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| **Author(s)**   | Hirai, Nobumitsu; Yamauchi, Masaki; Tanaka, Toshihiro; Hara, Shigeta                             |
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Decay of nano-islands on the surface of a Au(111) electrode in contact with sulfuric acid solution

Nobumitsu Hirai*, Masaki Yamauchi, Toshihiro Tanaka, Shigeta Hara

Department of Materials Science and Processing, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565-0871, Japan

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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).

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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 an electric double layer at the solid/electrolyte interface (e.g. chemomechanical 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 monoatomic 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 Al₂O₃ powder, the sample was electropolished in a solution of hydrochloric acid and ethanol (1:9) and annealed at 900 K in H₂ for 30 min. In situ images of EC-AFM were taken using Nanoscope IIIa (Digital Instruments)
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$_2$SO$_4$ 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$_2$SO$_4$ aqueous solution (pH = 1.1), prepared from H$_2$SO$_4$ (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$_2$SO$_4$ 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,

\[
J(R, t) = -\frac{2\pi R}{\Omega} \frac{\partial R}{\partial t} = \frac{2\pi R}{\Omega} \eta_S \left( \frac{\beta}{R} - \Delta \nu \Delta G \right).
\]

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

![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$_2$SO$_4$ 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.](image)

![Fig. 2. Time dependence of the number of atoms in the top layer for the multi-layered island shown in Fig. 1.](image)

![Fig. 3. Decay rate of the top layer of multi-layered islands on Au(111), immersed in 50 mM H$_2$SO$_4$, as a function of applied potential. The previous results with Au(100) are also plotted.](image)
difference between the atoms in the island and those on the
terrace, $\Delta G$ the excess free energy of atoms on the terrace
per unit area near the step edge due to the their super-
saturation and $\beta$ the free energy of step edge per unit length.
When $R$ is much smaller than the critical radius
$R_c(= \beta/\Delta v_{eq} G)$, the flux of atoms from the island is
constant with $R$, that is,
\begin{equation}
J(R, t) = \frac{2\pi \gamma \beta}{\Omega}.
\end{equation}

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
$\text{H}_2\text{SO}_4$ 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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