Unconventional features of Ag epitaxy on the Si(111)7×7 surface

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The population of Ag-occupied half-unit cells (HUC's) on Si(111)7×7 surface resulting from growth and annealing experiments is observed by scanning tunneling microscopy. The temperature dependence of Ag-object density and preference in HUC occupation are measured. The results are interpreted with the help of a coarse-grained kinetic Monte Carlo model. The key kinetic mechanisms affecting Ag motion are determined, in particular transient mobility of deposited Ag atoms and the existence of a highly stable configuration of six Ag atoms in a HUC. The attempt frequency and barrier to hopping of a single Ag atom between HUC's are estimated.

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I. INTRODUCTION

Metal films on semiconductor surfaces represent an example of films grown by *heteroepitaxy* on *reconstructed* surfaces. Such growth systems are extremely rich in different mechanisms that place adatoms arriving on the surface into their final positions and thus draw increasing experimental and theoretical attention.

Surface reconstruction plays a key role during first stages of growth of metal films on the Si(111)7×7 surface. Large (2.7 nm) triangular half-unit cells (HUC's) of two different types [faulted (FHUC's) and unfaulted (UHUC's)] divided by dimer rows and corner holes[1] form a highly corrugated surface potential for diffusing metal adatoms. At temperatures where mixed surface reconstructions are not formed, metal atoms cluster inside HUC's (Refs. 2–4) with stronger or weaker preference for occupying FHUC's. Recently, an exceptionally high preference of 0.95 has been found[5] in Tl/Si(111)7×7 growth at room temperature (RT), allowing us to prepare a well-ordered array of metal clusters on Si(111)7×7.

Ag and Pb that are nonreactive at low temperatures ($\lesssim$500 K for Ag) leave the 7×7 reconstruction unchanged[2,3] and thus have become model experimental systems for studying metal diffusion on the Si(111)7×7 surface. Basic information on diffusion processes for Pb/Si(111)7×7 comes from the work of Gómez-Rodríguez and co-workers.[6–8] During *in vivo* scanning tunneling microscopy (STM) experiments, they observed a high mobility of Pb atoms *inside* HUC's but low mobility *between* HUC's. They made an estimate of the rate of thermally activated hopping of single Pb atoms between HUC's (Ref. 6) and observed movement of Pb dimers inside HUC's.[7] In addition, they suggested nonthermal mobility of Pb adatoms deposited at RT.[6]

Several STM studies of growth of Ag on Si(111)7×7 have succeeded in distinguishing the appearance of growing Ag clusters[2,9,10] and single Ag atoms[11,12] on Si surface. However, details of Ag diffusion on Si(111)7×7 were rarely addressed. In our recent work,[13] we have found a transition from hit-and-stick nucleation of Ag at RT to diffusion-limited nucleation at $T \gtrsim 370$ K. The structure of the film grown at RT confirmed that limited mobility of Ag adatoms persists.

In this paper, we present results of extended growth and annealing experiments on a submonolayer Ag/Si(111)7×7 film. A coarse-grained kinetic Monte Carlo (KMC) model of growth plays a crucial role in our study, making it possible to draw conclusions concerning the origin of extra Ag adatom mobility at RT, as well as to determine the parameters of hopping of a single Ag adatom between HUC's and interactions between more Ag adatoms in a HUC.

II. EXPERIMENT

Series of samples with a constant amount of deposited Ag [0.090 monolayer (ML), $\approx$2.2 atoms/HUC, 1 ML $=7.83\times10^{14}$ cm^{-2}] at temperatures from RT to 540 K and two deposition rates $F_1=0.0010$ ML s^{-1}, $F_2=0.030$ ML s^{-1} (*growth experiment*) have been prepared by evaporation from a W filament in an ultrahigh vacuum (UHV) chamber of a homemade UHV STM system. Films with the same amount of Ag were prepared at RT at F_1 and subsequently annealed to temperatures up to 470 K for 300 s (*annealing experiment*).

