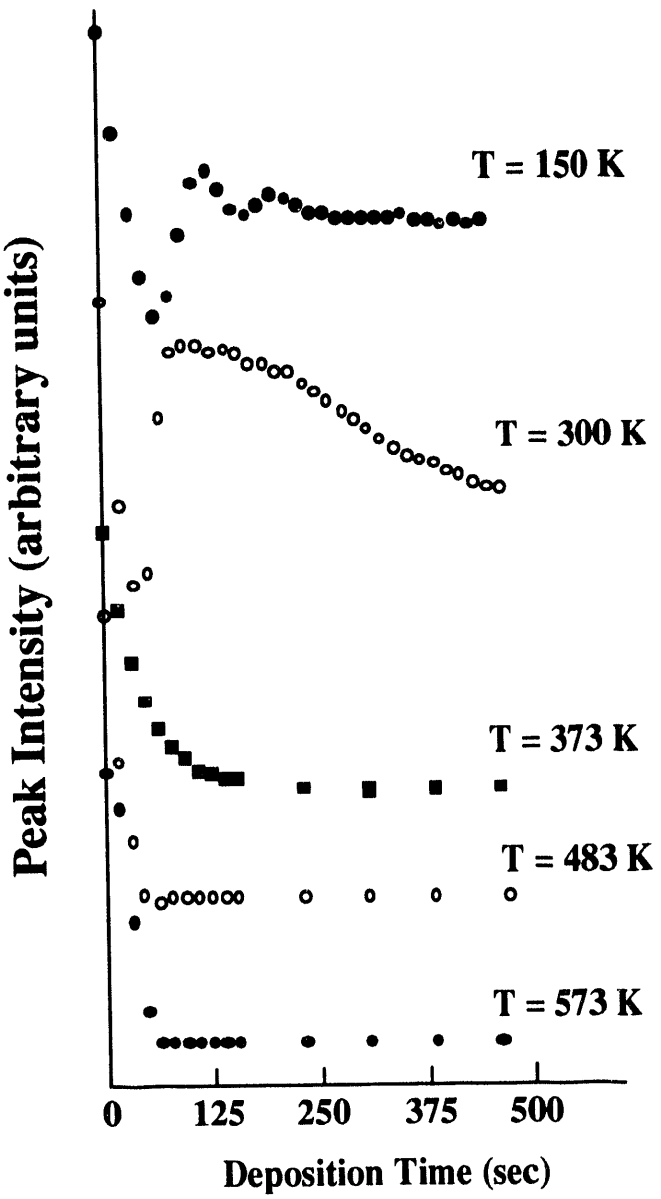

Figure 1 The normalized peak intensity of the specular beam vs. deposition time for different substrate temperatures at a deposition rate of ~1/125 ML/sec.

the assumption, based on [11], that thermally activated diffusion is not present for T≤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 flux. At higher 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 decrease. 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.

The results of the analysis to test for scaling are shown in figure 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 between the Ag

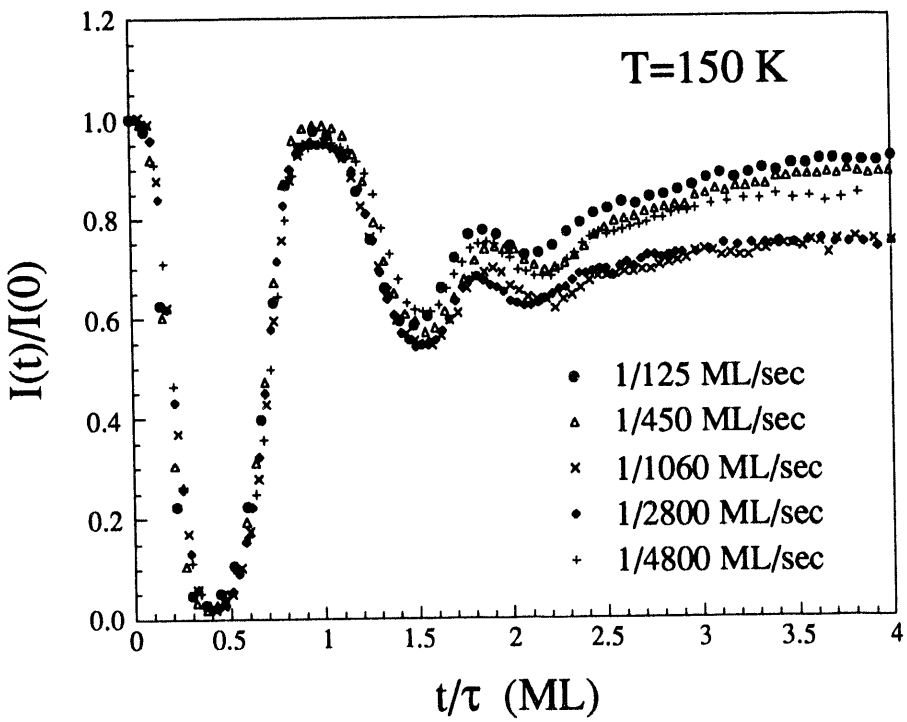

Figure 2 The normalized peak intensity of the specular beam, I(t)/I(0), vs. t/τ for different deposition rates at a substrate temperature of 150 K. τ is the period of the first oscillation. The number and amplitude of oscillations (since I(0) is the same) are flux independent.

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 adsorbed on Al(110) by measuring with STM the size of oxygen islands formed, and during Xe deposition on Pt(111) [12] 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 were operating then the FWHM of the $\sqrt{3}$ spots, measured after 1 ML of Ag has been deposited on clean substrates at T>473K, would be flux dependent, with narrower FWHMs observed at lower deposition rates because the atoms would have more time to join the growing domains. As figure 3 shows, for Ag deposited at a substrate temperature of 473 K with rates varying from 1/150-1/4800 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 scale of 10^{-12} seconds. The deposition rate was varied by only a factor of ~50 because of the 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

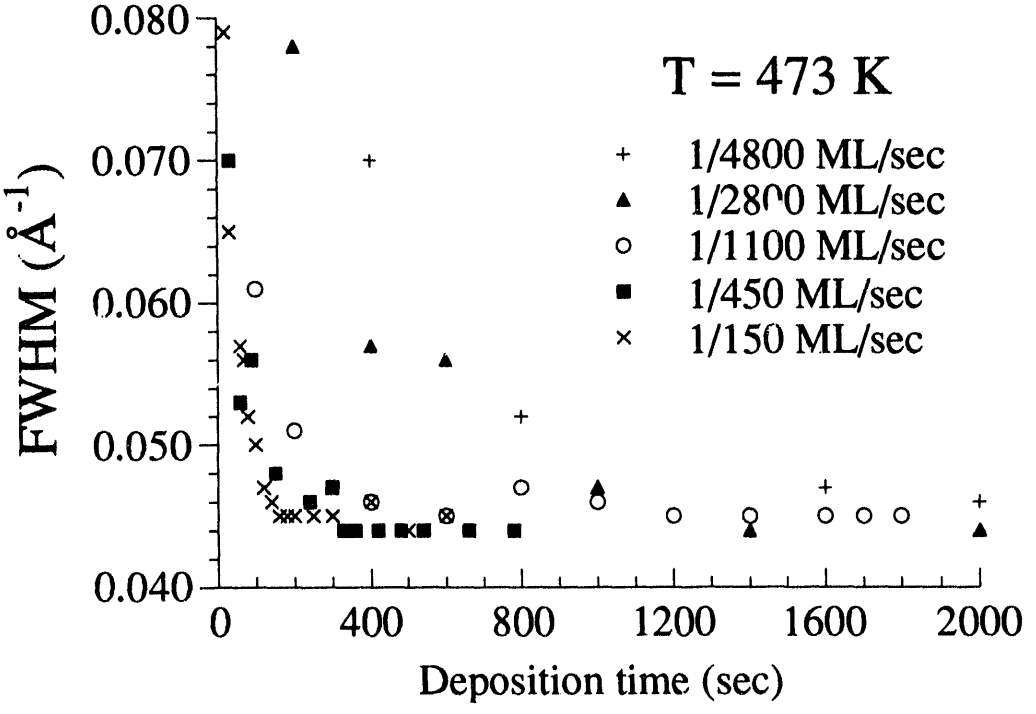

Figure 3 The FWHM of the (1/3,1/3) order spot of the $\sqrt{3}$ superstructure RHEED pattern vs. time for different deposition rates at a substrate temperature of 473 K. The final FWHMs are flux independent.

not simply limited by the supply of atoms: atoms join the growing domains at a constant rate (the atom arrival rate) because diffusion is so 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, 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 figure 4, this is not the case.

If we deposit a constant amount of Ag onto the clean Si(111)-(7 x 7) surface at a low temperature and then upquench the substrate to a temperature that lies 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 non-thermal 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 seconds 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 (1/3,1/3) order spot of the $\sqrt{3}$ diffraction pattern is plotted in figure 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 non-linear time dependence if the comparison is restricted to the 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 $\sqrt{3}$

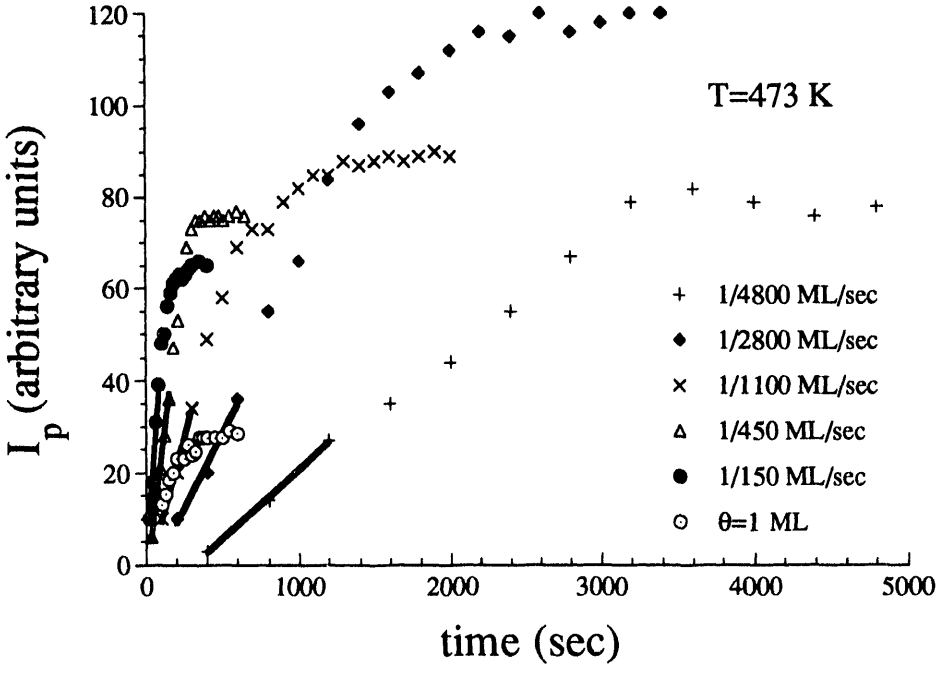

Figure 4 The peak intensity of the (1/3,1/3) order spot of the $\sqrt{3}$ superstructure RHEED pattern vs. Ag on Si(111) deposition time for different deposition rates at a substrate temperature of 473 K. The set of data labeled θ=1 ML is the peak intensity of the (1/3,1/3) spot vs. time after deposition 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.

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 non-thermal 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 flux experiments the atoms need to travel longer distances to initiate domain nucleation and, in addition, repulsive interactions lower the diffusion barrier for the annealing experiment. Since all these effects favor the annealing experiment, and we observe that the deposition rate of formation is faster than the annealing rate of formation at high enough deposition rates, it is safe to conclude that another source of mobility must be present in the deposition experiment. If the intensity is plotted vs. coverage (instead of time) then a family of different curves is obtained (no

scaling) 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 non-thermal 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 of Si deposition. 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.

CONCLUSION

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 for which 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 non-thermal 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] that 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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PAPER II

LOW TEMPERATURE AND FLUX DEPENDENT GROWTH PHENOMENA IN Ag/Si(111)

Low Temperature and Flux Dependent Growth Phenomena in Ag/Si(111)

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ABSTRACT

We have studied the growth of the Ag/Si(111) system for substrate temperatures in the range 150-473 K by using RHEED quantitative spot analysis. We have extended the temperature range for growth mode characterization to 150 K and found short-lived RHEED oscillations at this temperature that can be attributed to significant adatom mobility. By studying the flux dependence of the growth at 150 K, the diffracted intensity is found to be a function of the total amount deposited, and is independent of the deposition rate. This result implies that the average distance Ag atoms travel from the point of adsorption to the point where they are nucleated as part of the growing film is a constant value. This result and a comparison of the growth of the $\sqrt{3}$ structure at different deposition rates with the $\sqrt{3}$ growth during annealing of a constant coverage suggest that the adatom mobility observed in the low temperature experiment is non-thermal in nature. We suggest one possibility for the identity of this non-thermal mechanism.

INTRODUCTION

The growth of atomic structures on surfaces is predominantly controlled by surface diffusion. Surface diffusion is expected to be strongly temperature dependent, and typical barriers (E_d>0.3 eV) practically prohibit any mobility at low temperatures (T<150 K). Substantial growth, therefore, should not be present at these low temperatures unless some highly unusual transport mechanism operates. Several systems studied [1-5] with diffraction and STM, *have* surprisingly shown evidence for low temperature mobility in the range T=4-150 K. It is still not clear what the origin of this surprising mobility is. These results oppose the conventional wisdom that low temperature growth produces rough, columnar films. Theoretical work [6,7], in attempting to solve this puzzle, produced opposing results, which possibly depend on the details of the interatomic potential or the equilibration scheme (method of maintaining the constant substrate temperature) employed.

