CHEMISTRY LETTERS, pp. 2059-2062, 1994.

In Situ Observation of the Au-Hg Alloy Formation on a Gold Electrode Surface by Atomic Force Microscopy

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Bulk electrochemical deposition of mercury on Au(111) electrode surface in an acidic media, resulting in the formation of a Au-Hg alloy, has been studied *in-situ* by atomic force microscopy (AFM). AFM images revealed that small alloy protrusions form initially next to the Au grain boundaries and gradually increase in size with increased deposition time. More importantly, these protrusions are always accompanied by the dissolution of gold at the grain boundaries, leaving many apparent pits visible on the amalgamated surface.

Mercury amalgamation is a particularly important process from both a technological and fundamental perspective. For instance, precious metals (e.g., Au and Ag) can be separated from non-precious materials using amalgamation and the amalgams themselves are used extensively as a material for dental fillings. Despite its diverse applications, little is known about the surface morphology after amalgamation, especially at the nanometer-scale. There are a number of studies reported in the literature; however, most of these works are based on standard electrochemical techniques which provide only indirect information concerning changes at the surface.1-3) On the other hand, scanning tunneling microscopy (STM) and atomic force microscopy (AFM) are especially well suited for investigating surface structures with high resolution and are capable of *in-situ* imaging in electrochemical environments. Many researchers have reported on the electrochemical deposition, ranging from underpotential depostion (UPD) to bulk deposition, for various metal/electrolyte systems using STM and AFM.4-12) However to our knowledge, no one has investigated the bulk deposition of Hg on a metal surface using scanning probe microscopy. Hg deposition on a metal surface is quite unique in that the deposition process will directly result in the formation of a Hg alloy surface rather than simply depositing a bulk metal on top of the electrode surface. A similar electrochemical alloy formation has been reported for a Pb monolayer deposited onto a Au substrate.8) In this letter, *in-situ* electrochemical AFM is used to further understand the Hg amalgamation process on the nanometer-scale. In this particular study, the initial stages of Hg amalgamation of Au (111) thin films are investigated.

The gold electrodes were prepared by vacuum evaporation of Au onto glass at 300 °C and subsequently

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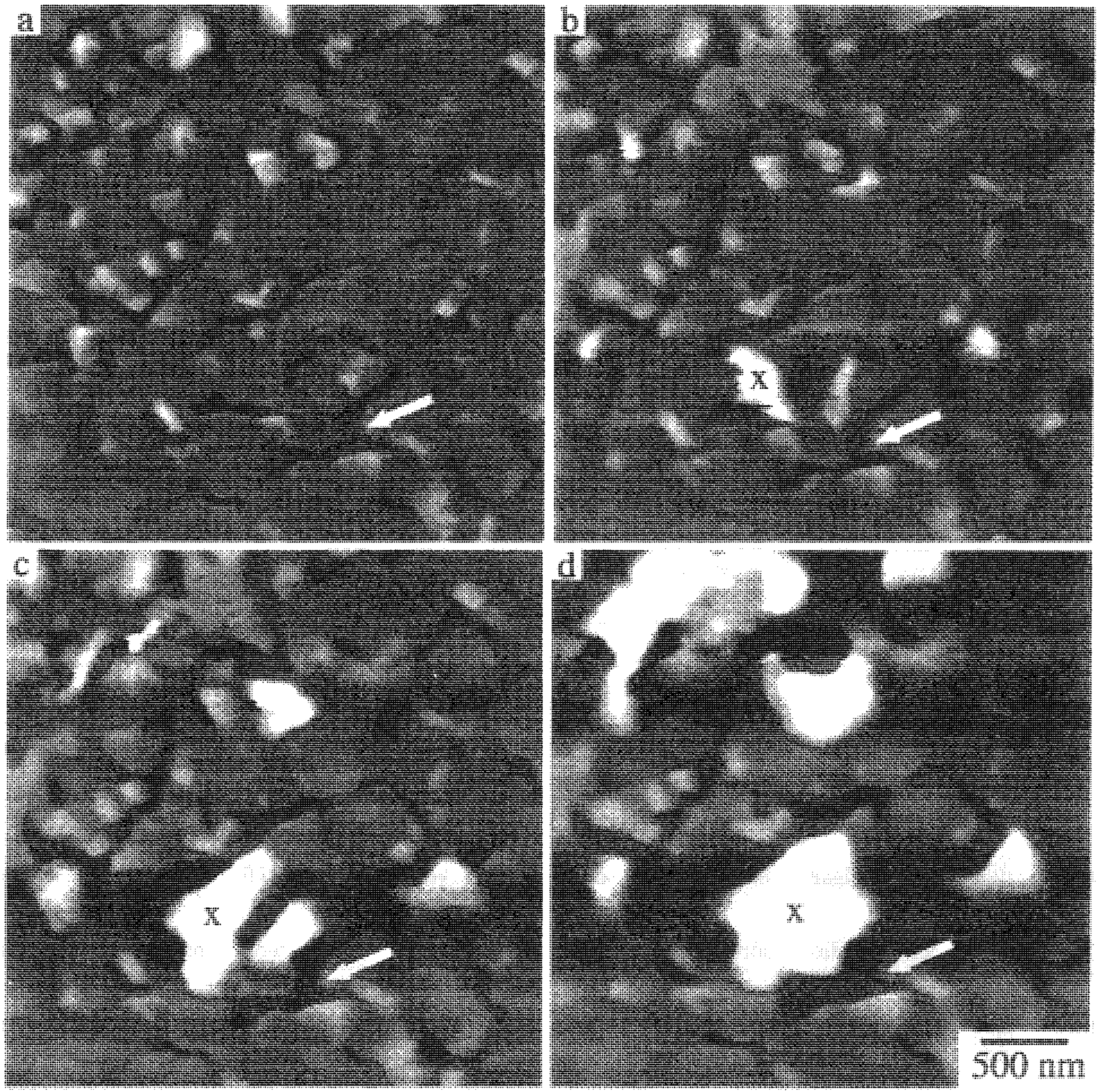

