Research Article

Strain Distribution of Au and Ag Nanoparticles Embedded in Al_2O_3 Thin Film

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Au and Ag nanoparticles embedded in amorphous Al_2O_3 matrix are fabricated by the pulsed laser deposition (PLD) method and rapid thermal annealing (RTA) technique, which are confirmed by the experimental high-resolution transmission electron microscope (HRTEM) results, respectively. The strain distribution of Au and Ag nanoparticles embedded in the Al_2O_3 matrix is investigated by the finite-element (FE) calculations. The simulation results clearly indicate that both the Au and Ag nanoparticles incur compressive strain by the Al_2O_3 matrix. However, the compressive strain existing on the Au nanoparticle is much weaker than that on the Ag nanoparticle. This phenomenon can be attributed to the reason that Young's modulus of Au is larger than that of Ag. This different strain distribution of Au and Ag nanoparticles in the same host matrix may have a significant influence on the technological potential applications of the Au-Ag alloy nanoparticles.

1. Introduction

The incorporation of multiple metals into a single system has induced intensive interest due to its promising applications. Therefore, the fabrication of alloy nanoparticles has become a major challenge. Particularly, Au-Ag alloy has been confirmed to be suitable for the application in surface plasmon absorption. These two noble metals have practically the same lattice constant and are chemically similar. Moreover, in the bulk phase they are miscible at all compositions. These properties provide the possibility to study the equal structures of different compositions without having to consider the influence of strong structural changes. By combining these two metals into a single entity, the catalytic performance of the material can be enhanced [1] and the surface plasmon absorption of Au-Ag alloy nanoparticles can be varied continuously between the absorptions of monometallic Au and Ag nanoparticles by changing the ratios of the precursors of Au and Ag [2].

On the other hand, nanocomposite films that consist of small metal nanoparticles embedded in metal oxides have

attracted attention because they are expected to have many useful electronic and optical properties as a result of quantum size effects [3, 4]. These systems have useful applications in catalysis, photocatalysis, sensors, and novel optoelectronic devices. However, substantial compressive strain can be induced during the growth process of nanoparticles embedded in a host matrix. The strain may also have much influence on the microstructure and physical properties of nanoparticles [5, 6]. Therefore, in order to understand and control the properties of Au-Ag alloy nanoparticles, the investigation on the interplay between the strain distribution of the alloy nanoparticles in a matrix and the state of individual Au and Ag nanoparticles is crucial for the technological potential applications of the Au-Ag alloy nanoparticles.

2. Materials and Methods

Au and Ag nanoparticles embedded in an amorphous Al_2O_3 matrix are fabricated by the pulsed laser deposition (PLD) method and rapid thermal annealing (RTA) technique,

respectively. Briefly, a KrF pulsed laser is used to ablate the target in a high-vacuum chamber. The wavelength of the excimer laser is 248 nm. The target to be laser ablated is prepared from a high-purity (99.99%) round Al_2O_3 target with diameter of 25 mm and one small high-purity (99.99%) Au/Ag square plate with length of 2 mm, respectively. During the PLD process, the center of the assembled Al_2O_3 -Au/ Al_2O_3 -Ag target is set to spin slowly around its central axis and the laser beam vaporizes the two-component materials alternately. The laser deposition is carried out in a high-vacuum system with a background pressure of about 8×10^{-7} torr. After the deposition, the samples are subjected to rapid thermal annealing at 400°C for 60 s in air ambient. The structure of the samples is examined by using high-resolution transmission electron microscope (HRTEM) with JEOL2010 microscope. The TEM electron diffraction pattern is matched against a simulated diffraction pattern generated by Java Electron Microscopy Simulation (JEMS) TEM simulating software [6].

3. Results and Discussion

Figure 1(a) shows the HRTEM image of Au nanoparticle annealed at 400°C , with its corresponding electron diffraction pattern on the top right corner. The diffraction pattern is matched against a simulated diffraction pattern generated by JEMS software for the Au nanoparticle embedded in Al_2O_3 thin film. It can be confirmed that the Al_2O_3 thin films still remain amorphous after annealing. It can also be seen that there is a single crystal Au nanoparticle with spherical shape embedded in Al_2O_3 matrix. The average size of the Au nanoparticles is approximately 5 nm. With the experimental and the simulated diffraction patterns, it can be deduced that the structure of the Au nanoparticle is cubic structure (space group Fm-3 m). Figure 1(b) shows the HRTEM image of Ag nanoparticle annealed at 400°C , with its corresponding electron diffraction pattern on the top right corner. It can be seen that there is a single crystal Ag nanoparticle with spherical shape embedded in amorphous Al_2O_3 matrix. The average size of the Ag nanoparticles is also approximately 5 nm. With the experimental and the simulated diffraction patterns, it can be deduced that the nanoparticle structure of Ag nanoparticle is face-centered cubic structure (space group Fm-3 m).

