Imaging diffusion fields on a surface with multiple reconstructions: Ag/Si(111)

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Abstract. Photoemission electron microscopy is used for studying the thermal decay of Ag islands grown epitaxially on a Si(111) surface. During the decay, the islands feed adatoms to the surrounding surface. The adatoms diffuse and eventually desorb, resulting in a radial coverage gradient that induces the formation of two concentric reconstructed zones, namely \((\sqrt{3} \times \sqrt{3})-R30^\circ\) and \((3 \times 1)\), around each island. We have developed a diffusion model to describe this multizone formation and demonstrate how diffusion constants can be determined for different reconstructed phases in a simple experiment.

Surface diffusion is a key process for ordering phenomena at surfaces. The formation of reconstructions and the interplay of adatoms and reconstructions with adatom concentrations are fundamental properties of metal/semiconductor systems, a knowledge of which might ultimately provide us with control over self-assembly processes on the nanoscale. Collective diffusion processes have been studied quantitatively for several decades \([1]–[7]\). There are essentially two types of measurement that have been carried out: (i) low-energy electron microscopy (LEEM)/photoelectron emission microscopy (PEEM) studies monitoring the mobility of molecular adsorbates \([8, 9]\) and metallic atoms \([10]\) after laser-induced thermal desorption and (ii) the spreading of artificially engineered patches of material observed using scanning electron microscopy (SEM) \([11]\), scanning Auger microscopy (SAM) \([12]\), biased-secondary electron imaging (b-SEI) \([13]\) and also PEEM \([6, 7]\).

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We have recently developed an experimental technique that provides a direct image of a diffusion field around a small Ag island on a Si(001) surface, by imaging a so-called ‘isocoverage zone’ (ICZ) [5], [14]–[16] in real time during the thermal decay of Ag islands on various Si(001) surfaces. Desorption of Ag atoms into the gas phase predominantly takes place from the surface after the Ag atoms have diffused to the surrounding surface, and not from the single crystalline surfaces of the Ag islands themselves [17]. Once introduced into the surrounding surface, the Ag atoms perform a random walk, and can induce a coverage-dependent surface reconstruction, the Ag/Si(001)-(3 × 2) [18, 19], when the local adatom concentration reaches a critical value. The Ag islands’ edges therefore serve as a reservoir source for diffusing adatoms, and the competing processes of surface diffusion and desorption produce a dynamically changing adatom concentration in the surrounding vicinity of the islands. This situation, in turn, causes the constant closed line of coverage, representing the critical coverage needed to form the Ag/Si(001)-(3 × 2), to move relative to the position of the island. This line of constant coverage, the ‘isocoverage’ line, is the boundary for the aforementioned ICZ surrounding the Ag islands.

Interestingly, once the coverage in the Ag overlayer falls below the critical coverage needed to maintain the Ag/Si(001)-(3 × 2) reconstruction, the surface reverts to the Si(001)-(1 × 2) reconstruction of the original substrate on which the Ag was deposited to form the islands, causing a difference in the local electronic structure. This difference in electronic structure between different reconstructed regions on the surface produces contrast in PEEM. The imaging of these different regions provides access to diffusion constants. The (an-)isotropic shape of the zone was found to reflect the (an-)isotropy of diffusion on the surface [15, 16]. Thus, via our LEE/PEEM-based imaging method, we are able to observe collective surface diffusion fields in situ and in real time during the decay of non-artificially grown Ag islands and the diffusive dynamics can be quantitatively analyzed without the further complications arising from silicide formation.

On the Si(001) surface, only one Ag-induced reconstruction is present, and the imaging of the ICZ is thus not suited for imaging gradients of the concentration, which would ultimately provide access to absolute values of the local adatom concentrations. Most metal/semiconductor systems, however, have a more complicated phase diagram than Ag/Si(001) and involve more than one adsorbate-induced reconstruction. The Ag/Si(111) phase diagram, for instance, exhibits two coverage-dependent reconstructions [20]–[24]. Here, we present experimental PEEM results for the Ag/Si(111)-(7 × 7) system and extend the diffusion model to describe multi-reconstruction systems. Our development and application of the diffusion model for multizone systems provides for the simultaneous determination of diffusion parameters for adatoms on different reconstructions.

