Effect of surface steps on the diffusion of adsorbates investigated with angle-resolved photoelectron spectroscopy

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To investigate the surface diffusion of chemisorbed H on Ag/Au(111) thin films with surface steps, we characterized the distribution of H atoms on the surface by measuring the Shockley states of these surfaces with angle-resolved photoelectron spectroscopy. Our results show that H atoms tend to diffuse and to remain on the terrace at the lower side of the surface steps during annealing. This diffusive behavior is explained qualitatively through the existence of an Ehrlich-Schwoebel potential barrier associated with the surface steps.

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The diffusion of atoms on a solid surface has long been of great fundamental and technological interest.1–3 Many processes, including epitaxial film growth, catalysis, and self-assembly of nanostructures, are closely related to the surface diffusion. Several factors, including the temperature, the surface structure, and the interaction between diffusing atoms and the substrate, determine how the diffusion proceeds. As far as the surface structure is concerned, a surface step is one factor that is important but less characterized.4 Previous authors suggested that the potential barrier resulting from a great change in the coordination number near a surface step, known as the Ehrlich–Schwoebel (ES) barrier,5–6 might be a dominant factor governing the diffusion of the surface atoms. Hindering the interlayer diffusion by an ES barrier at a surface step produces many interesting surface morphologies,7–11 but investigating the surface diffusion near and over a surface step remains a difficult task because of its dynamical nature and the atomic resolution required for its characterization. A microscope based on a scanning probe (SPM) reveals atom-resolved surface morphologies but only on a static surface. The microscopes for field emission of ions (FIM) or electrons (FEM) characterize surface diffusion through the observation of the motion of individual atoms, but the large electric field employed in these experiments limits the studied systems to mostly metallic adsorbates on the surfaces of tungsten, rhodium, and iridium.12–13

According to an alternative approach to characterize the surface diffusion, instead of observing the motion of individual atoms, the evolution of the surface might be explored by monitoring macroscopically measurable but atomically resolved signals. Previous authors have demonstrated that the measurement of the atomic-layer-resolved features in photoemission spectra makes practical characterizing the properties of a varying surface, such as the evolution of surface morphology12,13 and the adsorption and desorption of adsorbates.14,15

In this work, our objective was to investigate the surface diffusion of adsorbates in the presence of surface steps through adapting a spectrometric approach. Our prototypical system involved H atoms chemisorbed on Ag/Au(111). The evolution of the film surface was characterized by monitoring its atomic-layer-resolved Shockley states with angle-resolved photoelectron spectroscopy (ARPES).16,17 Our results indicate that the absolute Ag coverage plays no dominant role in the diffusion of the H atoms; instead, these H atoms preferentially remain on the surface of the lesser Ag coverage at an elevated temperature. This peculiar behavior is explained qualitatively with the existence of the ES barrier associated with the surface steps; we suggest that the surface step remains a decisive factor in the surface diffusion of adsorbates even when these adsorbates can diffuse over the step. This finding provides insight into how the surface structures, such as the steps, affect the surface diffusion of adsorbates, which might serve as key knowledge for the understanding and control of the surface morphology of thin films and nanostructures during growth and catalysis.

Our experiments were performed at an ultrahigh vacuum endstation installed at Beamline 21B1 of the National Synchrotron Radiation Research Center, Taiwan. Angle-resolved photoemission spectra were measured with the photon energy fixed at 21 eV. The resolution of the photoemission spectra was ∼30 meV in kinetic energy and ∼0.01/A in the wave vector of the photoelectrons. An Au(111) single crystal was cleaned with repetitive sputtering and annealing until the split Shockley state of Au(111) was obtained.18 Silver was deposited from a K-cell evaporator onto the sample with the sample temperature kept less than 100 K; the sample was subsequently annealed up to 260 K.17 Silver of nonintegral monolayers (ML) was deposited intentionally to create steps on the film surface; 1 ML denotes one atomic layer of Ag on Ag(111), ∼1.38 × 1015 atoms/cm2. The exact coverage of such films was characterized by analyzing the line shape of the Shockley states.19,20 Chemisorption of H atoms on the sample surfaces was induced with uv irradiation at a low temperature;15 the diffusion of the H atoms was activated on annealing. To monitor the adsorption, diffusion, and desorption of the H atoms, we measured the Shockley states continuously during the uv irradiation and annealing of the sample.