The deposition rate was measured by a quartz thickness monitor calibrated with an absolute accuracy of ±10%.[14] We used a Si(111) substrate with miscut ±0.25° and resistivity 0.01–0.005 Ω cm heated by passing dc current. The 7×7 reconstruction was obtained by a standard flashing procedure.[12] The substrate temperature was controlled by applied dc power and heating duration, and calibrated with ±15 K absolute accuracy.[15] Prepared samples were immediately quenched to RT (during the quenching, the difference between the substrate temperature and RT decreases to 1/2 during less than 4 s). STM images were taken at RT, on average 4 h after the sample was prepared. The pressure

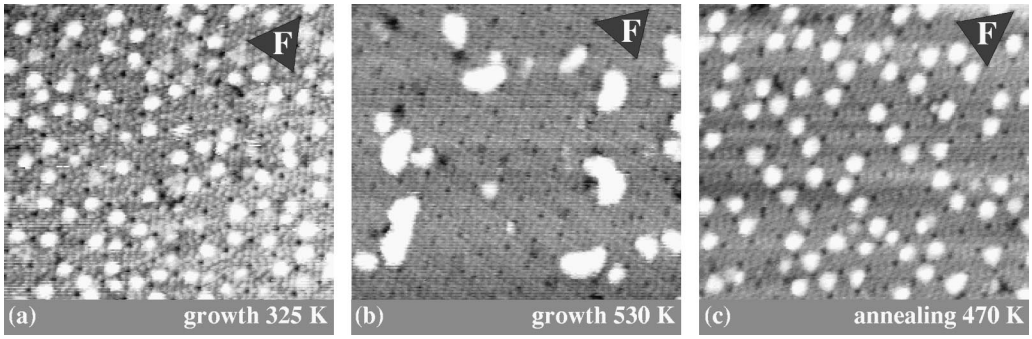

FIG. 1. Empty-state STM topographs of 0.09 ML Ag on Si(111)7×7. (a) After growth at lower temperatures, Ag clusters form inside HUC's. (b) At higher temperatures, coverage measured in HUC's saturates at ≈0.12 and islands larger than one HUC are formed. (c) Upon annealing a layer grown at RT (for 300 s at temperatures <470 K), no larger islands are formed and coverage saturates at ≈0.24. In the figures, orientation of FHUC's obtained from filled-state images is marked with a black triangle.

during all stages of sample preparation and manipulation did not exceed 2×10^{-8} Pa.

III. EXPERIMENTAL RESULTS

In both growth and annealing experiments, three quantities were measured: the density of Ag objects d_{Ag}, the coverage θ, and the preference of occupation of FHUC's P_F. As Ag objects, we considered nonempty HUC's (including HUC's with 1 Ag adatom) created in the growth experiment at lower temperatures [Fig. 1(a)] and in the annealing experiment [Fig. 1(c)] as well as Ag islands larger than 1 HUC, created in the growth experiment at higher temperatures [Fig. 1(b)]. The number of objects is normalized to the number of HUC's on the substrate, so that $0\leqslant d_{\mathrm{Ag}}\leqslant 1$. The coverage θ is a number of Ag-occupied HUC's normalized to the number of HUC's in the substrate. When no Ag islands >1 HUC are formed, $\theta=d_{\mathrm{Ag}}$. The preference P_F is determined as $n_F/(n_F+n_U)$, where n_F and n_U are numbers of occupied FHUC's and UHUC's, respectively ($0\leqslant P_F\leqslant 1$ from the definition).

Values of d_{Ag} and P_F obtained from the growth experiment are shown in Fig. 2(a). At temperatures $\lesssim$370 K, d_{Ag} does not depend on T, and it decreases at higher temperatures. This is due to the increase of the hopping rate of Ag adatoms between HUC's, which at a certain temperature T_c exceeds the arrival rate of Ag adatoms into a HUC and, as a result, nucleation of Ag starts to be diffusion controlled.[13] T_c increases with increasing deposition rate, and Arrhenius plots of d_{Ag} are linear as expected from classical nucleation theory[16] (Fig. 3). When d_{Ag} is less than $\approx$ 0.12, Ag islands larger than 1 HUC are formed, so that the coverage θ of samples remains approximately constant, $\theta\approx0.12$ (Fig. 3). This shows that a HUC has a limited capacity to accommodate adatoms;[17] $\theta=0.12\pm0.01$ at the given amount of deposited material corresponds to 18 ± 2 Ag adatoms in a HUC on average.

At RT, when thermally activated hopping is negligible, the short-range ordering of Ag-object positions,[13] and the low value of $d_{\mathrm{Ag}}\approx0.36$ cannot be a result of simple hit-and-stick growth. Instead, a *capture zone* of an Ag object including three neighboring HUC's has to be considered.[6,13] Two mechanisms that may contribute to the creation of the capture zone were suggested:[12,13] The transient mobility of an Ag adatom before it is accommodated on a Si(111)7×7 surface, and a considerable reduction of the hopping barrier for a hop of the Ag adatom to a neighboring *occupied* HUC.