Usually, the two basic approaches to calculate the strain distribution in materials are continuum elasticity and atomistic elasticity. Although atomistic elasticity is expected to give more reliable results, its application is limited by the number of atoms which can be taken into account. Finite-element calculation is a versatile computer simulation technique used for continuum modeling of deformation in materials [7]. The simulations are taken into account for the physical properties of many materials, including elastic anisotropy, thermal expansion, and three-dimensional object shape. Moreover, a general qualitative agreement between atomistic strain calculations and continuum elastic models has been demonstrated in nanomaterials [8, 9]. Recently, using the finite-element calculation to simulate the strain distribution

FIGURE 1: (a) HRTEM image of a single crystal Au nanoparticle embedded in amorphous Al_2O_3 matrix, with its corresponding electron diffraction pattern on the top right corner. (b) HRTEM image of a single crystal Ag nanoparticle embedded in amorphous Al_2O_3 matrix, with its corresponding electron diffraction pattern on the top right corner.

of nanoparticles has been widely reported [10, 11]. In this paper, the strain generated by the growth of Au and Ag nanoparticle embedded in an Al_2O_3 thin film is qualitatively simulated by finite-element (FE) calculations [5, 6]. Young's modulus is taken to be 170 [12], 76 [13], and 360 GPa [6] for Au, Ag, and Al_2O_3 , respectively. Poisson's ratio is taken to be 0.42, 0.38, and 0.24 for Au, Ag, and Al_2O_3 , respectively. In our simulation, the FE model for the strain calculations is based upon the following assumptions: a spherical, isotropic, linear-elastic nanoparticle is embedded in isotropic and linear-elastic matrix; the nanoparticle surface is welded to the matrix; the volumes change of the Au and Ag nanoparticles corresponds to a change in annealing temperature with taking the same temperature dependence of thermal expansion coefficient into account for the Au and Ag nanoparticles. Due to the nanoparticle residing in the matrix cavity which is too small, the matrix atoms are not being able to move rapidly enough to accommodate the growing nanoparticle, which results in the compressive strain on the nanoparticle. The strain distribution can be generated by the thermal expansion mismatch because of the growth of Au and Ag nanoparticles.

Figures 2(a) and 2(b) show the cross-sectional strain distributions for Au and Ag nanoparticles grown in Al_2O_3 thin films under the same condition, respectively. The inhomogeneous strain distribution can be found, which is distinguished by the different color as signed by the marks

FIGURE 2: (a) Cross-sectional strain distribution of Au nanoparticle. (b) Cross-sectional strain distribution of Ag nanoparticle.

in Figure 2. Correspondingly, Figures 3(a) and 3(b) show the X-Y plane strain profiles of Au and Ag nanoparticles embedded in Al_2O_3 matrix, respectively. Obviously, it can be seen that both the Au and Ag nanoparticles incur compressive strain from the Al_2O_3 matrix. Usually, the nanoparticles formation mechanism can be explained as follows. Firstly, the probability for nucleation increases at higher temperature, and the nuclei density is thus higher. Once sufficient surface energy is available, the number of nanoparticles increases rapidly as fresh nuclei are formed. On the other hand, the nanoparticles already formed by nucleation continue to grow by adatom attachment via surface diffusion, leading to agglomeration of bigger nanoparticles with increasing temperature [3]. Because of thermal expansion mismatch, the formation of nanoparticles in a matrix can be accompanied by the generation of compressive strain [14, 15]; that is, the Al_2O_3 matrix exerts a compressive strain on the Au and Ag nanoparticles due to the volume expansion of Au and Ag nanoparticles. Moreover, it should be noted that the compressive strain existing on Au nanoparticle is much weaker than that on Ag nanoparticle. This phenomenon can be attributed to the reason that Young's modulus of Au is larger than that of Ag. Thus, this different strain distribution of Au and Ag nanoparticles in the same host matrix may have a significant influence on thermal dynamical properties of Au-Ag alloy nanoparticles.

4. Conclusions

In summary, Au and Ag nanoparticles embedded in amorphous Al_2O_3 matrix are fabricated using PLD method and RTA technique, respectively. The HRTEM results reveal that the spherical Au nanoparticle with cubic structure and Ag nanoparticle with Face-centered cubic structure are formed in amorphous Al_2O_3 matrix, respectively. The strain distribution of Au and Ag nanoparticles embedded in the Al_2O_3 matrix is investigated. FE calculations clearly indicate that both the Au and Ag nanoparticles incur compressive strain from Al_2O_3 matrix. The compressive strain existing on Ag nanoparticle is much weaker than that in Au nanoparticle. This phenomenon can be attributed to the reason that Young's modulus of Au is larger than that of Ag. This different strain distribution of Au and Ag nanoparticles in the same host

FIGURE 3: (a) X-Y plane strain profile of Au nanoparticle. (b) X-Y plane strain profile of Ag nanoparticle.

matrix may have a significant influence on thermal dynamical properties of Au-Ag alloy nanoparticles.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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