The experiments were performed in an ultrahigh vacuum (UHV) LEEM [25]. PEEM was performed by illuminating the sample with UV light from a mercury discharge lamp. Precision-oriented (better than 0.1°) Si(111) substrates were cleaned by standard flash-annealing after degassing the samples at 600°C in UHV for several hours. Ag was deposited from an e-beam-heated tantalum crucible in a home-built evaporation cell [26, 27]. The Ag deposition took place at elevated substrate temperatures (500–690°C) and was monitored in situ with PEEM or LEE. The sample temperature was measured with an infrared pyrometer. For the desorption experiments, the temperature was rapidly increased to the desired desorption temperature (700–890°C), while an image sequence was recorded with the microscope.
Figure 1. The image sequence shows the time dependence of the island decay at 825°C. The time interval between the images is 2 s and the scale is the same in all images. The bright decaying triangle is the single crystalline Ag island, surrounded by a bright ($\sqrt{3} \times \sqrt{3}$)-R30° and a dark (3 x 1) reconstructed area. The outermost area shows the (7 x 7) reconstruction of the clean Si(111) surface. In (a)–(c), the ICZs are forming, whereas in (d)–(h), a quasi-static equilibrium is reached, while the size of the zones only decreases because of the island radius dependence shown in equation (1). After some time, the island vanishes ((i) and (j)) and the ICZs can no longer exist since their Ag-atom source, namely the island, is depleted. The slight anisotropy in (d)–(h) is due to a very small miscut and step alignment [16]. The images have been background corrected.

At elevated substrate temperatures, the initial deposition of Ag on Si(111) first leads to the formation of a low-coverage (3 x 1)-Ag reconstruction [20, 22, 23, 28], whereas during further deposition, the Ag/Si(111) system undergoes a phase transition and forms a high-coverage ($\sqrt{3} \times \sqrt{3}$)-R30°-Ag reconstruction [24]. Once the surface is completely covered by this phase, crystalline three-dimensional (3D) islands are formed, while the ($\sqrt{3} \times \sqrt{3}$) reconstruction is preserved between the islands. To prevent diffusion between the ICZs during desorption, it is necessary to achieve a low island density during growth. Ideally, the island-to-island distance is much larger than twice the diffusion length. The experimental observation indicates, however, that crosstalk can already be neglected when the island-to-island distances are about twice the diameter of the ICZs. Sufficiently low island densities of $\approx 50$ mm$^{-2}$ are achieved by depositing Ag at substrate temperatures of about 600°C, using low Ag deposition rates of $<1$ ML min$^{-1}$.

After island formation, the Ag flux is switched off and the sample temperature is raised rapidly to the desorption temperature. Figure 1 shows a sequence of PEEM images during a typical desorption experiment. Figure 1(a) shows the initial configuration of a bright triangular Ag island surrounded by a ($\sqrt{3} \times \sqrt{3}$) reconstructed background.

During desorption, in figure 1(b), a bright, ($\sqrt{3} \times \sqrt{3}$) reconstructed zone is maintained in the immediate vicinity of the island, but becomes surrounded concentrically by a darker, (3 x 1) reconstructed region. In figure 1(c), a second, slightly brighter, (7 x 7) reconstructed
zone can be observed surrounding the darker (3 x 1) zone. The specific phases associated with each contrasting region were confirmed by microdiffraction. In figure 1(d), two concentric zones of different grey levels and resembling different reconstructions can be clearly distinguished. During continued desorption (figures 1(e)–(h)), the two ICZs scale with the island size. Finally, in figure 1(i), the island’s Ag reservoir is depleted and the island disappears, followed by (first) the (√3 x √3) zone and (afterwards) the (3 x 1) zone. In figure 1(j), all Ag has been desorbed, leaving a clean (7 x 7) reconstructed Si(111) surface behind.

The (√3 x √3) and (3 x 1) reconstructions were the only Ag-induced reconstructions that we observed during our desorption experiments. The succession of the zones, (√3 x √3) in the vicinity of the island, then (3 x 1) and finally (7 x 7), shows that the coverage needed for the formation of the (3 x 1) is lower than for the (√3 x √3) reconstruction. This observation is consistent with the STM study by Nogami et al [23], where a (3 x 1) was always reported to be the separating phase between (√3 x √3) and (7 x 7) reconstructed areas. The phase diagrams of Ag on Si(111), as described by Nogami et al [23] and Le Lay et al [17], suggest that a (5 x 2) [23] reconstruction should also be present at some coverage. Neither during growth nor during desorption did we observe this reconstruction in the temperature regime investigated in this study.

We now develop a theoretical description of the experimental observation. The time dependence of the ICZ decay is similar to that described in our previous work [5]. After the ICZ is formed, a quasistatic equilibrium is reached (see figure 1). In contrast to compact Ag islands on Si(001), the Ag islands on the Si(111) surface are large and flat, and the island width changes more drastically. Accordingly, the radii of the zones on Si(111) show a stronger time dependence during decay than the radii of the zones on the Si(001) surface. More importantly, the previously found scaling law results from a single ICZ model, which we now generalize.