At RT, $P_F\approx0.59$, which means that the difference between FHUC's and UHUC's affects growth even at low temperatures. The possibility that P_F is due to hops of single Ag atoms out of UHUC's during 4-h sample relaxation at RT

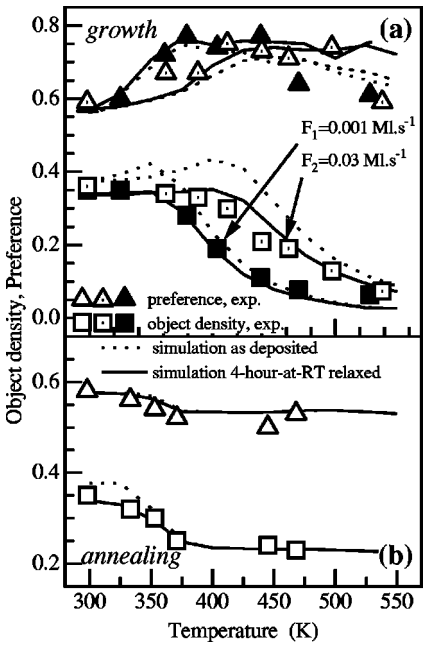

FIG. 2. Experimental (symbols): (a) The object density d_{Ag} and preference P_F of FHUC occupation as a function of the substrate temperature for 0.09 ML thick Ag layer grown at two different fluxes, F_1 and F_2. (b) The same quantities for an Ag layer grown at RT at F_1 and subsequently annealed for 300 s at different temperatures. The maximum experimental errors correspond to the symbol size. Simulation (lines): The results of the model described in text show *quantitative* agreement with all growth (a) and annealing (b) experimental data. In simulations, the experimental procedures were exactly followed, including the 4-h rest at RT before STM observation.

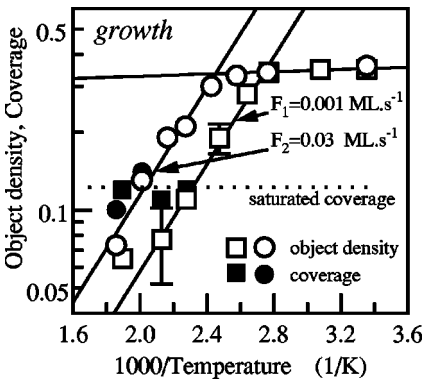

FIG. 3. Arrhenius plots of object density d_{Ag} from the growth experiment are linear as expected from standard nucleation theory. The coverage θ saturates at ≈ 0.12 by forming islands larger than 1 HUC. This is an indication of limited HUC capacity to accommodate more than ≈ 18 Ag adatoms: $\theta = d_{\mathrm{Ag}}$ for $d_{\mathrm{Ag}} > 0.12$.

(Ref. 13) can be ruled out if we consider the distribution of clusters consisting of n Ag atoms C_n of hit-and-stick growth with the capture zone including three neighboring HUC's for given amount of deposited Ag:[18] There are simply not enough HUC's occupied by single Ag atoms to shift P_F from 0.50 to 0.59. When thermal diffusion starts to play a role, P_F increases to ≈ 0.76 and then decreases again when islands larger than 1 HUC (consisting of neighboring FHUC's and UHUC's) are formed. Above T_c, the preference is caused by the difference of the hopping rates of Ag adatoms out of FHUC's and UHUC's.[13]

The results of the annealing experiment are shown in Fig. 2(b). As the annealing temperature increases, d_{Ag} is reduced from its RT value and saturates at ≈ 0.24 at $T > 380$ K. The preference P_F behaves in a similar way. Under the assumption of no Ag desorption, two conclusions can be made. First, some Ag *clusters* (more than 1 Ag atom inside a HUC) have had to disintegrate because the distribution C_n does not contain enough HUC's with one Ag atom to decrease d_{Ag} by 30% (cf. above). Second, (meta)stable Ag clusters do exist on the surface because saturation is reached.

The annealing experiment complements information about growth of Ag on Si(111)7×7 with information about cohesion of Ag clusters. The analysis of the experimental data using nucleation theory is thus possible. In the following, we describe a coarse-grained KMC model of Ag/Si(111)7×7 growth and use it to refine the overall picture of growth and to determine parameters of Ag diffusion on Si(111)7×7 surface.

IV. THE MODEL

Coarse-grained models have been used in studies of Si/Si(001)2×1 (Ref. 19) and Si/Si(111)7×7 homoepitaxy.[20,21] Since much of the experimental information about growth on reconstructed surfaces is available in units of surface reconstruction, considerable insight can be achieved by simple modeling of diffusion processes *between* unit cells without detailed description of adatom movement *inside* unit cells.