When adatoms *are* mobile, regardless of the substrate temperature, the deposition rate becomes an important parameter in the growth of atomic structures. Until recently [8,9] the role of the deposition rate has been largely ignored experimentally; typical growth experiments were performed at different temperatures with the same rate. Nucleation theory [10], however, clearly shows that the rate at which atoms are deposited onto the surface should greatly affect the growth. Relatively high deposition rates are expected to effectively shorten the distance adatoms diffuse before aggregation, while relatively low rates are expected to allow adatoms to diffuse over longer distances. The net result then should be different degrees of morphological roughness in films grown at different rates. In [8], a transition from a 2D to a 3D growth mode was actually observed by growing Pt/Pt(111) films at successively lower deposition rates.

Since most of the low temperature work [1,2], as well as the flux dependent experiments [8,9], have been performed on metallic systems, we concentrate, in the current study, on Ag/Si(111), a highly heteroepitaxial metal/semiconductor combination. Ag/Si(111) has been well studied with a multitude of techniques [11]; however, information about the low temperature and deposition rate dependent growth, and the diffusion coefficient of Ag on Si(111), is still not available. We present here the results of the low temperature (150 K) and high temperature (473 K, where the $\sqrt{3}x\sqrt{3}R30°$ superstructure forms) growth of Ag on Si(111)7x7 for different deposition rates in the range 1/125-1/4800 ML/sec (1 ML=$7.83x10^{14}$ atoms/cm^2). RHEED quantitative spot profile analysis is used in these experiments. Information about the film morphology can be obtained by monitoring the time dependence of the angular distribution of the diffracted intensity during growth.

The experiments were performed on a P-doped (0.05 Ω cm, 9.5x3.5x0.25 mm) Si(111) sample with the 5 keV electron beam incident parallel to the [110] direction. The base pressure in the UHV chamber was typically better than $5x10^{-11}$ Torr. The sample was cleaned by heating resistively to 1470 K for 2 minutes followed by slow cooling to RT from 1170 K. This procedure produced a sharp Si(111)7x7 RHEED pattern, and was followed before each experimental run was performed. The temperature was monitored with a W-Re thermocouple spot welded to one of the Ta clips which held the sample. For low temperature experiments, the sample could be cooled to 150 K via a Cu braid connected to a LN_2 dewar. At higher temperatures, the thermocouple measurement was checked with an optical pyrometer, and agreement between the two temperature probes was better than 95%. The absolute deposition rate was estimated from the first oscillation period at low temperatures, and from the observation of the onset of Ag(111) crystallite diffraction features near 1 ML [12]. A quartz crystal monitor was used to calibrate the relative rate, which is the important calibration for the flux dependent experiments we present. The

whole diffraction pattern, or selected regions, were collected with a video camera, processed with an image acquisition board, and stored on an IBM-AT computer to be further analyzed with specifically developed software. Peak intensity, FWHM, and integrated intensity can be extracted from the images.

RESULTS AND DISCUSSION

For the experiments below 473 K, we monitor the decay of the specular beam intensity of the RHEED pattern. Figure 1 shows the results of the growth for three different substrate temperatures in the range 150-373 K at a rate of 1/125 ML/sec. The specular beam peak intensity is plotted as a function of deposition time, and as expected, it decays because of destructive interference between the substrate and the overlayer. What is really surprising is the presence of a few short-lived oscillations at 150 K which disappear when the film is grown at room temperature (RT) and above. The RT growth mode for this system has been identified [12] before as Stranski-Krastanov, with small-sized Ag(111) crystallites of different rotational orientation formed near 1 ML. STM images [13] of submonolayer amounts of Ag deposited on Si(111)7x7 at 363 K and 403 K have also demonstrated the presence of Ag islands. In figure 2 we show the intensity distribution along the [112] direction (parallel to the shadow edge of the RHEED pattern) as a function of the momentum transfer vector $S_{[112]}$ for a constant value $S_{[110]}$=0.047 $Å^{-1}$, just outside of the specular beam, at different Ag coverages deposited at 150 K. At 1 ML Ag(111) crystallite features are seen centered near ±2.5 $Å^{-1}$, the value expected for the Ag(111) lattice constant. The Ag film grown at 150 K is thus structurally similar to that grown at RT. The intensity at $S_{[112]}$=0 is due to the broadening of the specular beam with increasing coverage. For the clean 7x7 surface (θ=0) the intensity at $S_{[112]}$=0 is due to Kikuchi lines (features resulting from inelastically scattered electrons) which disappear around 0.4 ML. The onset of the Ag(111) features actually occurs near 0.77 ML where, as seen from figure 2, they are barely above the background intensity. At this coverage the Ag(111) crystallites appear on the RHEED pattern as very diffuse streaks which are barely visible to the eye. Since considerable diffusion should be present in the system above RT, the disappearance of the

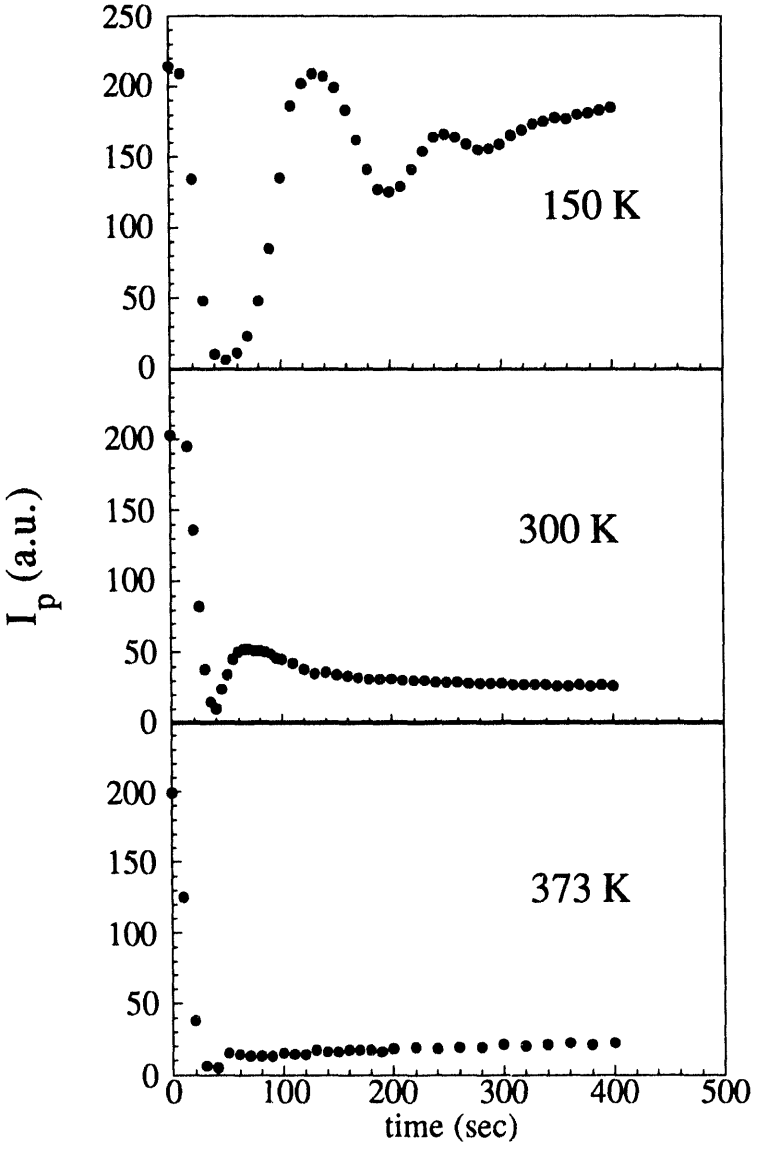

Figure 1 The specular beam peak intensity I_p as a function of deposition time during growth of Ag on the clean Si(111)7x7 surface for three different substrate temperatures. The deposition rate is ~1/125 ML/sec and the electron beam is incident at an angle of 1.6° directed along the [110] azimuth.

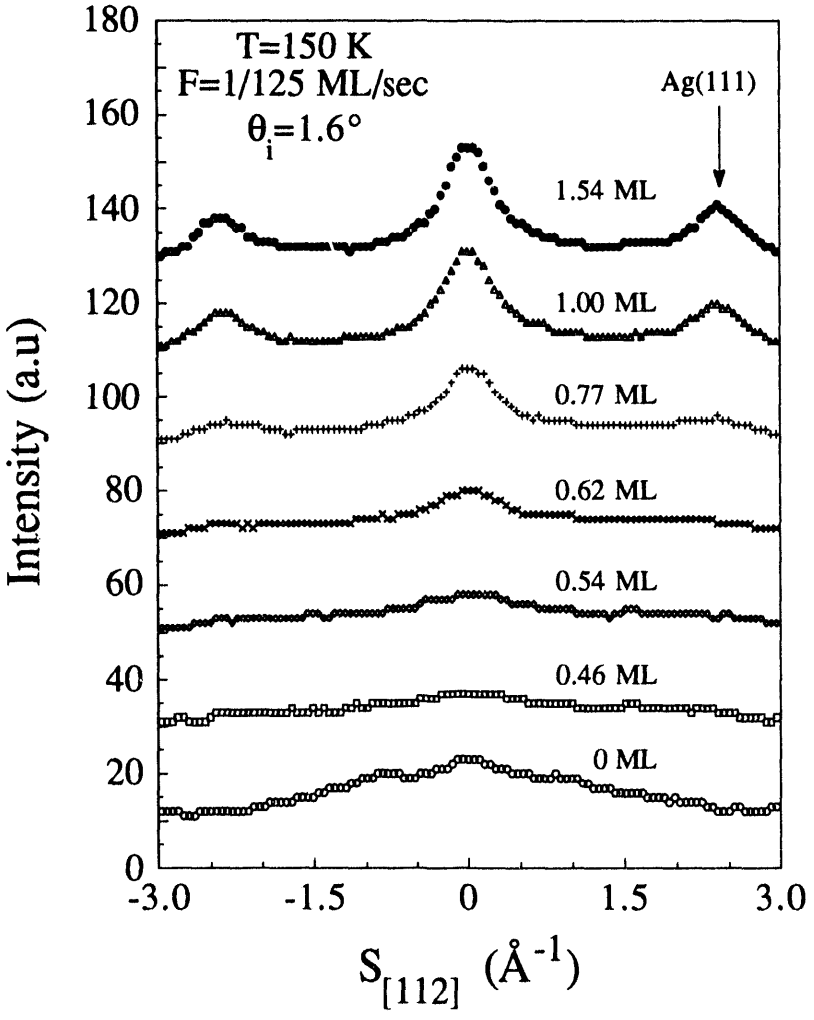

Figure 2 The intensity distribution as a function of $S_{[112]}$ along $S_{[110]}$=0.047 $Å^{-1}$ for different coverages deposited at 150 K. The formation of Ag(111) crystallites is observed for $\theta \geq 0.77$ ML.

short-lived oscillations at T>300 K in figure 1 results most likely from the adatoms being quickly incorporated in the growing islands. The puzzling question is why do we observe the 2-3 oscillations at 150 K. It is clear that if deposition was random, with no thermal diffusion, no oscillations would have resulted [14], and a monotonic decrease in the peak intensity, and broadening of the FWHM of the specular spot would have been observed. Figure 3 shows the spot profile of the specular beam for a coverage 0.69 ML deposited at a rate of 1/125 ML/sec. The profile is observed to have two components: a central-spike, and a wide, low intensity diffuse component. The low intensity diffuse part contains information about the Ag overlayer island distribution and the substrate separation size distribution, while the central spike merely reflects the long-range order of the crystal surface [15]. As pointed out in figure 3 the FWHM of the diffuse part is ~3 % of the Brillouin zone which is indicative of large Ag islands. Such a narrow FWHM would not have resulted if no adatom mobility were present during the growth. Similarly sharp features are present at other coverages over the duration of the observed intensity oscillations.

Despite the extensively studied processes on this system it is still not clear what is the diffusion barrier of Ag on Si(111). The kinetics of the formation of the $\sqrt{3}x\sqrt{3}R30°$ ($\sqrt{3}$) have been extensively studied [11] previously as well as the nucleation of large Ag islands on top of the $\sqrt{3}$ layer. These studies measured a diffusion activation energy E_d=0.40 eV for Ag on top of the $\sqrt{3}$. When several layers are deposited one deduces a much slower diffusion of Ag on Si(111) than the diffusion of Ag on $\sqrt{3}$, or on top of Ag islands, as seen with SEM micrographs [11]. The surface diffusion coefficient on the bare Si(111) can be obtained if submonolayer amounts are deposited. As mentioned above, submonolayer amounts of Ag have been deposited [13] on bare Si(111)7x7, and we employ a simple relation from nucleation theory [16], which relates the island density N to the diffusion

