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Decay of nano-islands on the surface of a Au(111) electrode in contact with sulfuric acid solution

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Abstract

The decay of nano-islands on the surface of a Au(111) electrode, in contact with 50 mM sulfuric acid aqueous solution under an applied potential in the range of 0.15–1.2 V, has been investigated using electrochemical atomic force microscopy (EC-AFM). The results are compared with those previously obtained for Au(100). With either orientation, it is found that the area of the top layer of multi-layered islands decreases linearly with time at any applied potential. It was also found that the decay rate, defined as the rate of decrease of the number of atoms in the top-layer of the islands per second, increases with the magnitude of the applied potential. Further, the decay rate of the top layer of the islands on Au(111) is almost the same as that on Au(100).

Keywords: Surface diffusion; Single crystal surfaces; Stepped single crystal surfaces; Gold; Atomic force microscopy; Metal–electrolyte interfaces; Solid–liquid interfaces; Surface structure; Morphology; Roughness; Topography

1. Introduction

The properties of a solid surface in contact with an electrolyte are of interest because of presence of a electric double layer at the solid/electrolyte interface (e.g. chemo-mechanical effect [1–4]). The state of this electric double layer at this interface can be controlled by means of an applied potential.

Atomic force microscopy (AFM) and scanning tunneling microscopy (STM) are powerful tools for the in situ observation of the electrode surface in an electrolyte [5,6]. Trevor et al. [7,8] and Honbo et al. [9] observed the topographic change of Au(111) and Au(100) surfaces with time in an acid solution, noting that chloride anions results in enhanced surface diffusion. The effects of anions in the electrolyte on surface diffusion have also been discussed in previous experimental work [10,11]. In recent years, it has been found that the dynamics of nano-features or mono-atomic steps on electrode surfaces are dependent on the applied potential [12–22]. The comparison between the above experimental results and theoretical considerations provides considerable insight into the influence of the applied potential and absorbed anions on surface dynamics. However, a comprehensive understanding of the dynamics of the electrode surface in electrolyte is still lacking. In order to understand these dynamics in detail, it is essential to obtain the dependence on the applied potential, simultaneously with other factors, such as surface orientation, temperature [17], anions in the electrolyte [16], electrode material [14], etc.

In this paper, the dependence of decay rates of nano-islands on Au(111) electrodes on applied potential have been investigated using electrochemical atomic force microscopy (EC-AFM) and are compared with decay rates on Au(100) electrodes reported previously [17].

2. Experimental

Au(111) disks (12 mm diameter, 2 mm thickness) were cut from a single crystal Au rod, grown using the Bridgman method. The sample preparation of Au(111) was almost the same as that reported previously [23]. After mechanical polishing with Al_2O_3 powder, the sample was electropolished in a solution of hydrochloric acid and ethanol (1:9) and annealed at 900 K in H_2 for 30 min. In situ images of EC-AFM were taken using Nanoscope IIIa (Digital Instruments)

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with an EC-AFM unit (Molecular Imaging). The potential of the working electrode was controlled by a potentiostat and referred to a reference electrode. Although the reference electrode actually used here was a Hg/Hg_2SO_4 electrode (0.65 V vs. normal hydrogen electrode; NHE), all potentials have been referred to NHE in this paper. The electrolyte used was 50 mM H_2SO_4 aqueous solution ($pH = 1.1$), prepared from H_2SO_4 (Wako, Superior) and MilliQ-water. The electrolyte was de-aerated with Ar gas for more than 2 h before each experiment. All experiments were performed at room temperature.