Fig. 1. A series of AFM images showing the Hg deposition process on the Au (111) electrode surface. The 'x' and arrow mark the locations of a protrusion growth and pit formation, respectively. The images were taken in intervals of 30 s, while maintaining a potential at - 900 mV. The height scale between 'black' to 'white' is 180 nm.

annealing at 400 °C for 2 h. The process is similar to that reported in the literature.$^{12)}$ 1 mM HgO was dissolved in 0.5 M H_2SO_4, which served as the supporting electrolyte. Pt wires were used as the reference and counter electrode which were affixed to the AFM electrochemical cell. All potentials were referred to this reference electrode. The AFM measurements were performed using a commercial system (Seiko SPA-300). Soft cantilevers (200 μm long with an integral pyramidal Si_3N_4 tip, exhibiting an spring constant of about 0.02 N/m) were used. The typical force applied for all the measurements was on the order of 10^{-9} N.

Figure 1 represents a series of 3 μm x 3 μm AFM images which were acquired sequentially at intervals of

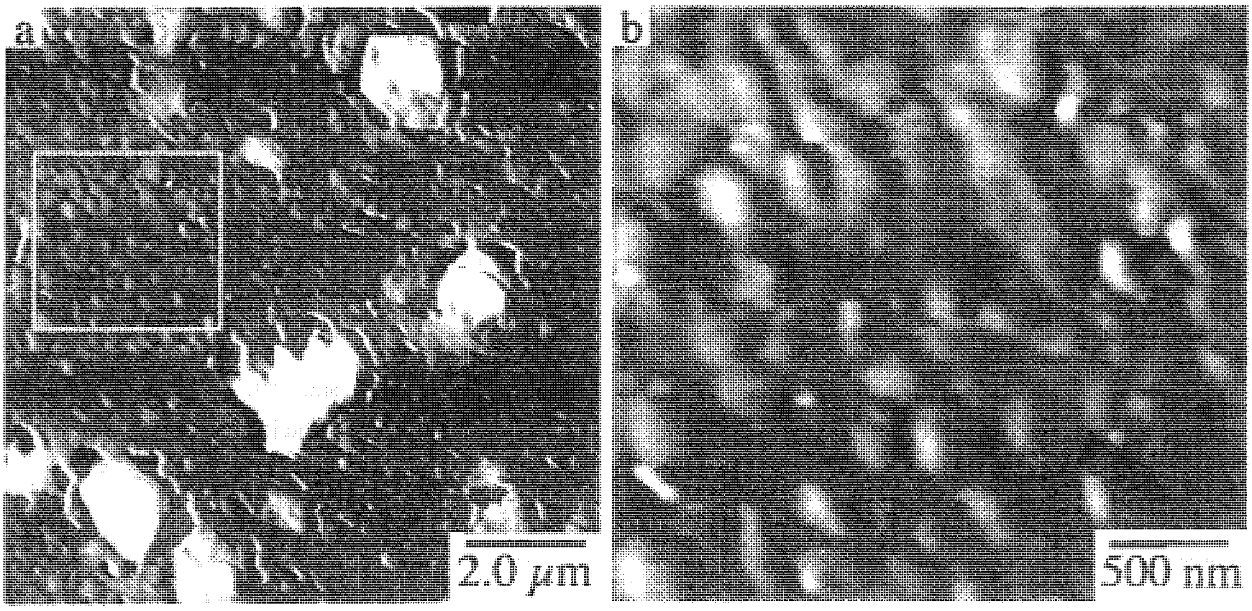

Fig. 2. (a) A 10 μm x 10 μm AFM image showing the amalgamated surface after 3 min. deposition at -900 mV. (b) A zoom image (white outline in Fig. 2a) taken at a initially smoother region shows that the smaller grain boundaries are filled in as the result of Hg amalagamation.

30 s while the electrode potential was being maintained at -900 mV. The average current density during deposition was approximately 142 μA/ cm^2, based on the assumption that Hg deposition took place uniformly over the Au electrode surface. Figure 1a shows a typical bare gold substrate prior to Hg deposition. The surface consists of Au (111) grains coalesced together which are separated by considerably 'deep' grain boundaries. These 'deep' boundaries (see arrow, Fig. 1a) are typical features after annealing under the conditions used here. After depositing for 30 s, local structural changes on the electrode surface are noticeably observed. Several small protruded structures have emerged (e.g., see 'x' mark in Fig. 1b) which corresponds to the bright areas in AFM images. Careful examination of these regions revealed that all the protrusions corresponded to locations at or near the Au grain boundaries. This observation follows the general tendency that bulk electrochemical deposition of metals occurs preferentially at the defect sites (e.g. grain boundaries), at least, during the initial stages of deposition. With increased deposition time, these small protrusions rapidly become larger (see 'x'marks in Figs. 1b-d).