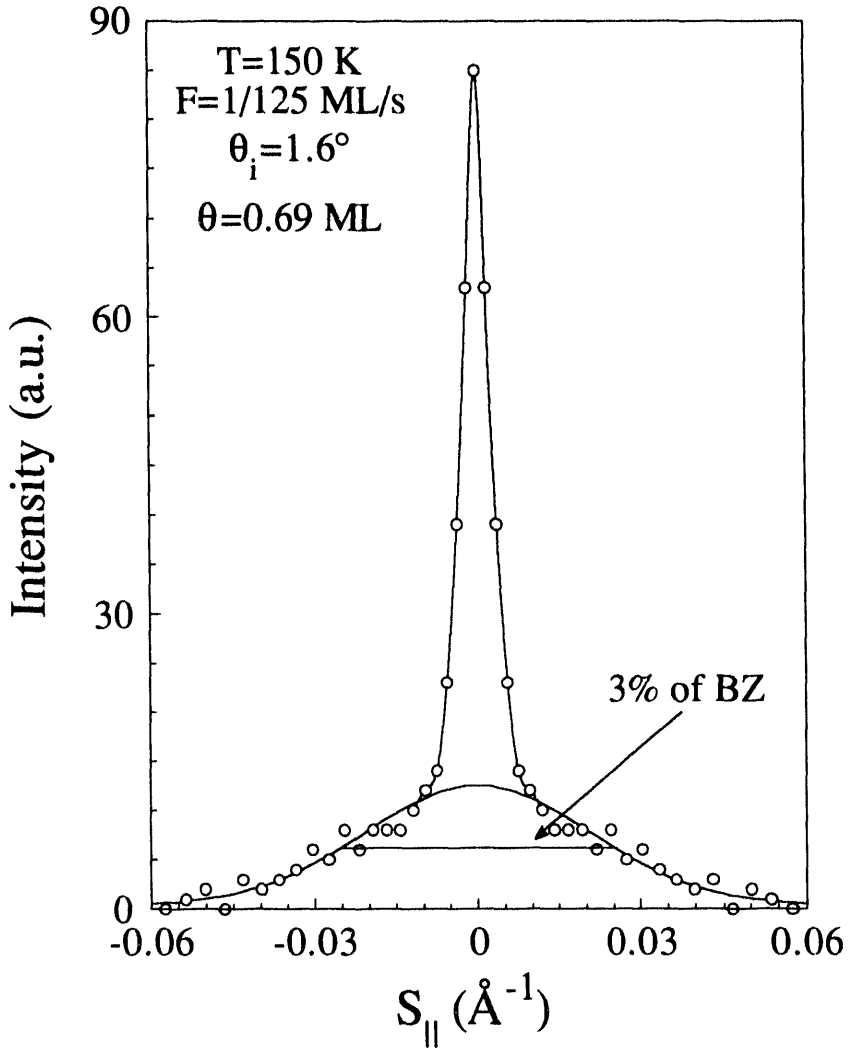

Figure 3 The intensity distribution of the specular spot, perpendicular to the shadow edge, as a function of the parallel component of the momentum transfer at a Ag coverage of 0.69 ML deposited on a 150 K substrate. The horizontal line represents the FWHM of the diffuse component of the profile and extends over ~3% of the Brillouin zone.

coefficient D, to estimate the diffusion barrier from the images shown in [13]. From [13] we estimate $N \cong 9.2 \times 10^{12}$ cm^{-2} at 363 K, and this implies a barrier of E_d=0.62 eV. This is in excellent agreement with the Si interatomic potentials used [17] in modeling of the bulk properties. If this value is used for T=150 K the typical diffusion distances expected are negligible over the time scale of the experiment. It is clear that the observed short-lived oscillations are not expected in a system with this high of a diffusion barrier, if thermal diffusion alone operates.

It is important to ask whether the presence of the (7x7) reconstruction, the diffraction features of which disappear during Ag deposition, has any effect on the growth, and therefore whether the observed specular beam decrease is a result of the change in the reconstruction and not the morphology of the growing film. Diffraction probes provide only statistical information about the film, so we do not have any information about possible changes within the substrate unit cell during the Ag deposition, which requires local microscopic experimental techniques. Previous work [18] on the growth of the $\sqrt{3}$ superstructure explained the evolution of the $\sqrt{3}$ spot under the assumption that the diffracted intensity of the $\sqrt{3}$ results from the changing domain morphology of the overlayer without any substrate complications associated with the disappearing (7x7) reconstruction. This is in agreement with recent studies of different aspects of the Ag/Si(111) system with STM [13] and LEEM [19] which do show that the (7x7) reconstruction remains intact during the deposition of Ag at temperatures higher than 150 K. Also, the growth of the GaAs(100) is performed in the presence of the (2x4) reconstruction, and still, the diffracted intensity variations have been exclusively attributed [20] to the changing film morphology and not the reconstruction. Since reconstructions are local rearrangements and the (7x7) is visible in our experiments during at least the deposition of almost the first Ag layer (the (7x7) spots do not change position but become diffuse and eventually disappear as Ag

deposition proceeds), it is safe to assume that the uncovered substrate remains unchanged, and the loss of specular beam intensity is a result of the Ag film only.

Another complication that can affect the interpretation of RHEED intensity variations is the possible onset of a transmission pattern. The main results of our paper are based on deposition of 1-2 Ag layers so it is irrelevant whether the observed pattern is thought of as a reflection or transmission pattern. Most likely, it is a reflection pattern because the specular beam remains unchanged, and the FWHM of the specular beam as shown in figure 3 is still narrow as the intensity increases toward its maximum value at 1 ML. (The narrow central spike is also still observed over the duration of the intensity oscillations) If transmission were to indeed occur at such a low coverage the crystals through which the electron beam would transmit would be extremely thin, and sharp features would be absent from the diffraction pattern. It is also in agreement with reference [12] that the growth mode at 300 K is a special case of the layer-by layer mode so at least the first layer wets the Si substrate and no transmission should occur.

It is important to develop an intrinsic test of identifying whether thermal diffusion is important in a low temperature experiment without relying on independent experiments, especially when data are not available to provide the value of the diffusion barrier. If we vary the deposition rate in a growth experiment then we expect the quality of the film to be sensitive to the rate at which the film is grown if thermal diffusion operates. At low deposition rates, we expect better grown film morphology for a given deposited Ag amount than for the same amount deposited at a higher rate, so the amplitude of a given oscillation, especially the first one, should be greater (if thermal diffusion operates, and is relatively slow-which would be the case for low temperatures), the lower the deposition rate. In addition, the intensity at the completion of each monolayer is expected to increase towards its initial clean surface value for perfect layer-by-layer growth attainable only at lower

fluxes. Because of increased nucleation on top of forming layers, deposition at higher rates (higher than rates where perfect layer-by-layer growth should occur) should lead to two or more levels being simultaneously occupied and growing, and cause a damping of the oscillation amplitude. The determination of the shape of the oscillations for different deposition rates when thermal diffusion operates is still an open theoretical problem, but for the present argument it is sufficient to merely state that different oscillation shapes should result for different deposition rates. We have studied the growth of Ag/Si(111) over a range in flux of 1/125-1/4800 ML/sec. As expected, the growth is slower at the slower deposition rates, but when the data are plotted in the form $I(t)/I(0)$ vs. t/τ, as in figure 4, where $I(t)$ is the value of the specular beam intensity at time t and τ is the period of the oscillations, it is remarkable, and highly non-trivial, that all the curves, at least for the first oscillation which is fully determined by diffusion of Ag on Si(111), collapse onto a single universal curve. This scaling implies that the film morphology simply depends only on the deposited Ag amount, irrespective of the deposition rate, and that thermal diffusion must be absent. The deposition rate variation was based on a cell temperature calibrated initially with a crystal quartz monitor, and later confirmed with the inverse of the observed period of oscillation. It is also important to note that the current experiment is not based on an absolute calibration rate, but only on the relative rate, as seen by the increase in the time required for the first intensity maximum, and the confirmation of an invariant oscillation shape.

One can pursue the puzzle further: if thermal diffusion does not operate in this system, what other non-thermal mechanisms can account for the observations? "Funneling" has been suggested [21] for the growth of fcc/fcc systems where binding site constraints within growing layers force correlation between atoms in lower layers before more layers can become populated. This results in very small islands and a rough surface because the correlation process is not perfect, and several successive layers are occupied simultaneously.

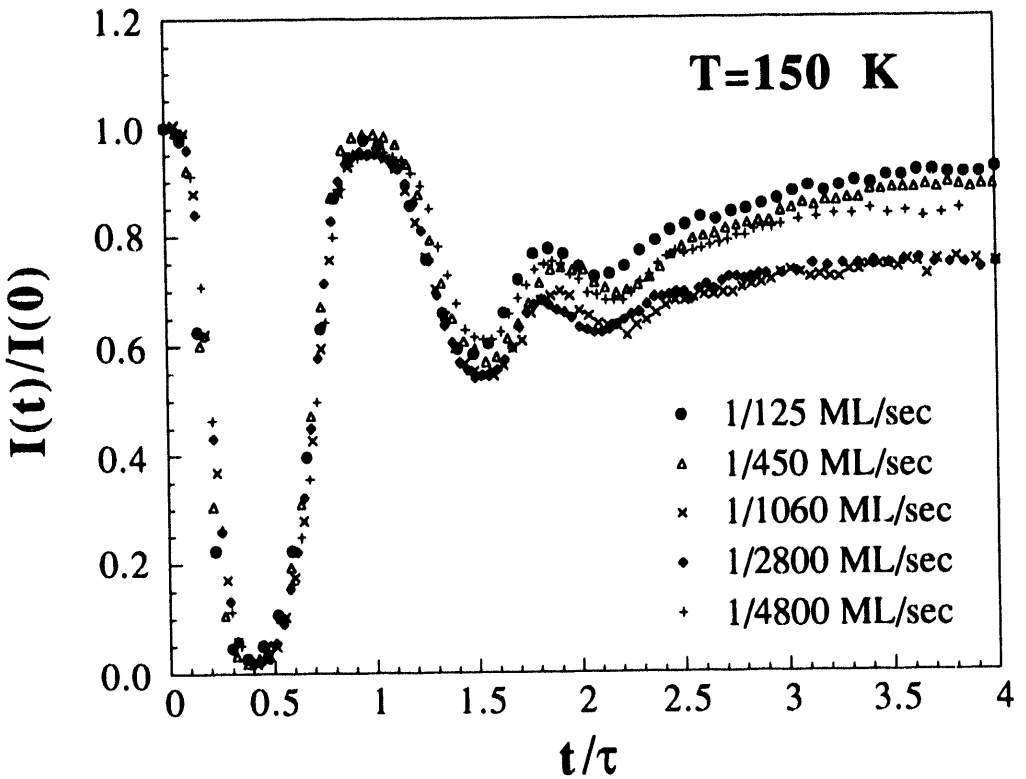

Figure 4 The normalized peak intensity of the specular beam during Ag deposition at 150 K for five different deposition rates plotted as a function of t/τ, where τ is the period of the first oscillation in each of the different growth experiments. Plotting the data in this manner facilitates comparison of the oscillations for different deposition rates.

A diffraction pattern should therefore reveal broad features and a dramatic drop in the intensity of the oscillation maxima during growth. Because of the sharp specular profile in figure 3, implying a smooth film and large domains, funneling can be ruled out as a possible mass transport mechanism in this system at 150 K. It is also not clear how the binding site constraint applies to Ag/Si(111).

Another possibility for the non-thermal mechanism is based [1] on the excess energy (2-3 eV) of an atom in the gas phase that needs to be dissipated to the substrate before the atom is adsorbed on the surface. If the transfer process is very inefficient, because of the substrate rigidity, then this can result in energy being retained by the atom causing it to hop several lattice sites away from the point of impact. Since this is a highly non-equilibrium process, completed on the scale of atomic relaxations-several picoseconds, it should result in a lateral displacement R_0 which is constant with respect to the macroscopic diffusion times available at deposition rates typically used in experimental growth studies. A constant displacement R_0 is consistent with the observed scaling at 150 K because, in the absence of thermal diffusion, the average island size L would simply be a function of the number of atoms available to form the islands (Ft), which in turn implies that the specular beam intensity, depending on L, would show scaling I(Ft) since F is proportional to the inverse of the period τ. It has been shown with Molecular Dynamics [7] that the stiffness of the Si lattice resulting from the high curvature of the interatomic potential and the 2-D topology of the potential energy surface in the unit cell can account for the inefficient energy transfer in this system. In general, scaling of the shape of the oscillations, even the first one is highly remarkable, and implies a constant, but not necessarily finite, diffusion length R (no diffusion, or infinitely fast diffusion are also consistent with the observations). Zero diffusion is ruled out by the observation of oscillations, and infinitely fast diffusion is ruled

out by several experiments, especially the formation of the $\sqrt{3}$ which is not formed instantaneously at higher temperatures than 150 K.

It is also important to mention that the observed structure in the specular beam variation with time is extremely sensitive to the angle of incidence of the electron beam. This is shown in figure 5 where the growth at 150 K is shown for four different angles of incidence, clearly showing the shape of the oscillations, and, in particular, the ratio of the successive maxima depends on the angle of incidence. The ratio changes from being close to one to almost zero where the oscillations are not present at higher angles of incidence (θ_i=6.0°). Since the scaling experiment in figure 4 was performed for a fixed angle of incidence the scaling argument is not affected by this angular dependent phenomenon. We do not have an explanation for this angular dependence, although it is known from other studies [22,23] that the oscillations are very sensitive to the angle of incidence. It is not yet well understood what the cause of the variation is, whether it is due to the oscillating step density (with changes in atomic scattering factor for steps) or simply the variation of the phase factor at different levels within the kinematic approximation. Since this is a heteroepitaxial system other possible causes might be present as well. We should note also that the ratio of the periods of the first and second oscillations not only is not one, but actually varies slightly within figure 5. We don't understand this variation, but since the scaling argument is based only on the first oscillation, it doesn't affect the main argument, especially if the Ag crystalline morphology after 2-3 layers can be different.