3. Results and discussion

Fig. 1 shows a series of EC-AFM images (200 nm × 200 nm), showing the decay of the top layer of a multi-layered island located on a Au(111)electrode, biased at 0.45 V in 50 mM H_2SO_4 aqueous solution. The top layer of the multi-layered island is indicated by white arrows. The orientation of Au (111) substrate is indicated by black arrows. Fig. 2 shows the time dependence of the number of atoms in the top layer of the multi-layered island. The number of atoms in the top layer, calculated from the area of the layer, decreases linearly with time. As with Au(100), it is found that the area of the top layer decreases linearly with time at any applied potential between 0.15 and 1.2 V, independently of the actual area of the top layer. It has been suggested by previous theoretical considerations [24] and previous investigation [18] that the decay rate is independent of the area of the top layer when the detachment of the atoms from the island is the limiting decay process. The flux of atoms from the island is given by the following equation,

$$J(R,t) = -\frac{2\pi R}{\Omega}\frac{\partial R}{\partial t} = \frac{2\pi R}{\Omega}\eta_S\left(\frac{\beta}{R} - \Delta\nu\Delta G\right), \qquad (1)$$

where R is the radius of the island, Ω is the occupied area of an atom in the island, η_S is the mobility, $\Delta\nu$ the density

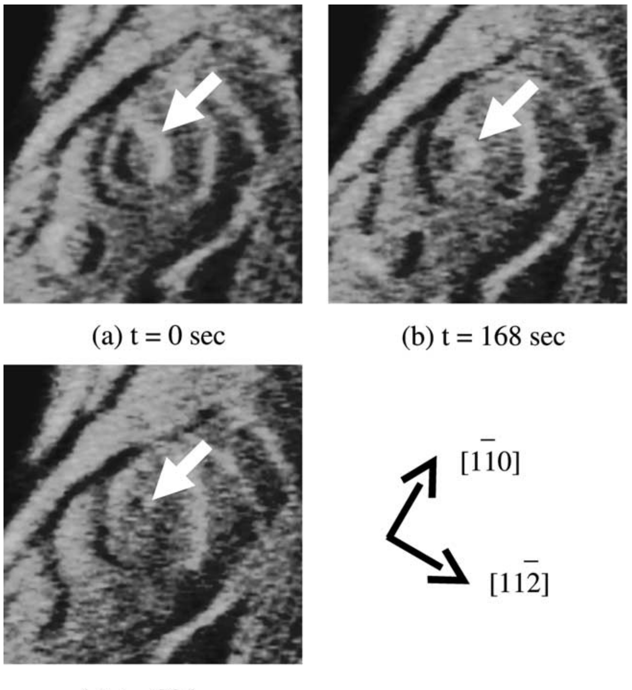

(a) t = 0 sec
(b) t = 168 sec
(c) t = 294 sec

Fig. 1. Series of EC-AFM images (200 nm × 200 nm), showing the decay of the top layer of a multi-layered island located on Au(111)electrode in 50 mM H_2SO_4 aqueous solution with an applied potential of 0.45 V. The top layer of the multi-layered island is indicated by white arrows. The orientation of Au (111) substrate is indicated by black arrows.

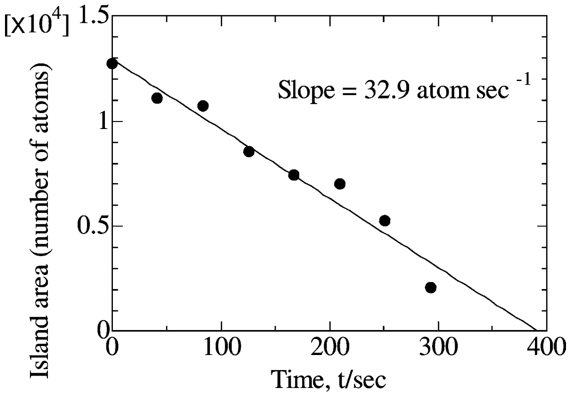


Fig. 2. Time dependence of the number of atoms in the top layer for the multi-layered island shown in Fig. 1.

