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Composition dependence on dispersion of Au/Cu bimetallic nanoparticles in nylon 11 thin films

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Abstract. Effect of composition on the dispersion of Au_xCu_{1-x} bimetallic nanoparticles into nylon 11 matrix has been investigated. TEM, EDX, and XPS depth profiling were used for characterizing the changes in the composition of the bimetallic particles and in the depth distribution of the particles in the nylon 11 layer caused by heat treatment in N_2 atmosphere. The island-like bimetallic particles were found to be formed on the nylon 11 surface before heat treatment. The results of XPS depth profiling revealed that, by the heat treatment, the Au_xCu_{1-x} bimetallic particles with $x \leq 0.55$ were not dispersed into the nylon 11 layer while those with $x \geq 0.70$ were homogeneously dispersed in the films, indicating the existence of critical composition for penetration of the bimetallic particles. By comparing the composition and structure of the bimetallic particles, the cause of these finding is discussed in terms of surface free energy of the particles.

PACS. 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 68.35.Fx Diffusion; interface formation

1 Introduction

Metal and semiconductor nanoparticles dispersed in polymeric matrices have recently been the subject of intensive research of various application fields, because such materials exhibit unusual physical and chemical properties based on size quantization effects of the nanoparticles. Bimetallic particles have also been the subject of intensive research of the surface chemistry and catalytic properties, because physical and chemical properties of metal particles can be improved by adding the other component to the monometallic particles [1,2]. The physical and chemical properties of such composite films are known to depend on microstructure of the composite film [3–5]. A wide variety of fabrication methods for polymer films containing small metal particles has been developed, including physical and chemical process, *e.g.*, plasma polymerization of organic monomers with simultaneous or alternating metal evaporation or sputtering [6–11], reduction of metal ions in organometallic compounds, and spinning of polymer solutions including metal complexes or metal colloids [12–16].

We have recently reported a novel method for the preparation of polymer thin films containing metal nanoparticles with relatively narrow size distribution [17,18]. This method relies on consecutive vacuum vapor deposition of a polymer and a metal, followed by heat treatment. The dispersion of the deposited metals can be achieved when the films are heat-treated at the temperature above the glass transition temperature (T_g) of the polymer. The structural relaxation of polymer matrix caused by heat treatment has proven to be responsible for the dispersion of metal nanoparticles [19]. In the previous work, it has been shown that the Au particles can penetrate into nylon 11 films by heat treatment in an inert atmosphere whereas the Cu particles cannot penetrate into the films [20]. In this paper, in order to investigate the cause of these finding, we have studied the effect of composition on the dispersion of AuCu bimetallic nanoparticles as well as their monometallic particles in vapor deposited nylon 11 thin films. The films containing the particles with different compositions were characterized by means of X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and energy dispersive X-ray (EDX) analysis. We show that there is a critical composition for the penetration of the bimetallic particles into bulk phase of the nylon 11 film, and discuss the dispersion mechanism in terms of the surface free energy of the particles.

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2 Experimental

The Au_xCu_{1-x} composite films were prepared by a vacuum vapor deposition technique. A glass vacuum chamber was first evacuated down to 1.0×10^{-5} torr, and a nylon 11 pellet (Aldrich) were then vapor deposited from a resistance-heated molybdenum boat. The deposition of nylon 11 was performed at a pressure below 5.0×10^{-4} torr at room temperature. The thickness of the nylon 11 film and deposition rate were 100 nm and $2.0\ \mathrm{nm\,s^{-1}}$, respectively, as monitored by a quartz crystal microbalance. The AuCu bimetallic particles were prepared by a co-evaporation technique. Gold and copper (both 99.99%) were simultaneously vapor deposited on the nylon 11 film from two separate alumina-coated tungsten filament under the control of two quartz crystals. The deposition rates of both components were controlled independently by the temperature of the evaporation source. Thus the molar ratio of the constituent metals could be varied by keeping the total amount of metal deposition (23.6×10^{15} atoms $\mathrm{cm^{-2}}$). These films were deposited on Si wafer for XPS measurement, thin carbon films supported on copper mesh grids for TEM observation. The obtained metal(s)/nylon 11 laminated films were then heat-treated at 100 °C for 10 min in N_2 atmosphere.

