Terrace diffusion of Au atoms on Ir(111)

Shohei Ogura and Katsuyuki Fukutani
Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo
153-8505, Japan
E-mail: ogura@iis.u-tokyo.ac.jp

Abstract. We evaluated the energy barrier and prefactor of the terrace diffusion of Au atoms on Ir(111) by scanning tunneling microscopy. From the temperature dependence of the island density, we found that the terrace diffusion barrier and prefactor are $0.097 \pm 0.009$ eV and $9.4 \times 10^9 \pm 1.6$ s$^{-1}$, respectively.

1. Introduction
Surface diffusion of atoms and molecules is a fundamental process in film growth and surface reactions. In particular, diffusion of Au atoms is an important topic, since Au has different chemical reactivities depending on its size and shape [1, 2] and the shape of Au islands is determined by the competition among deposition rate and various diffusion processes occurring on surfaces; terrace diffusion of monomers, corner and edge diffusions along an island [3, 4], and step-down diffusion from an island [5, 6]. A previous study has shown that Au thin films grown on Ir(111) also have an anomalous chemical reactivity for hydrogen dissociative adsorption [7]. A motivation behind the present work is to understand the Au diffusion parameters that determine the island size and shape. In this paper, we evaluated the terrace diffusion barrier and prefactor of the Au monomers on Ir(111) from the density of Au islands grown on this substrate measured by scanning tunneling microscopy (STM) as a function of sample temperature during Au deposition. Using the mean-field nucleation theory [8, 9] that connects temperature dependence of the island density with its diffusion coefficient, we derived the diffusion barrier and prefactor to be $0.097 \pm 0.009$ eV and $9.4 \times 10^9 \pm 1.6$ s$^{-1}$, respectively.

2. Experimental
The STM measurements were performed in an ultra-high vacuum (UHV) chamber equipped with a 4-grid optics for low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES), and a variable-temperature STM (OMICRON VT-AFM/STM). The base pressure was typically $1 \times 10^{-9}$ Pa. The Ir(111) surface was cleaned by successive cycles of Ar$^+$ ion bombardment at 500 eV, heating at 1100 K in $7 \times 10^{-6}$ Pa O$_2$ atmosphere, and final flashing at 1450 K. The average terrace width measured by STM was wider than 200 nm and each terrace is separated by monotonically high steps. Deposition of Au was conducted using heated tungsten coils loaded with a Au wire at a rate of $1 \times 10^{-3}$ monolayer(ML) s$^{-1}$ (1 ML = $1.57 \times 10^{15}$ atoms cm$^{-2}$ for Ir(111)) and sample temperatures in the range from 45 to 300 K. After the Au deposition, the samples were cooled to $\sim 40$ K and examined by STM. The deposited amount of Au atoms was estimated from the STM images. After the STM measurements of a sample...
Figure 1. STM topographic image of Au islands grown on Ir(111) at (a) 300 K, (b) 160 K, and (c) 80 K. Image sizes and Au coverages are (a) 1000 × 1000 nm², 0.13 ML (b) 200 × 200 nm², 0.09 ML, and (c) 100 × 100 nm², 0.29 ML, respectively.

surface, the surface was re-cleaned and a new Au layer was prepared on the clean surface. The STM data were recorded in the constant-current mode with a tunneling current around 0.2 nA and a sample bias voltage around −0.15 V. All STM images in the present paper are displayed as topographic topviews with higher areas denoted by brighter images.

3. Results and discussion
Figure 1 shows STM images of the Au islands grown on Ir(111) at various sample temperatures during Au deposition. Au islands reveal a two-dimensional dendritic shape as shown in Figs. 1(a) and 1(b). The Au islands on the terraces have a triangular envelope and their branches preferentially grow into the three \( \langle \bar{1}12 \rangle \) directions rotated by 120° with respect to each other, which reflects the three-fold symmetry of the Ir(111) substrate. This shape can be explained by the diffusion limited aggregation model with corner and edge diffusion [3, 4]. No nucleation of the second-layer islands is observed on the first-layer islands at this coverage, indicating that atoms deposited directly on an existing island can descend easily from the island, i.e., the energy barrier for step-down diffusion is relatively small and can be readily overcome even at 80 K.