We can extend our study further to test if the non-thermal component of the diffusion length is present at higher temperatures T>473 K, where the $\sqrt{3}$ is formed, since the energy involved is the condensation energy of the adsorbed atom, which is much higher than the substrate temperature change ΔT from 150 K to temperatures in the range where the $\sqrt{3}$ forms ($\frac{E_{condensation}}{k\Delta T} > 60$). We emphasize here that if the non-thermal diffusion

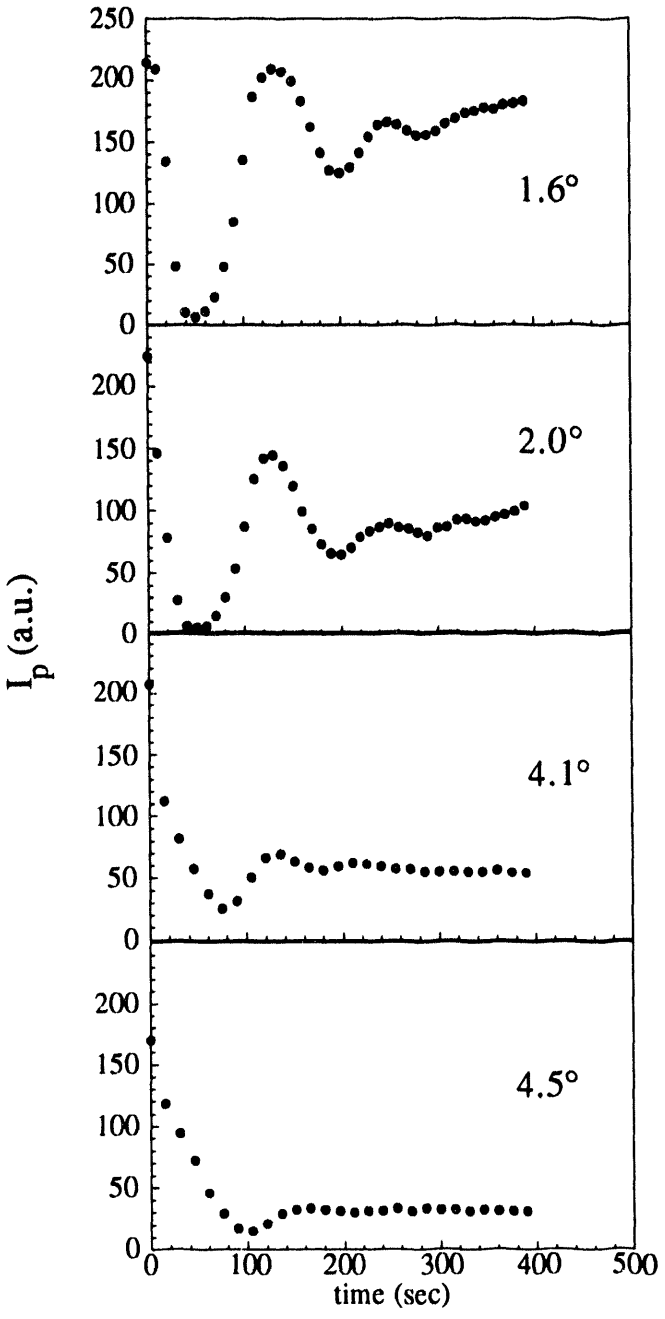

Figure 5 The specular beam peak intensity I_p as a function of Ag deposition time at 150 K for four different angles of incidence. The deposition rate is ~1/125 ML/sec for each.

component is present it will operate *along with* thermally activated diffusion to drive adatom mobility at these higher temperatures. For these high temperature experiments we monitor the time evolution of the fractional order $\sqrt{3}$ structure spots. Using the $\sqrt{3}$ superstructure has the advantage that a signal, solely dependent on the overlayer size distribution (without interference from the substrate size distribution as in the case with the specular beam) can be used to study the growth. We have studied the growth of the $\sqrt{3}$ structure at T=473 K for the same deposition rate range at which the growth at 150 K was studied. Figure 6 shows the peak intensity of the (1/3,1/3) order $\sqrt{3}$ spot as a function of deposition time for Ag deposited onto a substrate held at 473 K. We have also studied the growth of the $\sqrt{3}$ structure during the annealing at 473 K of two different coverages of Ag: 0.3 ML and 1.0 ML. For the annealing experiments, Ag was deposited onto the clean Si surface at 150 K. The substrate was then heated to 473 K, and the time evolution of the $\sqrt{3}$ structure observed. The peak intensity behavior of the (1/3,1/3) $\sqrt{3}$ spot during annealing is also plotted in figure 6. For all the experiments shown in figure 6 the angle of incidence was held at a constant 4.5° with the electron beam directed along the [110] direction. What is interesting in figure 6 is a comparison of the initial rate of formation of the $\sqrt{3}$ islands during annealing with the initial rate of formation of islands during deposition. In the annealing experiments thermally activated diffusion alone drives the adatom mobility. Since we observe (for sufficiently high deposition rates) that the rate of growth of $\sqrt{3}$ islands is faster under deposition than it is under annealing, this can be used as evidence of non-thermal diffusion being present during deposition. The comparison between the annealing and deposition might suggest that the annealing experiment will always be slower than the deposition experiment at high deposition rates, because the large number of atoms already on the surface during annealing would be expected to effectively block diffusion. However, if the comparison is restricted to $t \approx 0$ when blocking effects are negligible, it is possible (at least under the assumption of

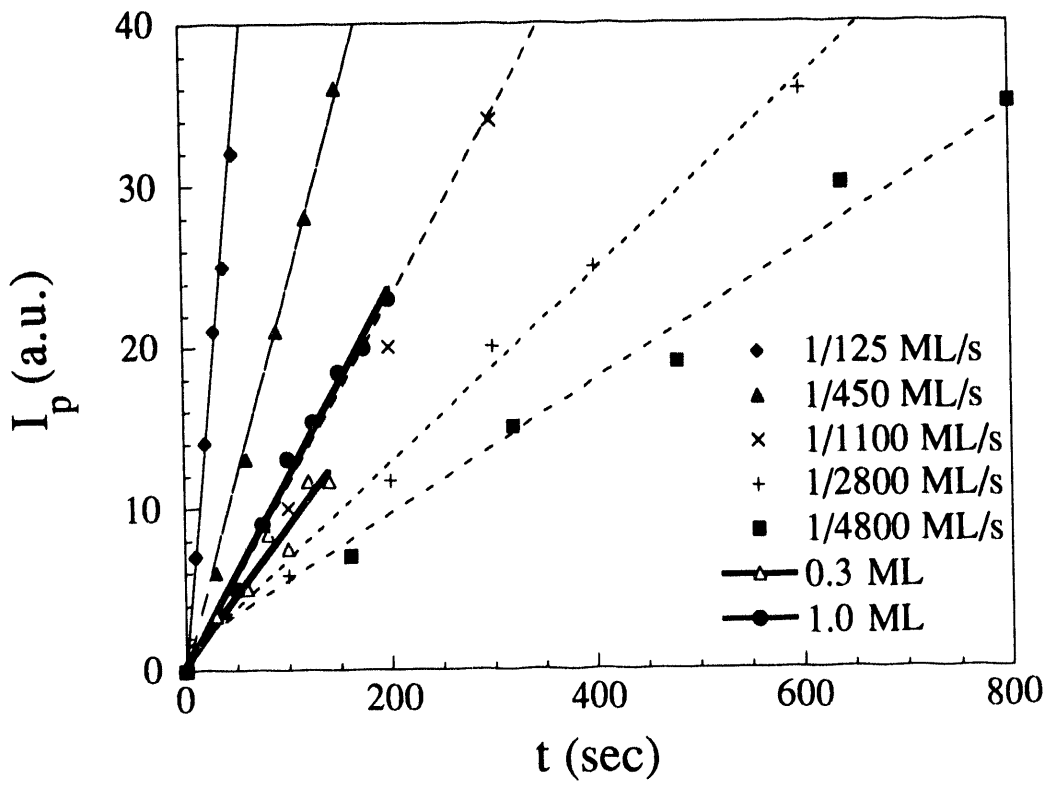

Figure 6 The peak intensity of the (1/3,1/3) order $\sqrt{3}$ spot as a function of deposition time for the growth of the $\sqrt{3}$ during deposition at T=473 K (1/125-1/4800 ML/sec) and for the growth during annealing at 473 K of a constant coverage of Ag deposited at 150 K. The thick lines are drawn to indicate the initial rate of formation of the $\sqrt{3}$ structure for the annealing experiments, and the thinner lines represent the rate of formation during deposition.

repulsive interactions ΔE between the Ag atoms) that the thermal diffusion in the annealing experiment would be faster than in the deposition experiment. The measured intensity can be assumed to be proportional to $I_p=NL^4$,where N is the island density and L is the average island size. Since $\theta=NL^2$ is the total amount of Ag then one has $I_p=\theta L^2$. Diffusion under the annealing experiment can be faster since $\frac{E_0-\Delta E}{kT_s} > \frac{E_0}{kT_s}$, where E_0 is the single particle diffusion barrier and T_s is the substrate temperature. That the domains in the deposition experiment grow faster than those in the annealing experiment implies $\theta_d L_d^2 > \theta_a L_a^2$. Since $\theta_d < \theta_a$ it follows that $L_d > L_a$, but since diffusion in the annealing experiment is expected to be faster, there must be an additional source of mobility in the deposition which is not present in the annealing experiment. This is consistent with the non-thermal component of the diffusion length invoked to explain the scaling of the specular beam at 150 K. That the rate of growth is faster during annealing of 1 ML than during annealing of 0.3 ML confirms that repulsive interactions are most likely present between Ag-Ag atoms. We can estimate the strength of the repulsive interactions that might be present because the $\sqrt{3}$ is not formed at T_a=150 K. We have $\frac{E_0-\Delta E}{kT_a} > \frac{E_0}{kT_s}$, which is valid if $\Delta E < E_0\left(1-\frac{T_a}{T_s}\right)$. This implies $\Delta E < \frac{2}{3}E_0$, consistent with repulsive interactions not being sufficient to form the $\sqrt{3}$ at the lower temperatures [11].

In figure 7 we have plotted, for the deposition experiments shown in figure 6, the peak intensity vs. θ, by converting the time axis to coverage (θ=Ft, where F is the deposition rate). We observe in figure 7 the expected result that the diffracted intensity does not scale with coverage when thermally activated diffusion operates. This is clearly different from the *scaling* observed at 150 K for the same variation of Ag deposition rate, and strengthens the conclusion that scaling is a useful indicator of whether thermal diffusion is present or not.

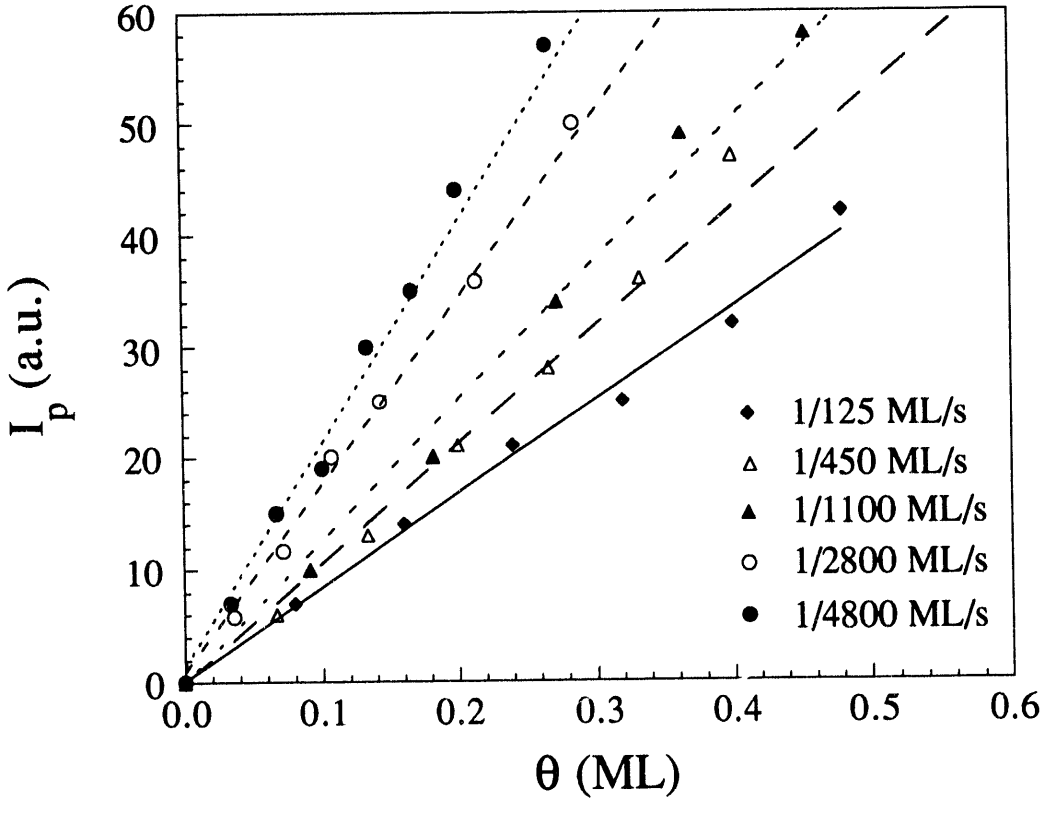

Figure 7 The $\sqrt{3}$ peak intensity plotted as a function of coverage for different deposition rates and a substrate temperature of 473 K.

Further evidence for the operation of a non-thermal mechanism can be found in figure 8, where the $\sqrt{3}$ spot profiles for five different 1 ML films grown at different deposition rates are shown. Though the peak intensity increases with decreasing deposition rate, the FWHM of each of the different profiles is the same within ±5%. Since the FWHM is inversely proportional to the average $\sqrt{3}$ domain size, this result implies that the average domain size is independent of the deposition rate. This suggests that the average diffusion length (the distance from the point of impact to the point where the adatom aggregates at high coverages) has a non-thermal component. Thermal diffusion is present during the formation of the $\sqrt{3}$ structure, and it is not clear how large the non-thermal component must be to explain the constant FWHM. This last experimental result is consistent with the main argument of this paper, but is much weaker evidence of the existence of non-thermal mobility.