Figure 1 shows the normally emitted curves of energy distribution measured for Au(111) with Ag at varied coverage. The Shockley states have binding energies that depend on the Ag coverage of the surface of the films;16,17 they are labeled with “Sn” when they originate from Au(111) covered with Ag at n ML. For Au(111) covered with Ag, two Shockley states are resolved in each spectrum, indicating that these
FIG. 1. Energy distributions of normal emission of Ag/Au(111) with the labeled Ag coverage; label “Au(111)” indicates that the surface was clean Au(111). The Shockley states on Au(111) covered with Ag at $n$ ML are indicated as $S_n$, where $n = 0, 1, 2, 3,$ and $4$.

Surfaces are atomically flat with the Ag films of only two distinct thicknesses coexisting on Au(111). This result agrees with previous reports on Ag/Au(111) grown with the two-step method. The two Shockley states in each spectrum are well defined, indicating that their corresponding surface domains are ordered and sizable and are separated with surface steps of which the height is one atomic layer.

Samples with varied Ag coverage were investigated. Figures 2(a) and 2(b) show data from 1.60- and 2.65-ML samples, respectively; data from a 3.70-ML sample are not shown; and “x-ML sample” denotes Au(111) covered with Ag at x ML. The spectra from the clean Ag/Au(111) surfaces are plotted at the bottom of Figs. 2(a) and 2(b); these two spectra also appear in Fig. 1. To deposit H atoms, the samples were exposed to photons of energy 21 eV with sample temperatures kept below 60 K. Previous authors reported that the chemisorption of H atoms on the surfaces of noble metals could be induced with irradiation of photons or ions. In photoemission measurements, the adsorption of H atoms appears as the deterioration of the Shockley states. After irradiation (90 min), the deterioration of the Shockley states, as shown in the spectra at 57 K in Fig. 2(a) and at 52 K in Fig. 2(b), was noticeable; the Shockley states were weakened and broadened. The deterioration was observed for both Shockley states in the spectra, indicating that H atoms adsorbed on the surfaces of the Ag films at both coverages.

To activate the surface diffusion of the adsorbed H atoms, the samples were slowly annealed, and the Shockley states were monitored continuously. Figure 2 shows representative photoemission spectra. At first glance, data in the two sets show a strong resemblance. For the 1.60-ML sample [Fig. 2(a)], state $S_1$ became severely broadened when the sample temperature reached 110 K, whereas state $S_2$ seemed little changed. $S_1$ stayed severely weakened and broadened until the sample temperature attained 195 K and suddenly recovered at 201 K. For the 2.65-ML sample [Fig. 2(b)], $S_2$ became broadened and weakened at 120 K and began to recover at $\sim 198$ K, whereas $S_3$ became slightly broadened because of the increasing sample temperature. A similar evolution in the spectra was observed for the 3.70-ML sample, with $S_3$ varying noticeably but $S_4$ little changed.

The nature of the evolution of Shockley states was explored by investigating the temperature dependence of their linewidths. These widths of the Shockley states were determined on fitting each spectrum to the sum of two Voigt functions and a polynomial background. All Gaussian widths (full width at half maximum, FWHM) were fixed to the resolution of the measurements (30 meV); the Lorentzian widths (FWHM) from the best fits were assigned to the linewidths. The fitting became problematic when the Shockley states were severely broadened, and the following procedure was performed. The difference in the binding energies of the two Shockley states in each spectrum ($\Delta E$) was first retrieved on fitting those spectra containing two clearly resolved Shockley