The depth distribution of Au and Cu in the films was measured by a X-ray photoelectron spectrometer, ESCA 750 (Shimadzu), using Mg-Kα X-ray source. Depth profiles were obtained by argon ion sputtering at a constant acceleration voltage of 2 kV, 10-15 mA ion beam current and 30° incidence angle. The mean size and composition of the particles were observed by using a JEOL JEM-2010 transmission electron microscope operating at 200 kV, equipped with EDX analyzer (NORAN Instrument, Inc.). The samples for cross-sectional TEM observation were deposited on a cured epoxy resin, according to a previous paper [19]. Thin cross sections with a thickness of *ca.* 60 nm were obtained with a Leica Ultracut UCT ultramicrotome using a diamond knife. These thin sections floating onto water bath were mounted on the carbon coated TEM copper grids. Before TEM observation, all the samples were again coated with thin carbon layer for the purpose to prevent electron charging up effects during TEM observation.

3 Results and discussion

Figure 1 shows TEM image and SAED pattern of the $Au_{0.43}Cu_{0.57}$/nylon 11 film before heat treatment. We can see that the island-like particles were formed on the nylon 11 surface, and the SAED pattern was completely indexed as that of fcc structure. EDX analysis of individual particles with an electron beam spot of 1 nm in diameter revealed that these particles were bimetallic (no monometallic particles were observed), and some selected particles with slight different sizes have nearly the same composition.

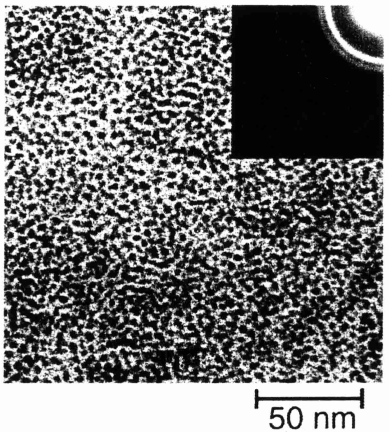

Fig. 1. TEM images and SAED pattern of as-deposited $Au_{0.43}Cu_{0.57}$ nanoparticles on the nylon 11 surface.

Table 1. Characteristic parameters of AuCu bimetallic particles as well as monometallic particles.

sample	mean size/nm	Au/Cu ratio (by EDX)
(a)	2.4	0/100
(b)	2.5	11.5/88.5
(c)	2.5	43.2/56.8
(d)	2.6	55.0/45.0
(e)	3.1	70.8/28.2
(f)	4.6	100/0

We performed the TEM observation for all the samples with different compositions. Table 1 summarizes characteristic parameters of the island-like particles with various compositions, obtained by the TEM observation and EDX quantitative analysis. Agreement for the compositions of AuCu bimetallic particles between those calculated by the initial amount of metal deposition and those measured by EDX analysis were fairly good. The mean size of monometallic Au particles is larger than that of monometallic Cu particles. For the bimetallic particles, the mean size increases as the Au/Cu ratio increases, *i.e.*, incorporation of Au into Cu results in the increase of particle size. This tendency can be explained by the initial growth mode of Au and Cu on the nylon 11 surface. In the case of low metal coverage, the metals tend to grow as islands due to their high cohesive energy during vapor deposition process [21], as can be seen in the present study (Fig. 1). The effect of composition on the particle size can be caused by the different surface diffusion coefficient of metal atoms on the nylon 11 surface, depending on the interaction energy between deposited metal atom and nylon 11 molecule. Therefore, it seems likely that the surface diffusion coefficient of Au atom is larger than that of Cu atom, *i.e.*, the interaction between Cu atoms and nylon 11 molecules (adhesion) is stronger than that between Au atoms and nylon 11 molecules. During co-evaporation process, deposited Au and Cu atoms are mixed and alloyed to be bimetallic islands at the nylon 11 surface, where the incorporation of Cu atoms into Au clusters may inhibit