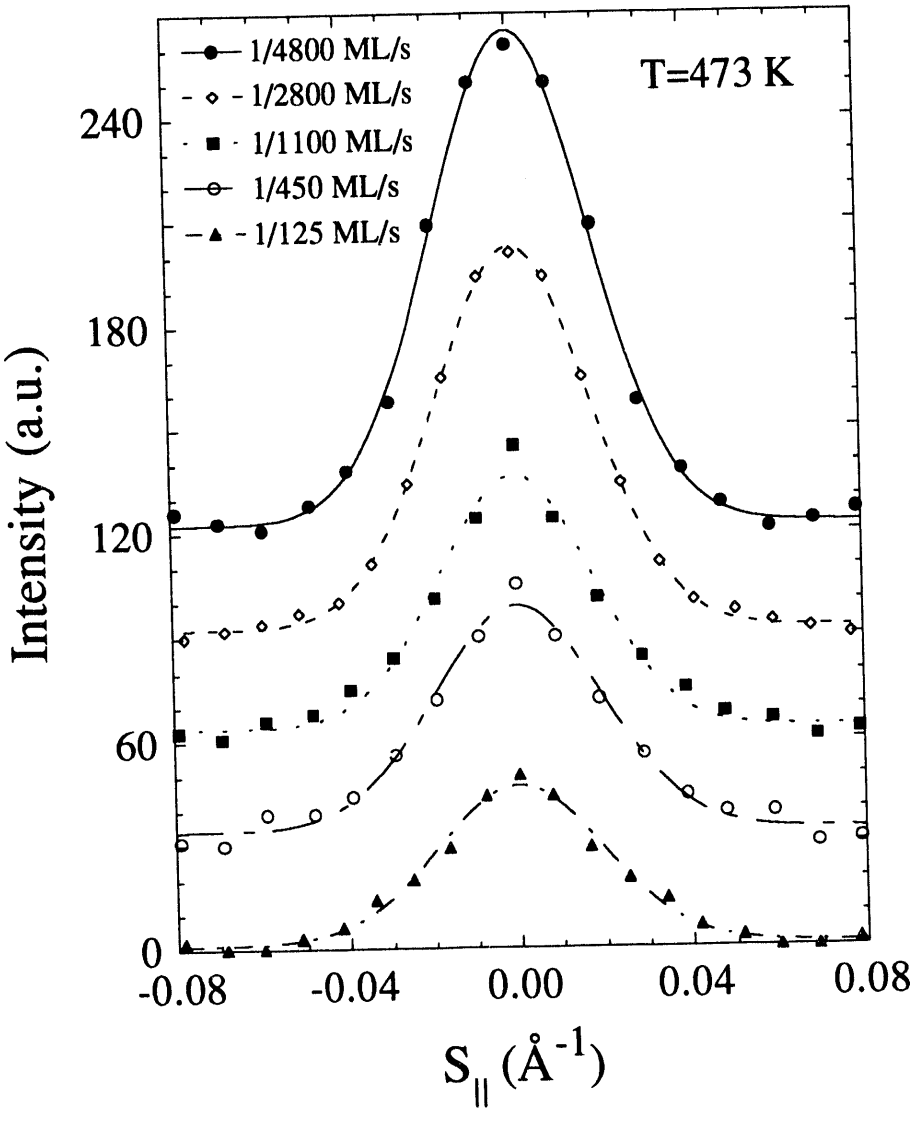

Figure 8 The $\sqrt{3}$ spot profiles for 1 ML films grown at different deposition rates at 473 K. The same FWHM for each profile indicates the $\sqrt{3}$ domains have an average size which is flux independent.

CONCLUSION

In summary, we have presented experimental evidence that non-thermal diffusion is present in the Ag/Si(111) system. It is based on the presence of short-lived oscillations at T=150 K that scale I=I(Ft) when the growth is performed as a function of deposition rate. Additional evidence for non-thermal diffusion is found in the growth of the $\sqrt{3}$ for T=473 K as a function of deposition rate. No scaling is observed for the $\sqrt{3}$ growth at different deposition rates, which strengthens the conclusion that the mobility observed at 150 K is non-thermal in nature. This technique (checking for scaling of the peak intensity) can be used in other experimental systems, where low temperature growth is observed, to determine whether the origin is thermal or non-thermal, especially in systems for which no independent measurements of the diffusion coefficient are available. We have also presented other high temperature experiments, which are not as decisive as the low temperature result in drawing the conclusion that non-thermal mobility operates, but nevertheless are consistent with this conclusion. We also note that a good deal of quantitative information about the growth in general can be obtained by studying the growth as a function of deposition rate.

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PAPER III

DIFFUSION OF Ag ADATOMS DURING THE Ag/Si(111) GROWTH

Diffusion of Ag Adatoms During the Ag/Si(111) Growth

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ABSTRACT

We have studied the growth of Ag on Si(111) to identify the growth mechanism over the temperature range T=150-723 K. We present evidence for non-thermal mobility from the scaling of the specular beam intensity decay at T≤300 K and from measuring the diffusion activation energy of the Ag/Si(111)-($\sqrt{3}$ x $\sqrt{3}$)R30° domain growth (for T>473 K) over a wide range of fluxes. We find the diffusion activation energy, E_d=0.24±0.05 eV, to be flux independent over a 30-fold increase in deposition rate, but half this value at lower fluxes.

INTRODUCTION

The growth of atomically controlled structures for the purpose of producing new materials with custom made properties has received great attention recently. The success or failure of the growth to form an optimal structure is determined by the interplay of the arrival rate and the mobility of the adatoms. Thus, the two important parameters which hold the key to successful fabrication are the rate of deposition and the substrate temperature. It is most common to search for the desired structures by varying the substrate temperature because of the strong temperature dependence of the adatom mobility. Less work has been performed by varying the rate of deposition to study surface growth. In the current study, we are interested in exploring the dependence of growth on both control parameters to deduce the underlying microscopic mechanisms that are crucially related to the quality of the grown structures. The experiments were performed with RHEED quantitative spot analysis which effectively monitors the evolution of a growing structure in real time.

We have concentrated our study on the heteroepitaxial system Ag/Si(111), a metal/semiconductor system, since most of the previous characterizations [1-4] of the grown structures have been performed on homoepitaxial metal/metal systems. There exists extensive work [5-11] on the Ag/Si(111) growth, obtained with several different techniques, to which we can compare the results.

The experiments were carried out in a UHV system with base a pressure of ~5×10^{-11} Torr. Ag was evaporated from a fully outgassed effusion cell, calibrated with a quartz crystal monitor, onto a well prepared Si(111)-(7 x 7) structure. The absolute deposition rate was obtained by observing low temperature intensity oscillations. Diffraction patterns were recorded with a high-gain video camera, digitized and stored in an AT-386 computer for further analysis. Selected regions of the pattern can be acquired to speed up the collection

time. The analysis involves the extraction of several quantitative measures (peak intensity, full-width-at-half-maximum (FWHM), and integrated intensity) of the diffracted spots as they evolve in time.

Previous studies of MBE growth with diffraction have produced phenomena that are still puzzling and controversial. The unexpected observation of low-temperature RHEED oscillations [4] has raised the question of what mechanism is causing the adatom mobility. It was suggested that the excess energy released by an atom after condensation is transferred into lateral motion that can transport the adatoms across the surface, the so-called transient mobility. Recent Molecular Dynamics simulations [12] of metal/metal deposition question whether transient mobility is operable on metal surfaces. At low temperatures, diffraction intensity oscillations were observed [1] for Pt/Pt(111) which disappear at intermediate temperatures and then reappear at high temperatures. This was explained by a two-barrier diffusion model, one at the center and the other at the edge of the islands. The latter decreases with the island size; thus, at lower temperatures, smaller islands nucleate and the edge-diffusion barrier is low enough to enhance interlayer mobility. The flux dependence in nucleation processes has been studied theoretically with a system of rate equations that incorporate all the relevant microscopic processes involved [5]. A scaling relation is predicted for the density of the observed islands at flux R, $N \propto R^p$, with the exponent, p, depending on the size of the critical nucleus [13]. Direct verification of this prediction with diffraction was reported recently on the Cu/Cu(100) system [14].

RESULTS AND DISCUSSION

Oscillations are surprisingly observed during Ag deposition at low temperatures. Figure 1 shows the decay of the specular beam as a function of time for various deposition rates at T=150 K. $t/\tau_{1/2}$ is used for the abscissa, where $\tau_{1/2}$ is the time it takes for the intensity to drop to half its initial value. It is clear that the data scale, i.e., there is only one characteristic time in the process, $\tau_{1/2}$. Scaling is also observed at temperatures up to 300 K, but with the number of oscillations decreasing with temperature. We can use this information to identify more detaiis about the growth mechanism. If thermal diffusion is the main driving force then the number of the observed oscillations would change as the deposition rate is varied. At higher growth rates the nucleation rate increases, and the surface is rougher. Thus, depending on the relative importance of interlayer and intralayer jumps between different levels, strong morphological flux-dependent changes in the growing structure are expected which will change the shape of the oscillations. The two-barrier model [1] suggested previously implies more oscillations and better layer-by-layer growth at higher growth rates because interlayer diffusion is enhanced with the increase in nucleation.

In general, if the diffracted intensity obeys scaling, $I\left(t / \tau_{1/2}^{n}\right)$, with a scaling exponent, n, different mechanisms will correspond to different values of n. For the present experiment, it is important to test if the exponent n=1 is compatible with the idea of transient mobility. The key difference between thermal diffusion and transient mobility is for the former, once an adatom is adsorbed on the surface it will move a distance $R \sim (Dt)^{1/2}$, where D is the surface diffusion coefficient, while, for the latter, the adatom will travel a fixed distance, R_0, after which, its excess energy is exhausted. The diffracted intensity measures the average growing domain size, L, which depends on the number of available atoms and

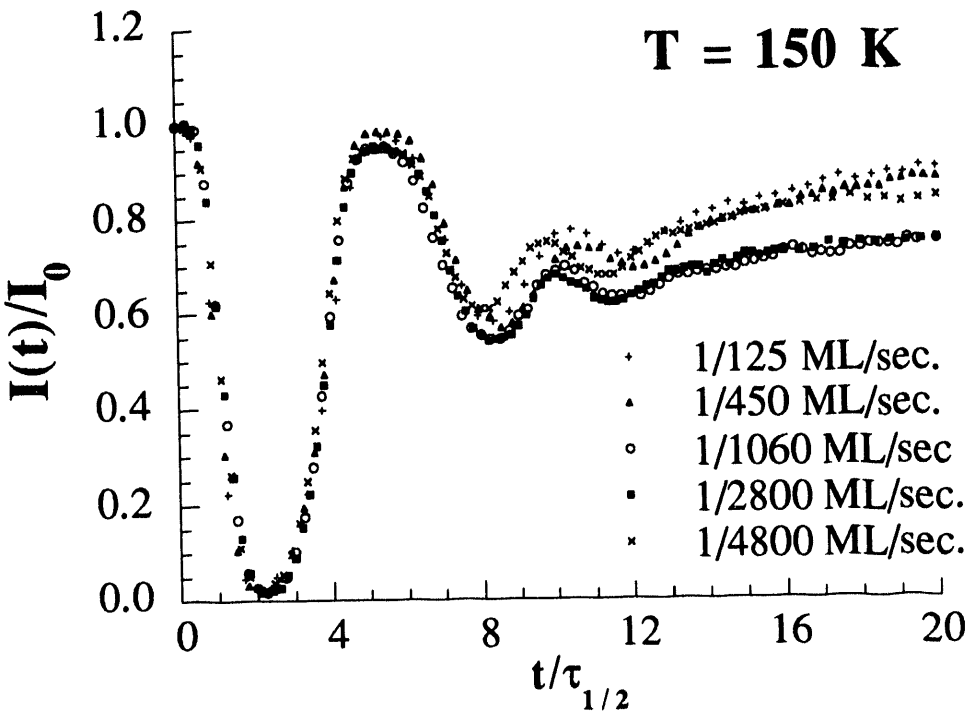

Figure 1 The normalized peak intensity of the specular beam vs. $t/\tau_{1/2}$ at 150 K for five different deposition rates.

the average distance they travel. So for the case of transient mobility, L is only a function of the product (Ft), where F is the growth rate, since R_0 is constant, thus confirming scaling; while, for the case of thermal diffusion, L has two time-dependent factors, the available number of atoms, (Ft), and the distance they travel, $(Dt)^{1/2}$. It is also likely that even for the case when both transient mobility and thermal diffusion are present, scaling of the data is possible if the thermal diffusion length is less than R_0. An STM study [6] of the initial nucleation of Ag islands after deposition on the Si(111)-(7 x 7) at T=363 K and T= 403 K reveals, for a coverage of 1/3, the formation of islands indicating Ag adatom mobility, but the relative importance of thermal diffusion vs. transient mobility cannot be determined since the islands were formed during direct deposition.