For the model, we consider a radial Ag coverage gradient, as depicted in figure 2, with critical coverages \( \theta_{i+1} \) necessary to form the reconstruction of the ICZ ‘i’ (i.e. between the radii \( R_i \) and \( R_{i+1} \)). In each zone, we assume only the corresponding excess coverage \( \phi_i = \theta_i - \theta_{i+1} \) to be mobile and to desorb, and \( \phi_i \) labels the critical excess coverage.
This situation can be described by a stationary drift-diffusion equation

\[ D_i \nabla^2 \phi - \phi / \tau_i = 0, \]

with zone-wise diffusion coefficients \( D_i \) and desorption times \( \tau_i \) (and consequently, with diffusion lengths \( \ell_i = \sqrt{D_i \tau_i} \)) and appropriate boundary conditions. In the limit that \( R_i, R_{i+1} \ll \ell_i \), and \( R_{i-1}, R_i \ll \ell_{i-1} \), in the circular geometry, the steady-state radii are found to obey

\[ R_i = R_{i+1} \left( \frac{R_{i-1}}{R_{i+1}} \right)^{\nu_i}, \tag{1} \]

where \( \nu_i = \frac{1 + (D_{i-1}/D_i)(\phi_{i-1}/\phi_i)}{1} < 1 \) for the \( i \)th ICZ. This reduces the problem of a myriad of diffusing adatoms to a simple power scaling law (equation (1)) that depends only on the diffusion constants and critical coverages of the two adjacent zones. Details of this model can be found in \([29]\).

For the outermost zone, which in our case corresponds to the Si(111)-(7 × 7) reconstructed area, the outer radius \( R_{i+1} \to \infty \), and it is replaced by the diffusion length \( \ell_i \) in equation (1). This coincides with the result of the single-zone theory outlined in our earlier work \([5]\).

The theory presented here suggests that in multizone systems, for each ICZ, the adjacent inner zone plays the role of the adatom supply. This result is supported by the experimental results in figure 3. Here, the time dependence of the radius of various zones is plotted as a function of time. The innermost zone disappears after the island and the outermost zone disappears after the inner zone. For the Ag/Si(111) system, this means that the inner, bright ICZ (supplied by the central island) in turn also feeds the outer, dark ICZ.

In the single zone case, data analysis using this technique has produced diffusion parameters that are consistent with known values for Ag diffusion \([30]\). Here, we use the generalization to the multizone systems to distinguish diffusion parameters on different reconstructions. In figure 3(b), the data from figure 3(a) are plotted in a double logarithmic scale, as shown in the legend. The fits shown represent the power laws according to equation (1). For the numerical analysis, the area of the triangular island is converted into a circle of the same area, as the specific shape of the island does not affect the shape of the zone. For the multi-ICZ case presented here, the results varied between 0.04 and 0.11 for \( \nu_1 \) and between 0.88 and 0.99 for \( \nu_2 \).

These results on the multi-ICZ on Si(111), with different diffusion constants for different reconstructions, have an interesting implication. Firstly, it is important to consider the critical values for the coverage needed to form the various reconstructions on Si(111). Although the exact coverages of the involved reconstructions have been under debate for many years, we will assume 2 monolayers to be the critical coverage to form islands, 1 monolayer as the critical coverage for the \( (\sqrt{3} \times \sqrt{3}) \) reconstruction \([23, 24, 31]\) and 1/3 of a monolayer as the critical coverage of the \( (3 \times 1) \) reconstruction \([23, 32, 33]\). The following argument, however, does not critically depend on the exact values for the coverages since the \( \nu_i \)s depend linearly on coverage, whereas the activation energy enters exponentially. With the typical values of \( \nu_1 = 0.08 \) and \( \nu_2 = 0.95 \), and assuming that the attempt frequency is roughly the same on all reconstructions, this results in the ratios \( D_0/D_1 = 17.25 \), \( D_1/D_2 = 0.026 \) and \( D_0/D_2 = 0.45 \) and illustrates that the diffusion constants are heavily dependent on the underlying reconstruction. We use \( E_{D_0} = 0.33 \) eV from the literature \([34]\) for the innermost \( (\sqrt{3} \times \sqrt{3}) \) reconstructed zone. The work by Hanbücken et al\([35]\) has been performed in a temperature and coverage regime that is
Figure 3. (a) The typical time dependence during Ag island decay for the island and the two ICZs. After the formation of the ICZ is completed after about 2 s the radius of the inner and outer zones shrinks slowly, similar to the behaviour on Si(001) for only one ICZ. When the island no longer exists, the supply of Ag adatoms disappears and the bright inner ICZ collapses. After the inner ICZ has disappeared, the outer dark zone collapses as well. This time-shifted behaviour suggests that the inner ICZ is the adatom reservoir for the outer ICZ. The diameter of the island has been enhanced by a factor of 4 for illustration.