In the present study, we focus on the temperature dependence of the island density. The island density increases with decreasing sample temperature, and as a consequence, the average number of atoms per island becomes smaller with decreasing sample temperature. The island density in the present paper is expressed by the number of islands per unit cell, i.e., in ML. The island densities are 8.4 × 10⁻⁷ ML at 300 K, 1.7 × 10⁻⁴ ML at 160 K, and 2.8 × 10⁻³ ML at 80 K. The mean island sizes, i.e., the mean numbers of atoms per island are 1.2 × 10⁵ at 300 K and 0.13 ML, 470 at 160 K and 0.09 ML, and 96 at 80 K and 0.29 ML.

According to a mean-field nucleation theory [8, 9] which assumes a constant monomer density outside the islands, the island density \( n \) per unit cell is given by \( n = \eta(D/F)^{-i/(i+2)}\exp(E_i/(i+2)kT) \), where \( i \) is the critical island size, \( E_i \) is its binding energy (\( E_1 = 0 \)), \( \eta \) is a numerical parameter as a function of coverage and \( i \), \( D \) is a terrace diffusion coefficient expressed in the number of unit cells visited by the adatom per unit time. \( D \) is given by \( D = (\nu_0/4)\exp(-E_t/kT) \) for two-dimensional diffusion, where \( E_t \) is the terrace diffusion barrier and \( \nu_0 \) is the prefactor. \( F \) is a deposition rate (atoms per surface unit cell and time), \( k \) is the Boltzmann constant, and \( T \) is the sample temperature. The critical island size of \( i \) implies that an island consisting of \( i + 1 \) atoms is the smallest stable island at respective temperatures; \( i = 1 \) when a dimer is the smallest stable island, and \( i = 2 \) when a trimer is the smallest one.

The island densities measured by STM as a function of sample temperature are plotted in Fig. 2. The Arrhenius plot shows three linear regions and the change in the slope indicates that \( i \) changes at these temperatures. In order to derive \( E_t \) and \( \nu_0 \) for the terrace diffusion by using the equation above, we determined the critical island size \( i \) from island size distributions. The
island size distribution $N_s(\theta)$, which corresponds to the density of the islands containing $s$ atoms at coverage $\theta$, is expressed in the form of $N_s(\theta) = \theta S^{-2} f_i(s/S)$, where $S$ is the average island size and $f_i(s/S)$ is the scaling function [11]. Since the shape of the scaling function $f_i(s/S)$ depends on $i$ [11], $i$ can be determined from the normalized island size distribution. Figure 3 shows the normalized island size distribution at 66 K obtained from the STM image. The solid line in Fig. 3 is the theoretical curve for $i = 1$ [10]. The island size distribution at 66 K well agrees with the theoretical curve. We also found that the island size distribution at 160 K agrees with the theoretical curve for $i = 1$. Therefore, we can conclude that the critical island size is 1 between 66 and 160 K. The island size distribution at 45 K, on the other hand, is similar to the curve for $i = 0$ [10]. This indicates that even monomers are immobile on the surface and that the island density is not determined by the adatom diffusion. Although the nucleation mechanism in the $i = 0$ region is not unambiguously determined at this stage, a possible origin is either post growth, transient mobility, or easy attachment [12]. We can only conclude that $i = 0$ below about 60 K. Since the island density is not sufficient to obtain statistically meaningful island size distribution and compare with the theoretical curve, we assume that $i = 2$ above 160 K.

In the $i = 1$ region, the slope of the line in the Arrhenius plot gives $E_t/3k$. From the slope of the line fitted to the data in the range of $66 \leq T \leq 160$ K shown in Fig. 2, we obtained the terrace diffusion barrier $E_t$ to be $0.097 \pm 0.009$ eV. From the intercept of the line in the $i = 1$ region, the prefactor $v_0$ can be also estimated to be $9.4 \times 10^{9\pm1.6}$ s$^{-1}$, by assuming that $\eta = 0.25$ [13]. $\eta$ is almost constant at the coverage between 0.1 and 0.5 ML [13].