FIG. 2. Energy distributions showing the evolution of Shockley states of uv-exposed Ag/Au(111) at (a) 1.60 ML and (b) 2.65 ML during annealing. The temperatures of measurement are labeled with the spectra. The Shockley states of Au(111) covered with Ag at 1, 2, and 3 ML are labeled $S_1$, $S_2$, and $S_3$, respectively. Spectra measured from clean surfaces are plotted at the bottom for comparison.
states. The variation of $\Delta E$ over the temperature range in our measurement was within 5 meV, which was much smaller than the energy resolution of the measurement ($\sim 30$ meV) and the linewidths of the surface states ($30 \sim 80$ meV). The spectra in the entire set were then fitted with $\Delta E$ fixed. Because of the very small temperature dependence, the error of the analysis resulting from the constant $\Delta E$ was minimal. In our analysis, $\Delta E$ was measured as 0.085, 0.065, and 0.045 eV for the 1.60-, 2.65-, and 3.70-ML samples, respectively.

Figures 3(a) and 3(b) show the temperature dependence during annealing of the linewidths of the Shockley states for the 1.60- and 2.65-ML samples, respectively; the variation of the linewidths is exhibited in the figures. The linewidths of $S_1$ of the 1.60-ML sample [Fig. 3(a)] and $S_2$ of the 2.65-ML sample [Fig. 3(b)] increase significantly beginning at $\sim 110$ K and decrease sharply at $180 \sim 190$ K, whereas the other Shockley states of the same samples show little variation. The 3.70-ML sample has the same fluctuation in the linewidths of its Shockley states. Authors of a previous report observed a similar phenomenon and suggested that the variation of the linewidth was caused by the diffusion and desorption of the H atoms on the surface; our results support this suggestion. The decrease in the linewidth of the Shockley states on Ag/Au(111) at varied Ag coverage all occurred at $180 \sim 190$ K, which is near the desorption temperature (180 K) of H on Ag(111). Furthermore, the fact that the desorption temperatures of H on Ag/Au(111) at varied Ag coverage are near each other and near that on Ag(111) indicates that the binding energies of H on Ag/Au(111) and Ag(111) are similar and have little dependence on the Ag coverage of the thin films. Ogura et al. observed a similar phenomenon, reporting that the Ag of one monolayer on Pt(111) already acts like Ag(111) for the chemisorbed H.

The experimental results in Figs. 2 and 3 enable the following conclusion. These systems possess surfaces of two Ag coverages coexisting and separated by the surface steps of the height of 1 ML. During annealing, the chemisorbed H atoms diffuse but tend to remain on the surface of the lesser Ag coverage. This conclusion is somewhat unexpected. The preferential sites of adsorption on a surface are generally dominated by the interaction between the adsorbate and the surface, but this interpretation is excluded as the dominant factor in this work because, as we observed, the interaction between H and Ag/Au(111) is near that between H and Ag(111) and shows little dependence on the Ag coverage. If the interaction on varied surfaces is similar, why do H atoms tend to remain on the surface of the lesser Ag coverage during annealing?

The existence of the ES barrier associated with the surface steps might provide a qualitative explanation of the peculiar behavior of the diffusion of H on Ag/Au(111). Figure 4 shows a sketch of potential energy of the adsorbate on a flat substrate with an island height of 1 ML. The potential energy is drawn under an assumption that the adsorbate preferentially remains on sites of larger coordination, which is appropriate in the current context because H preferentially adsorbs on the threefold hollow sites on Ag(111). The potential energy on the surfaces away from the steps is the same or similar, showing small fluctuations resulting from the variation of the coordination. The ES barrier appears at the step edges because of the much decreased coordination. For the sites away from the steps, such as sites A and D, the adsorbate diffuses on the same terrace when it can overcome the small potential barrier between sites. When the adsorbate on the upper terrace travels to site C and lacks enough energy to overcome the ES barrier, it is reflected back and remains on the same terrace. This reflected movement of the adsorbate was first reported by Ehrlich and Hudda in their FIM experiments on W tips. Site B has the least potential energy; the adsorbate tends to attach on the lower side of the step, as observed during the growth of many films. When the adsorbate gains energy to leave site B, it preferentially detaches to the same terrace because of the smaller diffusion barrier. A point of interest arises when the adsorbate at site C acquires sufficient energy to diffuse over...
the ES barrier and reaches site B. Because of the dissipative nature of the diffusion and the asymmetry of the potential energy at the surface step, once the adsorbate reaches site B, it is more likely to remain on the lower terrace. One might argue that, at a much elevated temperature, the ES barrier might become insignificant and the adsorbate then diffuses over the step freely in both directions, which should show as a severe broadening of both Shockley states in the spectra at a high temperature of annealing. This phenomenon was not observed in our work, and it suggests that the H atoms desorb from the surface of the lower terrace before their diffusion into the higher terrace becomes significant.