(b) The experimental results on the ICZ $R_1$ and island $R_0$ radii for comparison with the theory (see equation (1)) at 870 °C. The lines are fitted yielding the displayed values as the only variables. The outermost radius thereby yields the diffusion length $\ell_2$ for Ag atoms on the bare Si(111)-(7×7) reconstruction.

As our measurements have been performed at various temperatures, several sets of $v_i$ and $D_i$ with different values have been acquired. Each set, analyzed individually, leads to the same activation energy with a maximum deviation of 0.07 eV.

It is interesting to compare our value for diffusion on the (7×7) surface with known values from the literature. Jeong and Jeong [36] have calculated a diffusion barrier of 0.27 eV for
diffusion within a \((7 \times 7)\) half unit cell (HUC) and a barrier of 0.88 eV for diffusion between HUCs. The latter value was also roughly confirmed experimentally for single Ag adatom diffusion on Si(111)-(7 \times 7) \[37, 38\]. However, only the barrier for diffusion within a HUC is consistent with an earlier work by Hanbücken et al \[34\] and this study. Apparently, the calculated higher barrier for diffusion across HUCs does not play a role in our experiments: Sobotík et al \[38\] stated, in an STM study of diffusion of Ag on Si(111)-(7 \times 7), that ‘any defect or adatom’ within a HUC changes the electronic structure significantly. In our experiment, with coverages between \(\theta = 2\) monolayers (close to the island), \(\theta = 1/3\) monolayer (at the edge of the \((7 \times 7)\)) and \(\theta = 0\) monolayer at infinite distances, the situation of several adatoms within a single HUC is a likely scenario. As such, we believe that in our case the diffusion barrier within the \((7 \times 7)\) HUC is the relevant parameter. With this assumption, the experiments of Hanbücken et al \[34\], this study and the works by Jeong and Jeong \[36\] and Sobotík et al \[38\] seem to be in agreement.

Our results demonstrate that the imaging of ICZs is not only useful for measuring diffusion parameters, as was shown in our earlier work, but the imaging of multi-ICZ systems also provides access to diffusion parameters on different reconstructions. In fact, equation (1) implies a simple relation between the relative widths of different zones in a multizone system and the ratios of the corresponding diffusion constants. This can be most easily seen by considering two limiting cases. When \(D_i \gg D_{i-1}\), such that diffusion is much faster in zone \(i\) than in zone \(i-1\), we have \(v_i \approx 1\) and therefore \(R_i \approx R_{i-1}\), which implies that zone \(i-1\) (enclosed by boundaries of radius \(R_{i-1}\) and \(R_i\)) is much narrower than zone \(i\). On the other hand, \(D_i \ll D_{i-1}\), \(v_i \ll 1\) implies that \(R_i \approx R_{i+1}\), and zone \(i\) is narrow compared to zone \(i-1\). In general, our model predicts that faster diffusion on a reconstruction will yield a wider ICZ for this reconstruction.

In conclusion, the extended model shows that each zone acts as an adatom source for the neighbouring outer zone, just as the island is the adatom source for the innermost zone. We have shown that the relative widths of the zones basically reflect the diffusion constants relative to the other zones (see equation (1)), and that the diffusion parameter can vary dramatically between different reconstructions. For the Ag/Si(111) surface, we find the highest diffusion barrier \(E_{D_1}\) of \(\approx 0.61\) eV in the \((3 \times 1)\) reconstructed region, sandwiched between a higher coverage (\(\sqrt{3} \times \sqrt{3}\)) phase and the \((7 \times 7)\) phase of the bare Si(111) surface. Considering an \(E_{D_0}\) of 0.33 eV on the \((\sqrt{3} \times \sqrt{3})\) reconstruction \[34\] and \(E_{D_0} = 0.25\) eV on the \((7 \times 7)\) reconstruction, we conclude that the diffusion of an Ag adatom expelled by the island starts out fast, slows down in the \((3 \times 1)\) region and speeds up again in the \((7 \times 7)\) region. This finding is directly reflected in the widths of the zones relative to each other. Imaging ICZs in a multizone system is thus not only capable of acquiring diffusion parameters or diffusion anisotropy of the investigated system, but also provides an estimate for the diffusion barriers on different reconstructions in a very quick and simple experiment. Furthermore, by increasing the number of zones, this technique can also visualize diffusion gradients on the surface, since the critical coverage for each reconstruction is either known or can be determined in a simple growth experiment.

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