It should be noted that we neglected a small correction which should be considered when the island shape is fractal [14], since the islands are not extensively ramified between 66 and 160 K. The diffusion barrier would increase by about 10% at most, if the correction has to be applied.

It is reported that the terrace diffusion barrier and prefactor of Ag diffusion on Pt(111) are $0.168 \pm 0.005$ eV and $7 \times 10^{13\pm0.3}$ s$^{-1}$, respectively [15]. We compare this result with our present result, since both systems are diffusion of a noble metal on a fcc(111) surface of a transition metal. The terrace diffusion barrier of $0.097$ eV obtained for the Au diffusion on Ir(111) in the present work is slightly smaller than that for Ag on Pt(111). This difference would be intuitively attributed to the difference in the degree of lattice mismatch between the adatoms and substrate atoms. When adatoms having a larger atomic size are adsorbed on a surface having a smaller interatomic distance, they feel a less corrugated potential energy surface and the diffusion barrier becomes smaller. The atomic distance of Ir is smaller than Pt, whereas Au has a similar atomic size to Ag. Therefore, the diffusion barrier of Au diffusion on Ir is smaller than that of Ag diffusion on Pt.

The prefactor of $9.4 \times 10^{9\pm1.6}$ s$^{-1}$ is smaller than the usual value of $10^{12} - 10^{13}$ s$^{-1}$. Previous
studies [16, 17] show that the transition state theory breaks down when a diffusion barrier is lower than 0.1 eV, and that the prefactor decreases as the diffusion barrier decreases, and vice versa. Such a small prefactor is also explained by the multiple excitation model [17] or the long range interaction between diffusing monomers [18, 19]. Although we cannot conclude the reason for this small prefactor value at this stage, the present result is consistent with this tendency.

On the other hand, the slope becomes \( (2E_t+E_2)/4k \) in the \( i = 2 \) region, and the dimer binding energy \( E_2 \) is obtained to be \( 0.36 \pm 0.04 \text{ eV} \) by using \( E_t = 0.097 \text{ eV} \). The dimer dissociation barrier is \( E_t + E_2 \). It should be noted that the mean-field nucleation theory does not consider the dimer diffusion caused by successive corner diffusions, which affects the island density in the \( i = 2 \) region. This tends to increase the slope in the Arrhenius plot and leads to the increase of the prefactor \( \nu_0 \). Therefore, \( E_2 \) obtained here includes the effect of the dimer diffusion. The intercept of the line in the \( i = 2 \) region yields \( \nu_0 = 4.3 \times 10^{12 \pm 1} \text{ s}^{-1} \), which is larger than \( 9.4 \times 10^{9 \pm 1} \text{ s}^{-1} \) obtained from the \( i = 1 \) region. Because of the same reason as \( E_2 \), the prefactor \( \nu_0 \) obtained from the \( i = 2 \) region must be overestimated. Since we cannot distinguish the dimer binding energy and the dimer diffusion barrier at this stage, a further analysis such as a Monte Carlo simulation is needed to determine these values separately. Furthermore, since the island is extensively ramified at 300 K as shown in Fig. 1(a), the correction for the fractal shape should be taken into consideration.

4. Conclusions
We investigated the terrace diffusion of Au atoms on Ir(111). From the temperature dependence of the island density, we obtained the terrace diffusion barrier and prefactor of \( 0.097 \pm 0.009 \text{ eV} \) and \( 9.4 \times 10^{9 \pm 1} \text{ s}^{-1} \), respectively. This result can be used to control the island density, size, and shape by controlling the growth condition. We also obtained the dimer binding energy of \( 0.36 \pm 0.04 \text{ eV} \). However, since this value includes the effect of the dimer diffusion, a further analysis is needed to distinguish these values.

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