The simulation scheme is adopted from Ref. 20. Sites on a honeycomb lattice that represent HUC's of 7×7 reconstruction are assigned two parameters: an indicator of the presence of a stacking fault (faulted, unfaulted) and ''height'' n, which represents the number of Ag atoms in the Ag cluster inside the HUC. Only hops of single atoms are allowed. Hops are considered to be thermally activated with the activation energy $E_n^{F,U} = E_d^{F,U} + nE_a$ where the first term is a surface contribution (generally, different for unfaulted and faulted unit cells), and the second one models the Ag-Ag interaction as a *linear* function of the number n of Ag atoms in the cell. The attempt frequency ν_0 is assumed to be the same for FHUC's and UHUC's, and attempts of more Ag atoms to hop out of a HUC are considered to be independent, so that the hopping rate of an Ag atom out of a HUC can be written as $\nu_n^{F,U} = n\nu_0 \exp(-E_n^{F,U}/kT)$.

The HUC capacity in the model is not limited, and the model thus does not provide correct information about θ and P_F at temperatures where Ag islands larger than one HUC are formed. Simulations were performed on a 100×100 HUC lattice with periodic boundary conditions. The 4-h delay between sample preparation and observation was simulated by 4-hour-at-RT annealing of model runs.

V. SIMULATION RESULTS AND DISCUSSION

During work with the model, we focused on two targets: (1) choosing a minimal set of different kinetic mechanisms that describe observed growth and annealing phenomena and (2) determining the parameters for these mechanisms. The final version of the model, which gave *quantitative* agreement of simulated results with all available experimental data [Fig. 2(a,b)] included these kinetic mechanisms: (i) transient mobility of impinging Ag adatoms, (ii) hopping of Ag adatoms between HUC's on the surface and detachment of Ag adatoms from Ag clusters, (iii) the existence of stable Ag clusters of size $n > i^*$; and (iv) small differences between FHUC's and UHUC's.

(i) Transient mobility of an incoming adatom was implemented via an *incorporation routine*.[19] Such routine checks first (second, third, etc.) nearest neighbors of the landing position of the adatom and allows the adatom to choose the best final position according to a certain criterion (in our case, a random choice is made from occupied HUC's). d_{Ag} at RT is very sensitive to the choice of the search radius of the incorporation routine, the model with the incorporation routine searching first neighbors (INC-1) was taken as a template for further work. The incorporation routine yields $P_F = 0.5$; in the final version of the code, it was biased so that more FHUC's were occupied by allowing a few ($\approx 6\%$) of atoms landing in UHUC's with no neighbors to hop to a neighboring FHUC.

The transient mobility as the mechanism to cause the extra adatom mobility at RT was chosen after extensive (nonsatisfactory) tests of a model with biased thermal diffusion. The nonexistence of diffusion bias seems to be further supported by RT STM observations of low-coverage samples,[22] where a configuration of a single atom in a HUC next to a

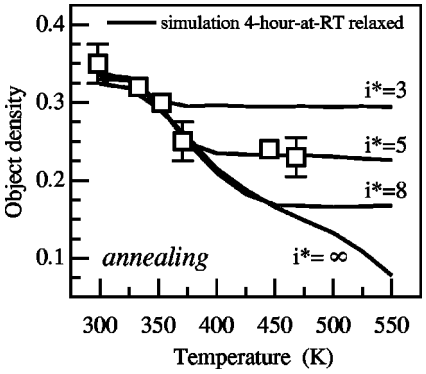

FIG. 4. Saturation of the object density in the annealing experiment can be tuned by introducing a critical cluster size i^*, above which an Ag cluster in a HUC becomes stable. The best fit is obtained at $i^*=5$. This suggests that the binding energy of an Ag cluster on Si(111)7×7 surface increases rapidly for arrangements of 6 or more Ag atoms in a HUC.

HUC with Ag cluster was found to be stable for more than 15 min.