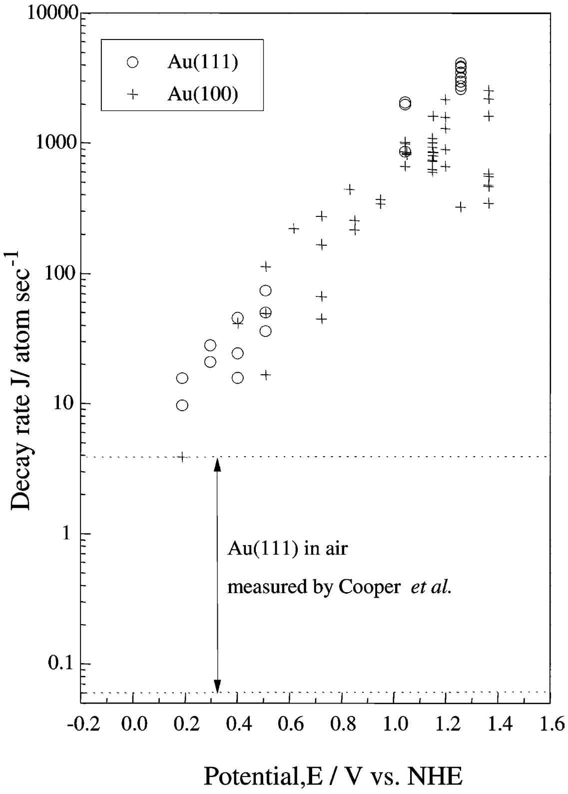
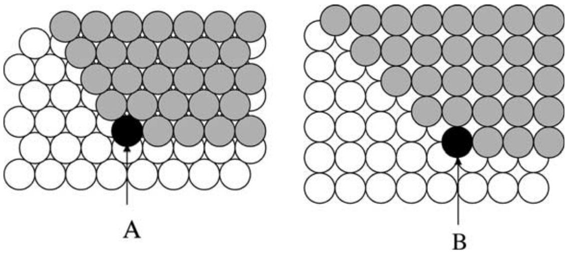


Fig. 3. Decay rate of the top layer of multi-layered islands on Au(111), immersed in 50 mM H_2SO_4, as a function of applied potential. The previous results with Au(100) are also plotted.



(a) Au(111) (b) Au(100)

Fig. 4. Schematic illustration of stepped surfaces of Au(111) and Au(100). Atoms at a kink site are shown as solid circles.

difference between the atoms in the island and those on the terrace, ΔG the excess free energy of atoms on the terrace per unit area near the step edge due to the their supersaturation and β the free energy of step edge per unit length. When R is much smaller than the critical radius $R_C(= \beta/\Delta\nu\Delta G)$, the flux of atoms from the island is constant with R, that is,

$$J(R,t) \cong \frac{2\pi\eta_S\beta}{\Omega}. \qquad (2)$$

As already described, the decay rate is independent of the area of the top layer at any applied potential between 0.15 and 1.15 V, but it is dependent on the value of the applied potential. Fig. 3 shows the decay rate of the top layer of multi-layered islands on Au(111) in 50 mM H_2SO_4 as a function of applied potential. The previous results on Au(100) [18] are also plotted in Fig. 3. As with Au(100), it is found that the decay rate increases when the potential of Au(111) increases in the range of 0.15–1.15 V. It is also found that the decay rate of the top layer of the islands on Au(111) is almost the same as that on Au(100). Fig. 4 shows a schematic illustration of stepped surfaces of Au(111) and Au(100). Atoms at kink site are shown as solid circles. When the detachment of the atoms from the island is the limiting process of the decay, it is thought that the atoms are mainly detached from kink sites, where an atom has the least number of neighbor atoms. Atoms at a kink site on Au(111) and Au(100) both have 6 neighbors, so that it is anticipated that the decay rate of the top layer of multi-layered islands on Au(111) would be almost the same as that on Au(100). The above consideration is in practical agreement with the our previous conclusion that the limiting process of the decay is not the surface diffusion of the detached atoms, but the detachment of the atoms from the island [18].

4. Conclusion

Decay of nano-islands located on a Au(111) electrode, in contact with 50 mM sulfuric acid aqueous solution and biased between 0.15 and 1.2 V, has been investigated using EC-AFM and compared with previously reported results for Au(100). Results and discussion yield the following conclusions:

1. As with Au(100), the area of the top layer of multi-layered islands on Au(111) decreases linearly with time at any applied potential.
2. The decay rate, defined as the rate of decrease of the number of atoms in the top-layer of multi-layered islands per second, increases with the applied potential.
3. The decay rate of the top layer of multi-layered islands on Au(111) is very similar to that on Au(100).

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