Electron-irradiation-induced sputtering of gold atoms from isolated nanometer-sized particles of Al$_2$Au

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Abstract

Electron irradiation effect on nanometer-sized Al$_2$Au particles has been studied using transmission electron microscopy. Particles of Al$_2$Au in sizes of around 25 nm in diameter have been irradiated with 200 keV electrons at room temperature. In bright field images, no appreciable changes in the size and in the microstructure of Al$_2$Au particles have been detected. However, careful analyses of the chemical concentration by the quantitative measurement of intensities of Debye–Scherrer rings using imaging plates show that gold atoms in Al$_2$Au particles were selectively removed by 200 keV electron irradiation. In separate annealing experiments, on the other hand, it is observed that aluminum atoms in Al$_2$Au compound particles were preferentially evaporated with increasing temperature. Based upon these results, it is concluded that the selective removal of gold atoms in nanometer-sized Al$_2$Au particles was induced not by heat-induced-evaporation of gold atoms but by knock-on displacement during 200 keV electron irradiation. It is suggested that the threshold energy for gold atom sputtering from Al$_2$Au nanoparticles is as low as less than 1.9 eV.

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1. Introduction

Nanometer-sized particles have attracted considerable attention from both scientific and technical points of view. This is because they show significantly different characteristics compared with the corresponding bulk materials [1–3]. Recent remarkable progress in fabrication techniques makes it possible to manipulate nanometer-sized particles in a variety of manners [4,5]. These nanometer-sized particles consist of $10^3$–$10^4$ atoms and the surface-to-volume ratio becomes remarkably large with decreasing size of particles. Surface atoms have some broken bonds and are therefore in a high-energy state compared with inner atoms. It is then expected that surface atoms make a great contribution to the unique properties exhibited in nanometer-sized particles. This is called as the ‘surface effect’. To get a fundamental understanding of this effect, a lot of work has been carried out to today. For example, in silicon with the covalent bond, the nature of the surface reconstruction was revealed by Takayanagi et al. [6], and it was shown that the surface effect is confined within a very thin surface region. In ionic nanocrystals, Perebeinos et al. reported that competition between the long-range Coulombic attractive and the short-range repulsive interaction induces an effective negative pressure which causes the lattice parameter to increase with decreasing size of particles [7]. On the other hand, it is well known that high-energy electron irradiation is useful to manipulate materials on an atomic level by the use of irradiation-induced atom displacements [8,9]. In fact, quite recently it was confirmed that knocking off of gold atoms from an embedded target Al$_2$Au precipitate and subsequent implantation into an aluminum matrix can be achieved by using 300 ~ 2000 keV electron irradiation [10]. This observation suggests a possibility that in the case of isolated, nanometer-sized particles of the Al$_2$Au compound, gold atoms on the free surface can be displaced from their lattice site by irradiation of electrons with an energy lower than 300 keV, since the displacement energy for atoms on the free surface can be reduced to a great extent, say, by ca. 50% [11]. In the present work, in an attempt to see whether or not the gold-atom displacement could be induced at such reduced electron energies, a series of in
situ 200 keV-electron-irradiation experiments were conducted using isolated, nanometer-sized Al$_2$Au compound particles.

2. Experimental procedures

Preparation of nanometer-sized Al$_2$Au compound particles was carried out using an evaporator installed in the specimen chamber of a Hitachi H-800 type 200 kV transmission electron microscope (TEM). The evaporator consisted of a spiral-shaped tungsten filament. The distance between the filament and a supporting film (substrate) was approximately 100 mm. An amorphous carbon film with a thickness of around 50 nm was used as the supporting film, and was mounted on a molybdenum grid. Using this evaporator, aluminum and gold atoms were evaporated from a lump of Al$_2$Au compound attached to the filament, onto the supporting film kept at room temperature (RT), and nanometer-sized Al$_2$Au particles were produced on the film. The lump of Al$_2$Au compound was obtained by clashing a bulk intermetallic compound of Al$_2$Au, which was produced by the arc-melting method prior to the TEM experiments. These nanometer-sized Al$_2$Au particles were then irradiated with 200 keV electrons at RT. Changes in bright-field images (BFIs) and selected area electron diffraction patterns (SAEDs) associated with electron irradiation, were monitored in situ. In addition to conventional films, imaging plates [12] were also employed so that the intensity of Debye-Scherrer rings could be digitalized and analysed in a quantitative manner. For the digitalization, an imaging plate processor (FDL5000) was used.