Because this is a heteroepitaxial system, it is possible to use information related only to the overlayer by concentrating on temperatures where the $\sqrt{3}$ structure is formed, and to search for evidence of transient mobility operating concurrently with thermal diffusion at these temperatures [15]. Figure 2 shows the final FWHM's of the $\sqrt{3}$ spot after depositing 1 ML of Ag for several different fluxes at T=473 K. These are flux independent and are larger than the instrumental FWHM. If only thermal diffusion is present on the surface then we would expect at lower deposition rates the final domain size to be larger, because the atoms will have more time to search and join growing domains; therefore, we should observe flux dependent final FWHM. If transient mobility is present and contributes a constant diffusion length, R_0, it can lead to a flux independent domain size. Is it possible that the constant FWHM's are limited by the atom supply because the deposition rates are so low that the diffusion time is instantaneous when compared to the deposition time? If this is the case, then the domains would grow at a constant rate, the rate of arrival of the deposited atoms, and the diffracted peak intensity would increase quadratic in time, $I_p \sim t^2$, because it is proportional to the square of the number of scatterers. Such quadratic time dependence is

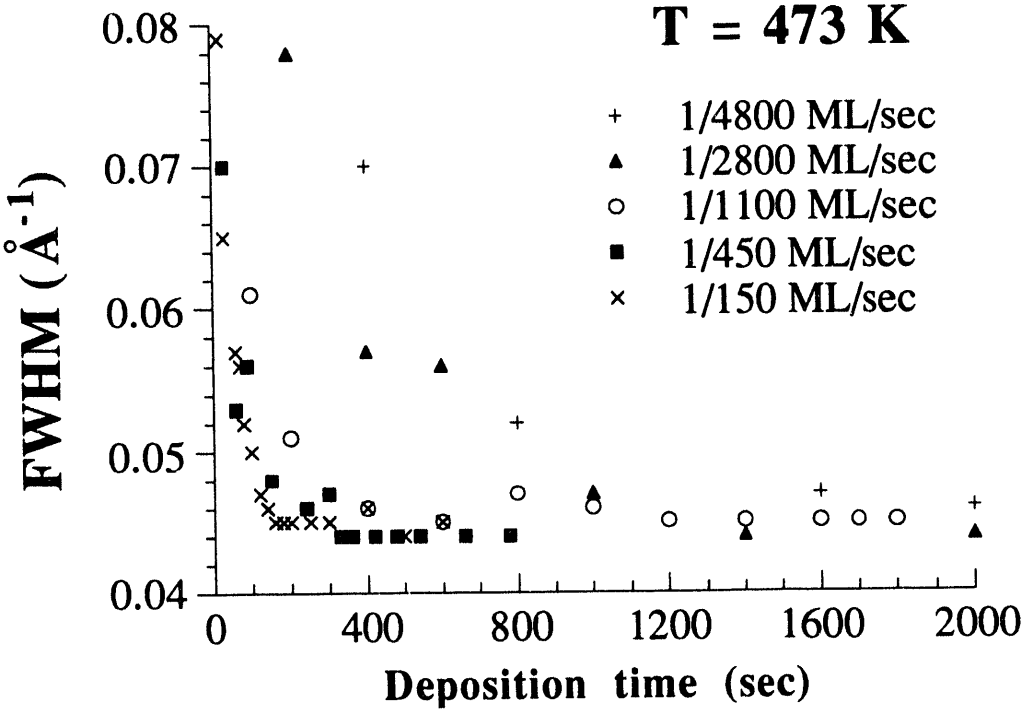

Figure 2 The FWHM of a $\sqrt{3}$ structure spot vs. Ag deposition time plotted for different growth rates and a substrate temperature of 473 K.

not observed as the linear time dependence in figure 3 shows. In addition, the measured activation energy should be zero if the growth is limited by the supply of atoms since, independent of temperature, the atoms reach the growing domains. As we describe shortly, we observe a non-zero activation energy.

The growth mechanism can be further identified if we monitor the initial growth of the $\sqrt{3}$ structure under constant Ag flux at T>473 K and, after annealing, at the same temperature, 1 ML of Ag deposited into a random configuration at 150 K. Both processes are determined by surface diffusion; during constant flux growth, the time dependence of the specular beam has been used to deduce [16] surface diffusion coefficients in the step flow regime and annealing experiments [17] of superstructures under constant coverage have been used to measure surface diffusion. At sufficiently high deposition rates ($\geq$ 1/1100 ML/sec) the domains grow faster under constant deposition than under constant coverage. This suggests that during deposition there is enhanced mobility over the expected thermal diffusion, that speeds up the formation of the domains. Since we are only measuring the initial rate of growth of the domains, with only a few atoms participating, blocking effects are not as important as for the late stages of the growth when more jumps are needed to add to the domain size. Although the deposited atoms need to move large distances to join other atoms, they are more efficient than those already adsorbed on the surface, which do not have to move as far, suggesting extra mobility.

A growth study of Cu/Cu(100) with He diffraction [14] has measured the island density from the separation of a superstructure satellite spot of the specular peak. An activation energy of E_d=0.28 eV was measured for monomer diffusion. Coalescence effects were ruled out. A more decisive experiment to rule out other many-body effects is to repeat the growth experiment as a function of flux. We have performed such experiments in this study. For constant deposition rate we vary the substrate temperature over the range T=473-

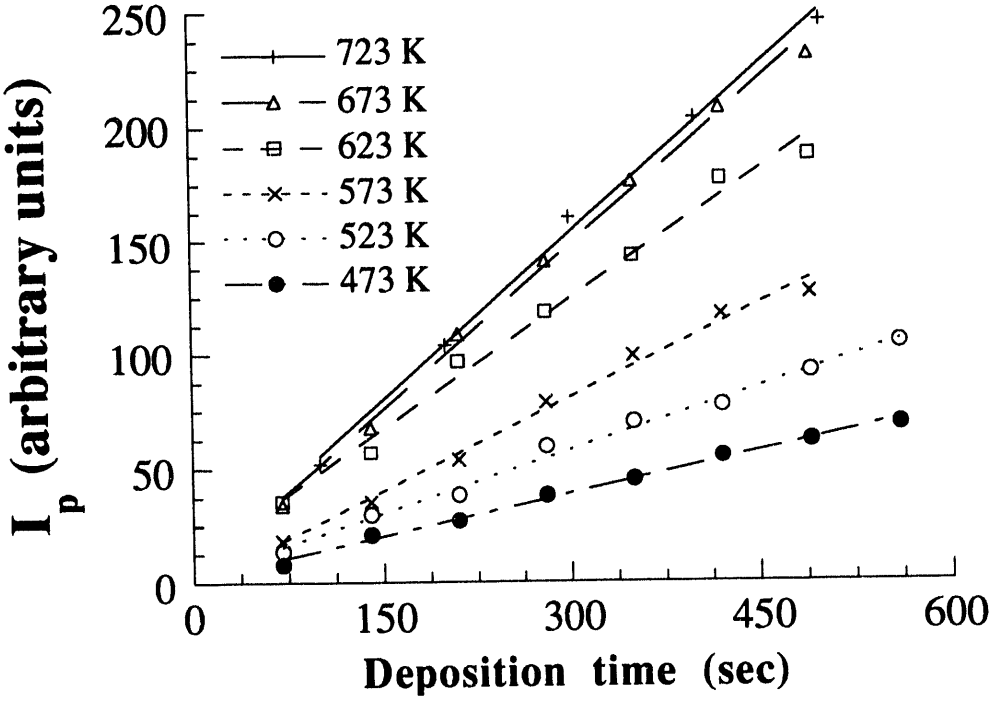

Figure 3 The peak intensity of a $\sqrt{3}$ structure spot vs. Ag deposition time for the initial growth of Ag for a deposition rate of 1/800 ML/sec and various substrate temperatures. Linear increase of the intensity with time is observed.

723 K to observe how the initial $\sqrt{3}$ rate of formation increases with temperature. Figure 3 shows the superstructure intensity vs. time for different temperatures with a constant growth rate. A linear dependence is followed and, from the initial slope vs. 1/T, an Arrhenius fit provides the activation energy. Although the functional form relating the diffusion coefficient, D, to the superstructure intensity increase is not known, we can assume that the intensity is a function of the unitless combination, Dt, which implies that D is proportional to the observed slope.

Our experiment uses not the island separation (which is proportional to the inverse of the square root of the island density) but the initial rate of growth of the $\sqrt{3}$ domains and it is not clear how the previous analysis [13] can be applied. Since one measures mainly the growth of islands, after the nucleation regime and atom attachment and detachment are more important, it is possible that we are more sensitive to clustering effects. Figure 4 shows how the activation energy, E_d, varies with Ag deposition rate. The measured activation energy, E_d=0.24$\pm$0.05 eV, is almost constant over the flux range of 1/30-1/800 ML/sec but drops gradually to half its value at lower growth rates. The measured values are below the diffusion activation energy expected [5], E_d>0.4 eV, and are consistent with the presence of transient mobility (coexistent with thermal diffusion) which suppresses the temperature dependence of the total diffusion length. The transient mobility diffusion length is temperature independent. The decrease in the activation energy with deposition rate is probably related to the formation of large $\sqrt{3}$ patches at the slower rates so the deposited atoms can land directly on top of them. The growth of the domains is accomplished with the diffusion and precipitation of the adsorbed atom on the already formed $\sqrt{3}$ islands, a process which is known [5] to have a lower barrier.

Recently reported changes [5] of the $\sqrt{3}$ coverage from 2/3 to 1 involve parameters which are outside those used in our experiment.

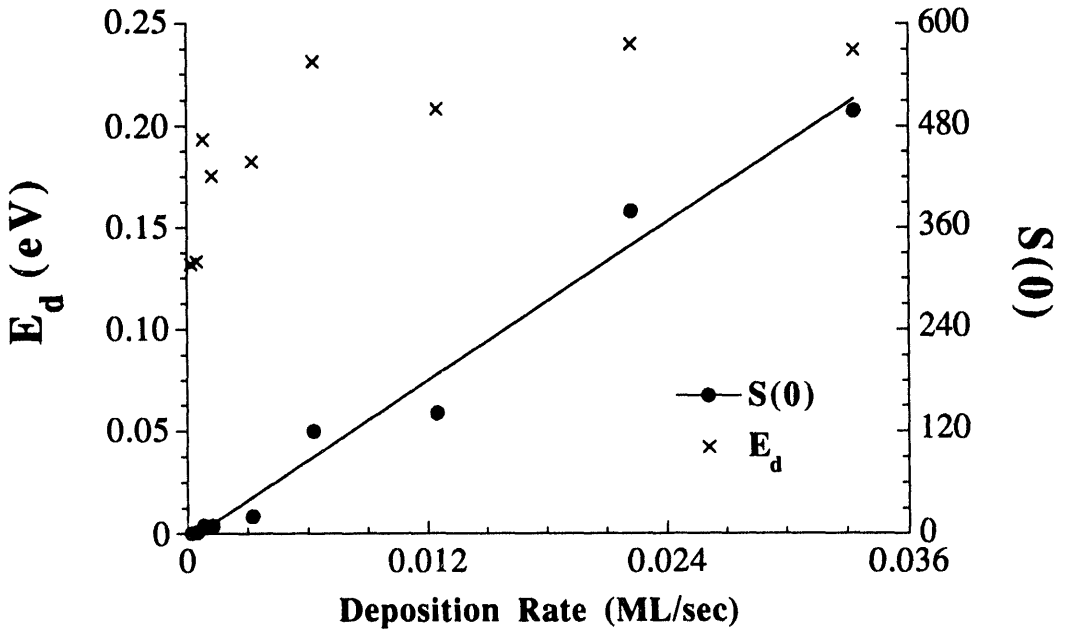

Figure 4 The measured diffusion activation energy, E_d, and the prefactor obtained from the temperature dependence of the initial slopes for the different deposition rates data, as in figure 3.

Figure 4 also shows the measured prefactors for the different growth rates. (What is plotted is the 1/T=0 intercept raised to the natural logarithmic power.) It is clear that the prefactor follows almost a linear relation with the deposition rates. Is this expected? If we look back at figure 3, what is really plotted on the ordinate is a quantity that is effectively the $\sqrt{3}$ domain size initially obtained at temperature, for a fixed time. The number of available atoms (for a fixed time) participating in the growth of the domains increases with deposition rate. If the data are plotted at constant coverage, by dividing with the deposition rate, then a constant prefactor is obtained as expected.

Recent Molecular Dynamics simulations [18] of the deposition of Si on Si(111) have demonstrated that the adsorbed Si atoms display oscillations in their kinetic energy, suggesting transient mobility. The slow dissipation of the energy of incoming atoms can be attributed to the strong covalent bonding between the Si atoms in the substrate. This strong bonding produces a "rigid" substrate that cannot absorb the incoming energy quickly. Since the rigidity of the lattice depends on the Si-Si bond, and not so much on the nature of the deposited atom, we expect the Ag-Si interaction to have a minimal effect so that transient mobility could be present in the Ag/Si(111) system. This phenomenon accounts for the extra Ag adatom mobility observed in an STM study [10] of Ag on Si(100)-(2 x 1). In addition, transport measurements [19] of the film resistance at 80 K, studied with a 4-probe technique, show the onset of conductivity at θ=0.9 ML and almost full metallic behavior after 2-3 layers, which suggests the formation of smooth films.

CONCLUSION

In conclusion, we have presented evidence that the scaling of the specular intensity at $T \leq 300$ K with $t/\tau_{1/2}$, for different deposition rates, suggests the presence of transient mobility that can explain the observed quasi-layer-by-layer growth at low temperatures. The evolution of the growth of the $\sqrt{3}$ structure at T>473 K leads to a flux independent FWHM. Parallel experiments under constant coverage and constant flux conditions, are also consistent with the presence of transient mobility. The activation energy measured is $E_d = 0.24 \pm 0.05$ eV, which is constant over a 30-fold increase in deposition rate. By emphasizing both flux and temperature dependent measurements, better control over the growing structures can be attained.

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PAPER IV

FLUX DEPENDENCE OF THE Ag/Si(111) GROWTH

Flux Dependence of the Ag/Si(111) Growth

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ABSTRACT

We have studied the initial stages (1-2 ML) of the growth of Ag on Si(111) as a function of temperature T and deposition rate F to identify the operating diffusion mechanism. The specular beam intensity at 150 K shows short-lived oscillations which depend on the total amount of Ag deposited, irrespectively of the deposition rate, and suggest the absence of thermal diffusion at this low temperature. Growth studies at higher temperatures T≥473 K, monitoring the formation of the $\sqrt{3}x\sqrt{3}R30°$ structure as a function of deposition rate, measure a non-thermal component R_0>50 Å to the diffusion length. The temperature dependence of the $\sqrt{3}$ growth is used to measure an activation energy $E_d = 0.24 \pm 0.05$ eV.

INTRODUCTION

The growth of atomically controlled structures for the purpose of producing new materials has received great attention recently. The success or failure of the growth to form an optimal structure is determined by the interplay of the arrival rate and the mobility of the adatoms. Thus, the two important parameters which hold the key to successful fabrication are the rate of deposition and the substrate temperature. It is most common to search for the desired structures by varying the substrate temperature because of the strong temperature dependence of the adatom mobility. Less work has been performed as a function of deposition rate. In the current study, we are interested in exploring the dependence of growth on both control parameters to test if lower deposition rates produce smoother films as expected. The experiments were performed with RHEED quantitative spot analysis which effectively monitors the evolution of a growing structure in real time.