However more importantly is the observation that the Au grain boundaries neighboring the protrusion sites are also modified during the deposition process. This phenomenon is clearly seen by following the series of arrows in Fig. 1. Along each of the protruded regions, the Au grain boundaries become increasing larger with further deposition time which eventually form pit-like structures. This observation is in contrast to conventional metal deposition where the underlying substrate shows no significant surface perturbation. Moreover, since excess Hg in contact with Au is known to cause amalgamation, the Hg atoms will continue to preferentially diffuse into the Au electrode along these grain boundary sites. However from our observation, it is clear that not only the Hg atoms are mobile but that the Au atoms must also migrate as well during amalgamation to account for the AFM observations. We are currently conducting more detail studies to elucidate the driving mechanism behind the Au migration and will be the subject of a later publication.

Figure 2a shows a 10 µm x 10 µm AFM image which was obtained after depositing for 3 min. at -900 mV. Similar structures were repeatedly observed over various parts of the amalgamated surface. Compared with the bare gold surface, significant changes in surface structure are easily distinguished as a result of the Hg deposition at this potential. First, there are several protruded alloy lumps on the electrode surface. Moreover, we can clearly observe that the appearance of such structures is always accompanied by several pits surrounding the protrusion and agrees with our earlier observation mentioned above. In addition, cross sectional examination of the AFM images showed that the depth of these pits is always approximately 120 nm, which corresponds to the same thickness as that of the vacuum-deposited gold film. This suggests that the Au grains in the pits have fully dissolved into either the Au-Hg alloy protrusions or neighboring areas during the Hg deposition process. Lastly, the regions lying between the protrusions on the amalgamated surface are also modified during Hg deposition as shown in Fig. 2b. We find that the distinct 'deep' grain boundaries seen prior to deposition appear less well-defined and in some cases completely disappearing after amalgamation. These areas are generally smoother than the protruded-structure regions prior to deposition. This observation indicates that the newly formed alloy surface can also partially fill the smaller grain boundaries in order to accommodate the extra Hg inside the Au electrode.

In summary, we applied *in-situ* electrochemical AFM to observe the bulk deposition of Hg on the Au(111) electrode surface, resulting in the formation of a Au-Hg alloy. The formation of protrusions on the surface is always accompanied by the dissolution of gold at neighboring grain boundaries which lead to many pits surrounding the structure. At more smoother areas, the grain boundaries of the Au electrode surface is rearranged due to the formation of the Au-Hg alloy.

The authors would like to that Mr. H. Sakai with helping in the preparation this manuscript. This research work was support by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

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(Received August 5, 1994)