The electron microscope was equipped with a turbo-molecular pumping system to achieve a base pressure of around $3 \times 10^{-5}$ Pa in the specimen chamber. The electron flux used in irradiation experiments was approximately $1.5 \times 10^{20}$ e m$^{-2}$ s$^{-1}$.

3. Results

Fig. 1 shows a typical sequence of electron micrographs of the changes in nanometer-sized Al$_2$Au particles during a 200 keV electron irradiation experiment. Fig. 1(a) and (a') show a BFI of as-produced Al$_2$Au particles on an amorphous carbon film and the corresponding SAED, respectively. As seen in Fig. 1(a), Al$_2$Au particles are randomly dispersed on the amorphous carbon film. The mean diameter of Al$_2$Au particles is approximately 25 nm. Debye–Scherrer rings in the corresponding SAED (Fig. 1(a)) can be consistently indexed as those of a crystal with the CaF$_2$ structure belonging to the space-group Fm3m. This is the same structure as that of bulk Al$_2$Au compound [13]. This fact indicates that deposition of aluminum and gold atoms onto the supporting carbon film was carried out rather uniformly over the film and that the composition of particles produced was within a concentration range where the alloy took the CaF$_2$ structure. Fig. 1(b) and (c) show BFIs of the same field as in Fig. 1(a) after 200 keV electron irradiation for 0.9 and 1.8 ks, respectively. Fig. 1(b') and (c') show SAEDs corresponding to Fig. 1(b) and (c), respectively. In association with irradiation, dramatic changes have been caused neither in BFIs nor in SAEDs. However, a close examination on the intensity of Debye-Scherrer rings has revealed a systematic change in the relative intensity of

![Fig. 1. A sequence of electron micrographs of the changes in nanometer-sized Al$_2$Au particles during 200 keV electron irradiation. (a) BFI of as-produced Al$_2$Au particles on an amorphous carbon film and (a') the corresponding SAED, (b) BFI of particles after irradiation for 0.9 ks at RT and (b') the corresponding SAED, (c) BFI of particles after irradiation for 1.8 ks at RT and (c') the corresponding SAED.](image-url)
the 111 ring with irradiation. Fig. 2(a), (b) and (c) show the intensity profiles of Debye–Scherrer rings in Fig. 1(a), (b) and (c), respectively. The profiles in Fig. 2 were obtained using imaging plates. It is seen from Fig. 2 that the relative intensity of the 111 Debye–Scherrer ring decreased with increasing total dose of electrons. Namely, the intensity of 111 ring normalized by, for example, that of 220 ring monotonically decreased during irradiation. This fact indicates that gold atoms were selectively removed from Al2Au particles during irradiation, as will be discussed in detail in the discussion part. In fact, the selective loss of gold atoms from Al2Au particles during irradiation was confirmed also by EDS analyses which were conducted separately [14]. It is of interest to note here that the selective sputtering of gold from Al2Au particles during irradiation was also observed during 150 keV electron irradiation [14].

In an attempt to elucidate which of the two elements (i.e. Au and Al) evaporates preferentially from Al2Au particles upon heating, an in-situ annealing experiment was carried out, using the TEM. Fig. 3(a) and (a') show a BFI of as-produced Al2Au compound particles at RT and the corresponding SAED, respectively. The mean diameter of particles in Fig. 3(a) is approximately the same as that in Fig. 1(a). The Debye–Scherrer rings in Fig. 3(a') are again consistently indexed as those of the Al2Au compound with the CaF2 structure. Fig. 3(b) and (b') show a BFI of the same area and the corresponding SAED after heating up to 970 K, respectively. The mean diameter of particles decreased by this annealing, as seen from a comparison of Fig. 3(a) with (b). The Debye–Scherrer rings in Fig. 3(b') are consistently indexed as those of the AlAu compound with the CsCl structure [14,15] superposed with those of the γ-AlAu2 compound with the MoSi2 structure [16]. In the SAED (Fig. 3(b')), the Debye–Scherrer rings from the Al2Au compound with the CaF2 structure are absent. Namely, by the annealing at 970 K, the original Debye-Scherrer rings of the Al2Au compound were replaced with those of the AlAu compound and of the AlAu2 compound, both of which are gold-enriched phases compared to the original Al2Au compound. This observation indicates that, upon heating, aluminum atoms, not gold atoms, in Al2Au particles preferentially evaporated. Based upon this result, it is concluded that the selective loss of gold atoms in nanometer-sized Al2Au particles shown in Fig. 1, was induced not by temperature rise due to electron irradiation but by preferential knocking-off of gold atoms driven by elastic collision with 200 keV electrons.