The trend of the evolution of the surface states observed in our experiment should be insensitive to the exact H coverage as long as the lower terrace of the stepped surface is not fully covered with H. Our ARPES measurement is not capable of determining the exact H coverage, but a rough estimate of the H coverage may be possible. The previous study showed that H/Ag(111) has a (2 × 2) reconstruction with the H atoms staying on the threefold symmetric hollow sites; the H coverage is 0.25 ML for an ideal H/Ag(111)-(2 × 2) surface. For the 1.60-ML sample, 40% of the total surface is the lower terrace, which is Au(111) covered with the Ag of 1 ML. During annealing, all H atoms diffuse to the lower terrace. Although severely broadened, the spectra [158 and 187 K in Fig. 2(a)] show the existence of S1, suggesting that the H coverage is less than 0.1 ML (40% × 0.25 ML).

For heteroepitaxial thin films and nanostructures, the surface electronic states can be modulated significantly with overlayer coverage; the binding energy of the adsorbate can show a strong dependence on overlayer coverage, influencing the diffusion of the adsorbate among the surfaces of varied overlayer coverage. Because the binding energy of H on Ag/Au(111) depends little on the coverage of the Ag overlayer, the surface of the Ag/Au(111) thin film acts like the Ag(111) bulk surface for the diffusion of the H atoms; H on Ag/Au(111) is considered a prototypical system to investigate the pure step effect on the surface diffusion of an adsorbate.

The ES barrier is commonly comprehended with an argument involving the coordination. This argument works well when the adsorbate and the atoms of the substrate are the same species. Because H atoms on Ag(111) preferentially occupy the threefold hollow sites, the ES barrier estimated qualitatively from the argument of the coordination number is expected to be applicable. For those adsorbates composed of one or more atoms that preferentially occupy the bridge or on-top sites, the variation of the surface potential energy experienced by the adsorbate near a surface step might diverge from a traditional ES barrier. In these cases, the surface step is expected to continue to play a role in the surface diffusion of an adsorbate, but its influence might differ much from our observations in the present experiments.

The ARPES that we used determined qualitatively the surface distribution and desorption of adsorbate on monitoring in real time the atomic-layer-resolved signals over a macroscopic area. Although this spectral approach is powerful, it has its limitations. The detailed mechanism for an adsorbate diffusing over a surface step can be complicated. For example, does the adsorbate displace substrate atoms at the surface step during diffusion?5,7 Surface steps of two types exist on the (111) surface: do surface steps of the separate types have distinct effects on the adsorbate diffusion? The technique that we employed seems incapable of addressing these questions. Future experimental and theoretical investigations are required to determine a detailed mechanism of the diffusion of an adsorbate over a surface step.

Our experiment serves as a demonstration that the surface steps play an important role in the diffusion of adsorbates on a surface not only at a lower temperature but also at a moderate temperature at which an adsorbate can diffuse over the surface steps. With the existence of an ES barrier at a surface step, the adsorbates (H atoms in this work) preferentially remain within the same terrace at a lower temperature but diffuse to the lower terrace at an elevated temperature. With a designed arrangement of the surface steps operated at a specified substrate temperature, one might control the direction of the surface diffusion of varied adsorbates. Our result is prospectively important technologically and might become key knowledge concerning the growth and construction of nanostructures and the design of catalytic surfaces.

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