(ii) The parameters of thermally activated hopping of Ag atoms between HUC's, ν_0 and $E_d^{F,U}$, and the bonding energy of an Ag atom in Ag clusters E_a were found by fitting to experimental results a simplified model that takes into account the nonbiased incorporation routine INC-1, hopping of Ag adatoms between HUC's, and the linear increase of the bonding energy of an Ag cluster with its size. FHUC's and UHUC's are not distinguished, $P_F=0.5$, $E_d^F=E_d^U=E_d$, $\nu_n^F=\nu_n^U=n\nu_0\exp[-(E_d+nE_a)/kT]$. The values of ν_0, E_d, and E_a influence the positions and slopes of the Arrhenius parts of $d_{\mathrm{Ag}}(T)$ in the growth experiment and the position and slope of the non-saturated part of $d_{\mathrm{Ag}}(T)$ in the annealing experiment. The best fit is obtained for $\nu_0=5\times10^{9\pm1}$ s^{-1}, $E_d=(0.75\pm0.10)$ eV, $E_a=0.05$ eV. Parameter error bars were estimated by varying E_d and ν_0 to induce changes in simulated $d_{\mathrm{Ag}}(T)$ within error bars of $d_{\mathrm{Ag}}(T)$ obtained from the experiment. The low value of E_a that indicates a rather weak interaction of Ag atoms inside a HUC is surprising but not unlikely. Recent theoretical calculations[23] show that there exist three nonintersecting closed diffusion paths for metal adatoms inside a Si(111)7×7 HUC so that metal adatoms can move independently with minimal mutual interactions.

(iii) Saturation of $d_{\mathrm{Ag}}(T)$ in the annealing experiment [Fig. 2(b)] can be achieved by introducing a critical cluster size i^* of the largest unstable Ag cluster. Clusters of more than i^* Ag atoms are made stable artificially, by setting the activation energy of an Ag atom hop out of such a HUC equal to, say, 5 eV, $E_n^F=E_n^U=5$ eV, $n>i^*$. The best fit is obtained for $i^*=5$ (Fig. 4), i.e., the smallest stable cluster consists of six Ag atoms. Our results are in agreement with the observed shape and symmetry of the smallest ringlike Ag cluster stable at 90 °C, which was estimated to consist of six Ag adatoms in a HUC.[2]

The necessity to introduce stable clusters of size $n>i^*$ into the model should be interpreted as a correction to the assumption of the linear increase of the bonding energy of an Ag cluster with its size: The bonding energy increases much faster than linearly for clusters of ≈6 (and more) atoms. However, larger clusters should not be considered absolutely stable, if only because the limited capacity of a HUC is observed in the experiment.

(iv) The preference of FHUC occupation, P_F, of the simulated data is obtained by small modifications of the just described simple model. At RT, the incorporation routine is biased as described earlier. In order to obtain the increase of P_F at T_c in simulation of the growth experiment, the difference between activation energies for hopping of Ag atom out of UHUC's and FHUC's is introduced. The difference applies only for clusters smaller than s^* atoms, otherwise the P_F at $T>T_c$ comes out too high ($P_F\to1$): $E_n^U=E_d^U+nE_a$, $n=1,2\ldots$, $E_n^F=E_d^F+nE_a$, $n<s^*$, $E_n^F=E_n^U$, $n\geqslant s^*$ (cf. above). The increase of P_F at T_c is determined by s^* and $\Delta=E_d^F-E_d^U$. The maximum value of P_F increases with s^* and/or Δ, so the upper estimate $\Delta\leqslant0.05$ eV can be obtained at $s^*=2$.

By introduction of incorporation bias, i^*, s^*, and Δ, the final model version was obtained. None of these corrections influences the modeled $d_{\mathrm{Ag}}(T)$ in growth and annealing experiments used to fit ν_0, $E_d^{F,U}$, and E_a in a significant way. This allows us to use parameters ν_0 and $E_d^{F,U}$ from (ii) as an estimate of the hopping rate of a single Ag adatom between HUC's on the Si(111)7×7 surface.

VI. CONCLUSIONS

Extended growth and annealing experiments interpreted using a coarse-grained KMC model allowed us to obtain a comprehensive view of adsorption, surface diffusion and mutual interactions of Ag adatoms on Si(111)7×7 surface at temperatures between RT and ≈540 K, where Ag/Si(111)$\sqrt{3}\times\sqrt{3}$ mixed reconstruction is not formed. The growth system can be characterized in a following way:

(1) The hopping rate of a single Ag adatom between HUC's on the Si(111)7×7 surface are estimated to be $\nu_1^{F,U}=\nu_0\exp(-E_d^{F,U}/kT)$, $\nu_0=5\times10^{9\pm1}$ s^{-1}, $E_d^F\approx E_d^U=(0.75\pm0.10)$ eV, $E_d^F-E_d^U\leqslant0.05$ eV.

(2) The nontrivial structure of the Ag layer observed at low temperatures where thermally activated hopping of Ag adatoms is negligible is caused by transient mobility of impinging Ag adatoms.

(3) The stability of an Ag cluster in a HUC is weak but increases substantially for six or more Ag atoms in a HUC. In the observed temperature range, HUC's have limited capacity to accommodate Ag adatoms.

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