4. Discussion

The structural factor, \( F_{hkl} \), is given by the following equation [17].

\[
F_{hkl} = \sum_{i=1}^{n} f_i e^{-2\pi i (h x_i + k y_i + l z_i)}
\]

where \( f_i \) is the atomic scattering factor of component \( i \), and \( (x_i, y_i, z_i) \) is the lattice site of the component \( i \) in the unit cell. The lattice sites of gold atom in Al2Au with the CaF2 structure are \((0,0,0), (1/2,1/2,0), (1/2,0,1/2), (0,1/2,1/2), (1/4,1/4,1/4), (3/4,1/4,1/4), (1/4,3/4,1/4), (1/4,1/4,3/4), (3/4,3/4,1/4), (1/4,3/4,3/4), \)
(3/4,1/4,3/4), (3/4,3/4,3/4) [18]. The structure factor of Al2Au can be calculated by substituting these values of \((x, y, z)\) into Eq. (1); then
\[
F_{hkl} = \left\{ f_{\text{Au}} + f_{\text{Al}} e^{-i\pi(h+k+l)/2} + f_{\text{Al}} e^{i\pi(h+k+l)/2} \right\} 
\{ 1 + e^{-i\pi(h+k+l)} + e^{i\pi(h+k+l)} + e^{i3\pi(h+k+l)} \}
\] (2)

From Eq. (2), the following extinction rule can be derived.
\[
F = 4(\delta_{\text{Au}} + 2\delta_{\text{Al}}) \text{ if } h,k,l \text{ are all even and } h + k + l = 4m \text{ (m:integer)}
\]
\[
F = 4(\delta_{\text{Au}} - 2\delta_{\text{Al}}) \text{ if } k,k,l \text{ are all even and } h + k + l = 4m + 2 \text{ (m:integer)}
\]
\[
F = 4\delta_{\text{Au}} \text{ if } k,k,l \text{ are all odd}
\]
\[
F = 0 \text{ if } k,k,l \text{ are mixed (odd and even)}
\]

The structure factor of the 111 reflection, \(F_{111}\), is composed of only \(\delta_{\text{Au}}\), whereas that of such reflections as 220 is composed of both \(\delta_{\text{Au}}\) and \(\delta_{\text{Al}}\). This fact suggests that \(F_{111}\), and therefore the relative intensity of the 111 reflection, is a direct measure of the gold-atom occupancy on the gold sublattice in the Al2Au compound. Based upon this premise, the monotonic decrease of the relative intensity of the 111 reflection with 200 keV electron irradiation shown in Fig. 2, indicates the decrease of the gold concentration in Al2Au. Namely, it is indicated that gold atoms were selectively sputtered out from Al2Au during 200 keV electron irradiation. This is consistent with the result of separate EDS experiments [14].

From the experimental results given in Section 3, as well as the discussion mentioned above, it seems safe to consider that gold atoms on the surface of Al2Au nanoparticles can be preferentially removed by knock-on collisions with 150 ~ 200 keV electrons. The maximum energy transferred from a 150 keV electron to a gold atom is evaluated to be 1.9 eV [19]. Since the displacement energy for atoms within a crystal is less than 1.9 eV, it is concluded that the selective removal of gold atoms in nanometer-sized Al2Au particles was induced not by heat-induced evaporation of gold atoms but by knock-on displacement during 200 keV electron irradiation. It is suggested that the threshold energy for gold atom sputtering from Al2Au nanoparticles is as low as less than 1.9 eV.

5. Conclusion

Particles of Al2Au around 25 nm in diameter, were irradiated with 200 keV electrons at room temperature. Careful analyses of the chemical concentration by the quantitative measurement of intensities of Debye–Scherrer rings using imaging plates show that gold atoms in Al2Au particles were selectively removed during electron irradiation. In separate annealing experiments, on the other hand, it is observed that aluminum atoms in Al2Au compound particles were preferentially evaporated with increasing temperature. Based upon these results, it is concluded that the selective removal of gold atoms in nanometer-sized Al2Au particles was induced not by heat-induced evaporation of gold atoms but by knock-on displacement during 200 keV electron irradiation. It is suggested that the threshold energy for gold atom sputtering from Al2Au nanoparticles is as low as less than 1.9 eV.

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