We concentrate our study on the heteroepitaxial system Ag/Si(111), which has a large epitaxial mismatch when compared to previous studies [1-5] performed mostly on homoepitaxial systems. This is a well studied system [6-8] with several different techniques, but our work emphasizes lower temperatures extending the range to 150 K, focuses on the flux dependence, and deals with the diffusion energetics of Ag on bare Si in the initial stage of the growth, i.e., submonolayer regime.

The experiments are carried out in a UHV system with base a pressure of ~5 x 10^{-11} Torr. Ag is evaporated from a Knudsen cell, calibrated with a quartz crystal monitor. Although the relative deposition rate, and not the absolute rate, is sufficient for the conclusions reached in our experiment, the latter is determined from the oscillation period observed at low temperatures and the onset [9] of Ag(111) crystallite features near θ=1 ML.

Diffraction patterns are recorded with a high-gain video camera, digitized and stored in an AT-386 computer for further analysis.

Several puzzling observations have already been reported which deviate from the expectations of nucleation theory. Diffraction intensity oscillations have already been observed [1-5] in several epitaxial systems (mostly fcc metals deposited on fcc metals) at low temperatures where no thermal diffusion is expected, unless the diffusion barrier is low, (E_d<0.1 eV). It is still not clear what the origin of this low temperature mobility is. Proposed mechanisms, which require further experimental verification, involve the adatom accommodation process itself which imparts lateral displacement to the incoming atom [1] or binding site constraints [10] that produce spatial interlayer correlations. The atoms "funnel" [10] the particle down to the lowest level, thus suppressing columnar growth. Experiments at higher temperatures T>400 K on the Pt/Pt(111) system [11] have shown that the cluster density does not decrease, and the average cluster size does not increase with temperature, being limited to certain "magic" sizes. In addition, although it has been realized for some time [12] that the interplay between arrival and diffusion rates leads to simple scaling relations $N \propto \left(\frac{F}{D}\right)^x t^y$ between the island density N, the flux F, the diffusion coefficient D, and the time t, experimental confirmation of the theoretically predicted value of the scaling exponents has been met with partial success [13].

RESULTS AND DISCUSSION

It is surprising that we observe short-lived oscillations for the Ag/Si(111) system at 150 K, which disappear at higher temperatures, as shown in figure 1. A[illegible] oscillations are of poor quality (which is expected given the strong epitaxial mi[illegible]ey are similar to other low quality oscillations [3-5] which require the presence of adatom mobility. It has been well documented [14] that ballistic deposition with no lateral motion simply leads to monotonic intensity decrease. In addition, the Ag deposition is performed in the presence of the 7x7 reconstruction with the superstructure spots gradually disappearing as the Ag is deposited. We attribute the loss of specular intensity to destructive interference between the substrate and overlayer domain distribution. The reconstruction simply gives the local symmetry of the substrate unit cell, and is not related to long range morphological changes. In this system this assumption was used [8] to interpret the kinetics of the formation of the $\sqrt{3}$ as simply a result of th[illegible]ging overlayer morphology, without any interference from the reconstruction.

The observed oscillations sensitively depend on the angle of incidence θ_i. Although the detailed dependence is complicated, in general the trend is reduced oscillation amplitude as θ_i increases up to θ_i=6° where the oscillations disappear. Such dependence on the angle of incidence has been observed [15] previously. We do not have an explanation, but for the current study, which centers on the kinetic aspects of the growth and the role of flux, the dependence is not essential since θ_i is kept constant.

In order to identify further the unusual aspect of the oscillatory behavior observed at T=150 K, we have varied the deposition rate over the range F=1/4800-1/125 ML/sec. As explained before we expect the overlayer morphology to improve as the deposition rate is reduced, so better quality oscillations, with higher amplitude, should be present. Figure 2

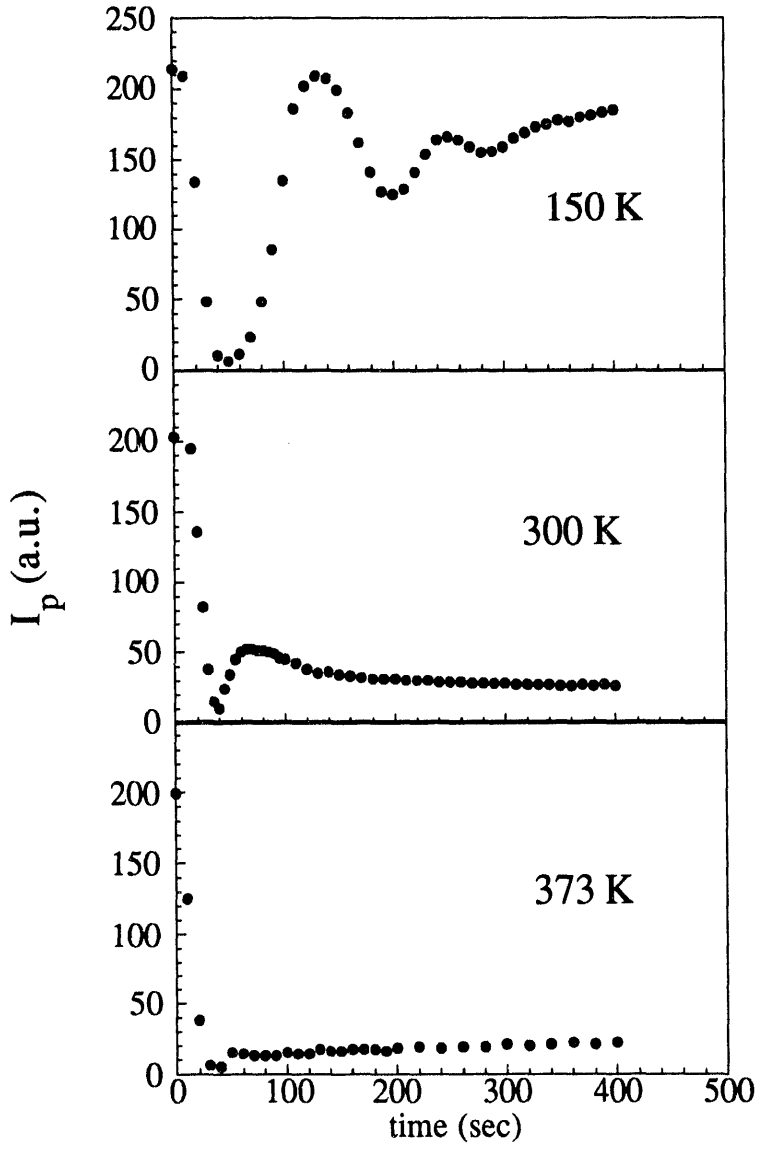

Figure 1 The specular peak intensity vs. Ag deposition time for three different substrate temperatures for a deposition rate of 1/125 ML/sec. The short-lived oscillations observed at 150 K disappear at higher temperatures.

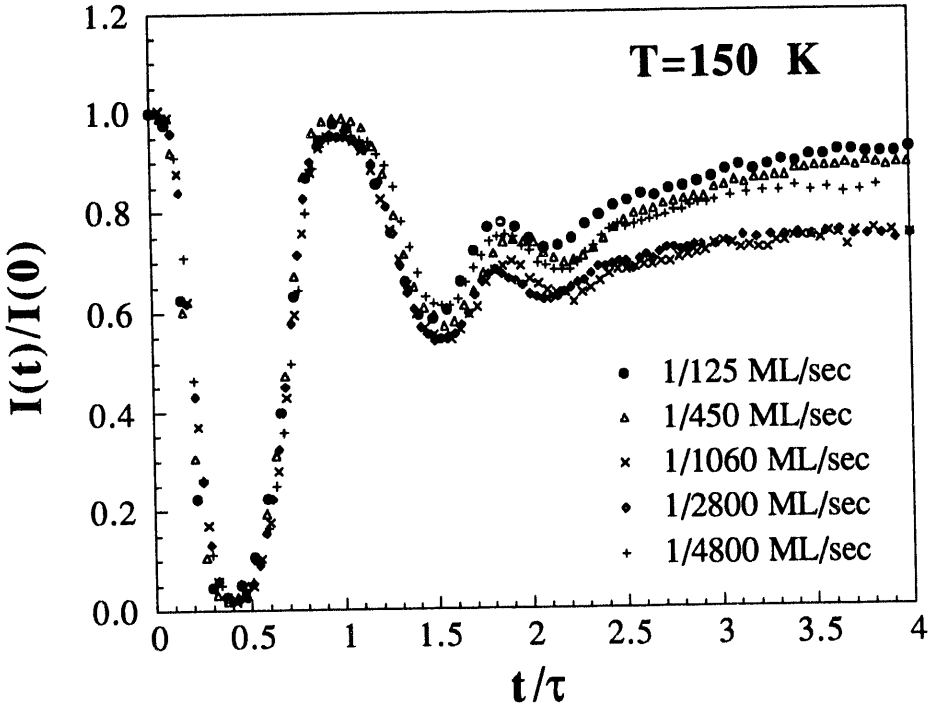

Figure 2 The normalized specular peak intensity vs. t/τ for five different deposition rates at 150 K. τ is the period of the first oscillation.

shows the observed specular beam intensity at different deposition rates plotted as I(t)/I(0) vs. t/τ, where τ is the first oscillation period. Since I(0) is constant, corresponding to the clean surface (within 5% reproducibility), the data demonstrate not only that the amplitude of the first oscillation, and that of the successive weaker ones (within 10%), is flux independent, but the entire shape of the oscillations is also flux independent. (We have subtracted a constant 10% of I(0) background which forces the first minimum to be close to zero.) Deviations from scaling at higher coverage (θ>1 ML) cannot be related to coalescence because in the absence of thermal diffusion scaling should hold for the resulting interconnected domain network.

The scaling of the specular beam intensity, especially during the formation of the first oscillation, is consistent with the film morphology being dependent only on the total amount of Ag on the surface, and not on the rate of deposition. In general, one expects the intensity to be a function of the amount (Ft) and the typical diffusion distance R an atom travels, I(Ft,R(t)). For larger R one expects to have larger average domain sizes L and therefore higher specular intensity. Since for different deposition rates we observe the same shape of the oscillations, this suggests that R is constant. So if one writes for the diffusion length $R = R_0 + (4Dt)^{1/2}$, it can be concluded that D≈0 at T=150 K, i.e., there is no thermal mobility. This result is consistent with a recent STM study [7] that has imaged Ag islands at substrate temperatures T=363-403 K. If the island density is measured from the shown image at 363 K, $N(cm^{-2})=9x10^{12}$ cm^{-2}, and nucleation theory [12] is assumed, an activation energy E_d≈0.65 eV is extracted. If this value is used to calculate the diffusion coefficient at 150 K, a negligible value $(4Dt)^{1/2}$≈0 results for the thermal component of the diffusion length. In other growth studies where it is not clear if the origin of the needed mobility is thermal or not (because the diffusion barrier is unknown) the flux dependent experiment presented in this study can be employed as a method to identify the nature of the mobility.

A constant non-thermal diffusion length R is also compatible with the two extreme values, $R_0=0$ or $R_0=\infty$. A zero value $R_0=0$ is ruled out by the presence of the short-lived oscillations (i.e., monotonic decrease is expected for ballistic growth), and an infinite diffusion length $R_0=\infty$ (or low deposition rate F) is ruled out because of the $\sqrt{3}$ growth rate observed at higher temperatures. The $\sqrt{3}$ superstructure intensity monitored at $T\geq 473$ K should follow t^2 time dependence if the diffusion is high relative to the deposition rate since every atom would join the domains "instantaneously" and the domain area would grow linearly in time. The superstructure intensity is proportional to the number of scatterers squared, so it would increase like t^2. Figure 3 shows the superstructure intensity vs. time for a given deposition rate at different temperatures, and it is clear that the time dependence is linear, thus ruling out extremely fast diffusion $R_0=\infty$, or low deposition rates. In addition, a zero activation energy should be measured since the atoms would reach the growing domains independent of temperature. As we describe shortly, a non-zero activation energy is found.

The formation of the $\sqrt{3}$ can be used additionally to test the proposed relation $R = R_0 + (4Dt)^{1/2}$ with $D\neq 0$ at these higher temperatures. This system is especially useful for monitoring epitaxial growth since the $\sqrt{3}$ diffraction spots give exclusive information about the overlayer configuration without any interference from the substrate. Integral order beams have information about both the substrate and overlayer domain size distributions so it is difficult to decouple the individual contributions. The growth of the $\sqrt{3}$ is monitored over a flux range F=1/4800-1/30 ML/sec at different temperatures, and the peak intensity obeys a linear time dependence. The available diffusion time t is expected to decrease with F^{-1}. The peak intensity follows $I_p \propto NL^4$ (with N the island density and L the average domain size), and for a constant coverage $\theta=NL^2$, $I_p^{1/2}$ is proportional to L. At low coverage, one expects the average island size L to be simply proportional to the diffusion

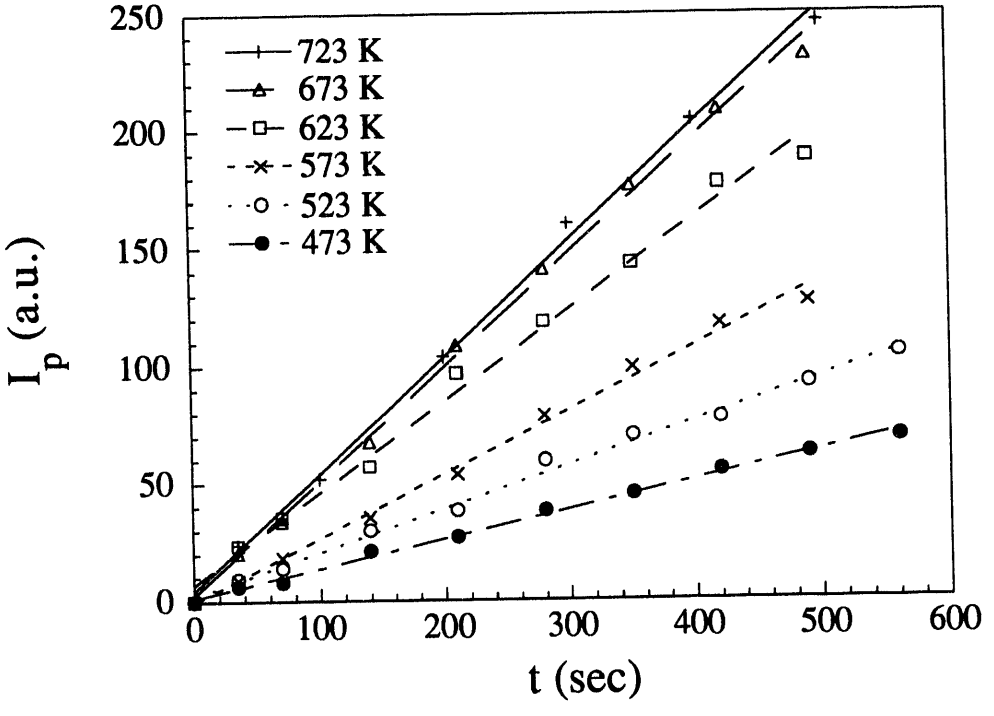

Figure 3 The peak intensity of a $\sqrt{3}$ structure spot vs. Ag deposition time for the initial growth of Ag for a deposition rate of 1/800 ML/sec and substrate temperatures T=473-723 K. Linear increase of the intensity with time is observed.

length R. $I_p^{1/2}$ should then depend linearly on $F^{-1/2}$ so a non-zero intercept in $I_p^{1/2}$ would imply a non-zero value of R_0 in $R = R_0 + (4Dt)^{1/2}$. The values of $I_p^{1/2}$ obtained for low Ag deposition θ=0.2 are plotted as a function of $F^{-1/2}$ in figure 4 for different temperatures. Especially at the lower temperature T=473 K, the relation is linear, but with a non-zero intercept. We can estimate the value of R_0 to be in excess of 50Å at T=473 K by translating the arbitrary units on the y-axis to Angstroms if we use the measured FWHM (=0.052Å^{-1}) at the end of the θ=0.2 deposition shown in the inset of figure 4. Because of the linearity between I_p and t, the same estimate of R_0 is obtained if a different coverage is used for the fit. It is important to emphasize that even if a different relation $L \sim t^{1/3}$ [16] based on nucleation theory, relating the average domain size and time (so that $I_p^{1/2}$ is plotted as a function of $F^{-1/3}$), is used, a non-zero intercept also results. At higher temperatures the data deviate from linearity (because of the increased role of 2-D desorption and island dissolution). For these higher temperatures there is also a non-zero intercept, although its temperature dependence is currently under investigation.

As reported before [17], other experiments support the conclusion that non-thermal mobility is present. First, Ag is deposited in a random configuration at T=150 K and then upquenched to T=473 K to form the $\sqrt{3}$ structure. When this constant coverage experiment is compared to the constant deposition experiment at T=473 K for early times $t \approx 0$ (when small domains, 2-3 atoms across, are formed), it is found that the rate of growth (as measured from the slope of the I_p vs. t curves) is lower in the annealing than in the deposition experiments for fluxes $F \geq 1/1100$ ML/sec. Is this result always true, i.e., the annealing will be slower than the deposition experiment so there is no useful information from the comparison? Because the comparison is restricted to very early times , blocking effects are minimal, and if repulsive adsorbate-adsorbate interactions are present in this system, as suggested previously [6], it is possible that the initial growth rate of the annealing

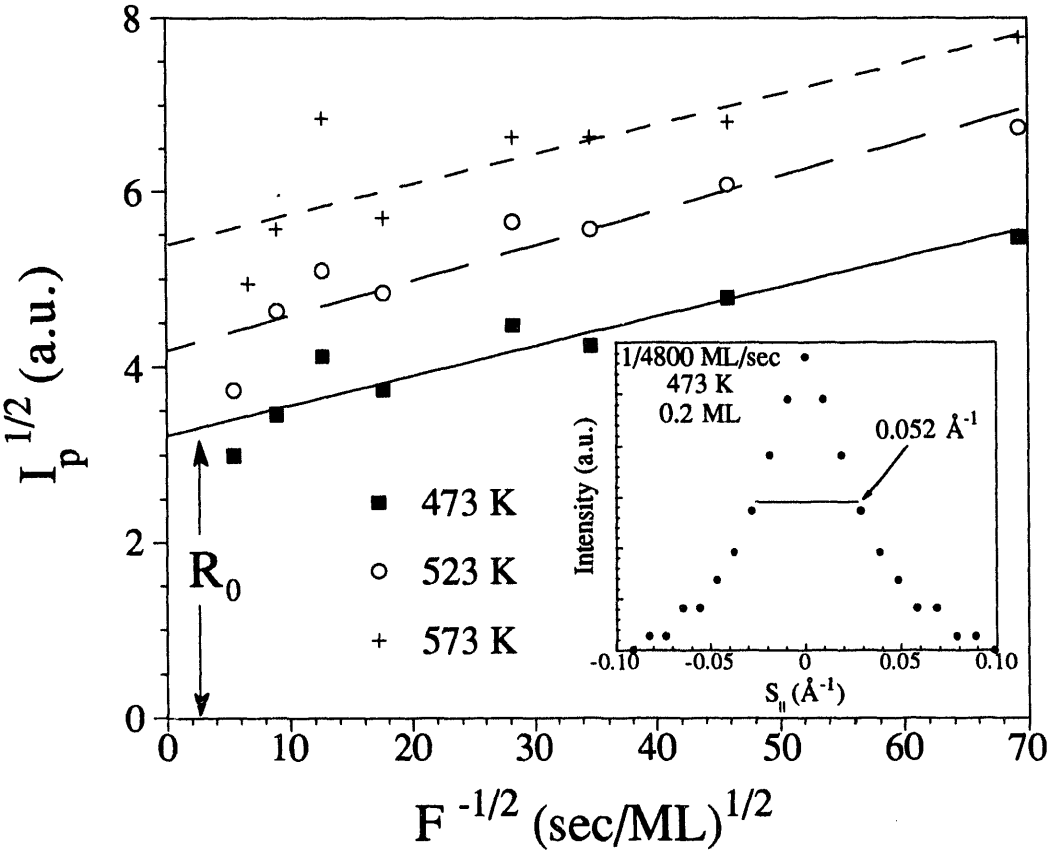

Figure 4 The square root of the $\sqrt{3}$ peak intensity $I_p^{1/2}$ as a function of the inverse square root of the flux $F^{-1/2}$ for a fixed coverage of 0.2 ML. A non-zero intercept R_0 is observed. The magnitude of R_0>50 Å can be estimated by measuring the FWHM of a typical $\sqrt{3}$ spot profile at 0.2 ML shown in the inset.

will be faster than the rate of the deposition experiment (the repulsive interactions would lower the barrier). Since this is not observed, it has been concluded [17] that an additional source of non-thermal mobility is present during deposition.

It has also been reported before [16] that the final FWHM attained, well above the instrumental resolution, during the growth of the $\sqrt{3}$ at different fluxes is independent of deposition rate. Although this late time regime is marginally related to the question of whether a non-thermal mechanism operates (since the late time growth is affected by blocking and multi-particle correlations), the constant FWHM is rather surprising and is consistent with the overall conclusion that additional non-thermal mobility operates.

The temperature dependence of the growth, as shown in figure 3, can be used to extract the activation energy of diffusion. I_p vs. t is linear, and under the simple assumption that for dimensional consistency I_p should be a function of the combination (Dt), it follows that I_p is simply proportional to D. The slopes of the growth curves in figure 3 are plotted vs. 1/T in an Arrhenius plot to extract the diffusion activation energy E_d. If the data shown are converted to I_p vs. θ plots (by simply multiplying the time by the flux θ=Ft) the same E_d is obtained, while the prefactor (in arbitrary units; no absolute length scale is determined for the abscissa because it requires accurate spot profile analysis, to be reported in future work) is different. A low diffusion activation energy E_d=0.24±0.05 eV is measured for fluxes F=1/160-1/30 ML/sec, while it drops to half this value for lower fluxes. The effective prefactor in the I_p vs. t plots changes almost linearly with flux (while the corresponding one obtained from I_p vs. θ is constant). What is the meaning of this low E_d value? In principle, the growth experiment under constant deposition measures a combination of the bare substrate-adatom diffusion barrier, the contribution of the adsorbate-adsorbate interactions, and any non-thermal contribution to the diffusion length we have hinted at previously. Because of the low value measured and because of the wider temperature range used in the

current experiment (250 K instead of 50-100 K ranges typically used in diffusion studies) it would be difficult to determine the individual contributions of each separate barrier. All three processes are present during the whole temperature range so it would be difficult to observe the temperature independent regime, expected for the non-thermal component observed in other studies [13]. Other experimental techniques [6] have been used previously to measure surface diffusion in the Ag/Si(111) system, but usually at higher coverage (θ>1 ML) when the deposited Ag has already formed large islands either on bare Si or on top of the $\sqrt{3}$, a different regime than the one in the current experiment which focuses on the θ<1 regime. The value we measure is lower than the values obtained by employing the other techniques; the lowest value obtained for the diffusion of Ag on top of the $\sqrt{3}$ is E_d=0.4 eV. The difference can be attributed to the different configurations probed [18].

CONCLUSION

In summary, we present low temperature experiments that show short-lived specular beam intensity oscillations whose shape is surprisingly flux independent, suggesting a constant, non-zero diffusion length. This constant component R_0>50 Å is measured at higher temperatures, where the $\sqrt{3}$ forms, by monitoring the superstructure growth as a function of deposition rate. The growth of the $\sqrt{3}$ at different temperatures is used to extract a diffusion activation energy $E_d \leq 0.24$ eV which is well below values measured with other techniques and with the system in other overlayer configurations. It is clear from the series of experiments described above that the flux dependence, when analyzed quantitatively during growth, can reveal many surprising aspects of mass transport in epitaxial systems.

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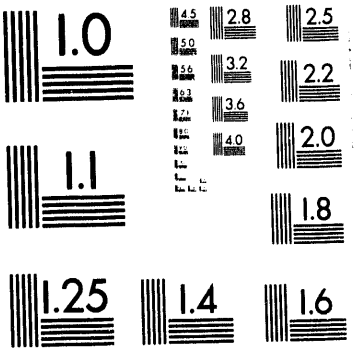
GENERAL SUMMARY

We have used RHEED to quantitatively study the low temperature (150 K) and flux dependent growth of Ag/Si(111). The main result is the scaling of the specular peak intensity, i.e., the specular intensity is a function I(Ft) of the total amount deposited. The implication of this result is that the adatom diffusion in these experiments occurs over a time which is small compared to the average time between single atom adsorption events for the range of deposition rates used. Since, as concluded from the finite time needed to form the $\sqrt{3}$ structure at higher temperatures, the deposition rates used are not negligible when compared to the *thermal* diffusion rate, we can conclude that thermal diffusion is absent in this system at 150 K and that some other mechanism drives the growth.

Possible mechanisms which can explain these unexpected results are funneling [8] and transient mobility [5]. The latter is the likely explanation for this system. Funneling can be ruled out because of our observation of sharp diffraction features indicating the formation of large Ag clusters which are not expected to be present in the funneling model. Since transient mobility occurs while the depositing atom reaches equilibration with the substrate lattice (which takes place on the order of 10^{-12} seconds), it is consistent with the observation of fast diffusion compared to deposition time for our range of deposition rates. In fact, any range of deposition rates attainable experimentally would not be able to include rates high enough to be sensitive to transient mobility. Transient mobility is also consistent with the total diffusion length having a constant, non-thermal component added to the component due to thermally activated diffusion. Under transient mobility, an atom will move on the surface until its latent heat of condensation is dissipated to the lattice.

From the high temperature data, by plotting the $\sqrt{3}$ peak intensity $I_p^{1/2}$ (which is proportional to the average island size L) vs. the deposition rate $F^{-1/2}$ (which is the average


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6

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available diffusion time), we confirm the presence of a non-thermal component R_0 of the diffusion length R, and estimate a lower bound (50 Å) for the magnitude of R_0 which is quite large (>10 substrate lattice sites). This large value for R_0 supports the conclusion formed (that a non-thermal component operates *along with* thermally activated diffusion to drive the growth at higher temperatures) from the constant FWHM at 1 ML, and the comparison between the deposition and annealing growth results. A similar length (10 lattice sites) was estimated [5] for the transient mobility diffusion length for metallic atoms on fcc(001) surfaces.

Further evidence for transient mobility in this system of Ag/Si(111) is found in Molecular Dynamics simulations [13]. For the deposition of single Ag atoms on Si(111) these simulations display a large degree of lateral mobility for Ag atoms depositing near a potential energy surface maximum. It has been concluded that this motion most likely is a result of inefficient energy transfer because of lattice rigidity. A comparison between potentials used in this work and in the metal/fcc(001) simulations [12], where no transient mobility was observed, reveals that the Si(111) potential is a factor of 3 higher in curvature, near the bottom of the well, than the fcc(001) potential, confirming the importance of the rigidity in the interatomic potential. We could perhaps suggest, based on the lattice rigidity of Si(111), that transient mobility should be related to covalent bonding. We can thus make a general conclusion: low temperature and flux dependent growth studies have revealed interesting behavior which is not expected according to the traditional understanding of ultrathin film nucleation. Clearly, much more investigation is required involving a diversity of experimental systems and techniques before a theory universally describing atomistic processes at surfaces can be formulated; it may be found that such a theory cannot be universally applied.

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