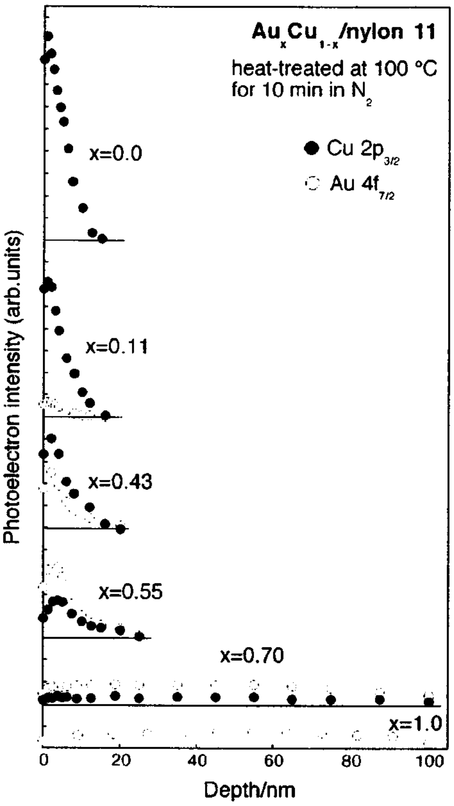

Fig. 2. Depth distribution of Au and Cu in the nylon 11 film heat-treated at 100 °C for 10 min in N_2 atmosphere.

the growth of bimetallic islands due to higher interaction energy of Cu with nylon 11 matrix than that of Au atoms.

Figure 2 shows the depth distribution of Au and Cu obtained by XPS depth profiling for the sample with different metal compositions, heat-treated at 100 °C for 10 min in N_2 atmosphere. These films were deposited on Si wafer substrate to prevent charging up effects during XPS measurement and argon ion sputtering process. The depth scales in Fig. 2 were corrected by taking into account for the sputtering time and Ar ion current. The Cu $2p$ and Au $4f$ photoelectron spectra were measured for a appropriate sputtering interval. For the Cu monometallic particles, no indication of oxidation state for Cu was observed in the Auger electron spectrum (not shown here), and the Cu $2p$ photoelectron intensity is localized at the surface, indicating that the Cu particles cannot penetrate into the nylon 11 layer. The photoelectron signal of Cu and Au for the $\mathrm{Au}_x\mathrm{Cu}_{1-x}$ bimetallic particles with $x = 0.11$, 0.43 and 0.55 is also detected only at the surface region. On the other hand, both Au and Cu are dispersed homogeneously in the nylon 11 matrix for the sample with $x = 0.70$, quite similar in profile to those of Au monometallic particles ($x = 1.0$).

From the XPS data obtained, composition of the bimetallic particles was calculated quantitatively using the area of Au $4f_{7/2}$ and Cu $2p_{3/2}$ photoelectron spectra. In Fig. 3, the Au contents in the bimetallic particles are plotted against the depth of the films. The composition of the particles is found to be nearly constant in the depth direction of the matrix film, and average composition (x_{ave}) is consistent with those obtained by EDX analysis (Table 1).

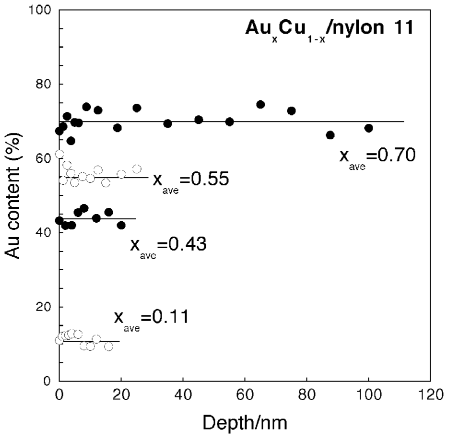

Fig. 3. Compositions of AuCu bimetallic nanoparticles in depth direction of the nylon 11 matrix.

Cross-sectional TEM images for the sample with $x = 0.55$ and 0.70 after heat treatment are shown in Fig. 4. We can see that the $\mathrm{Au}_{0.55}\mathrm{Cu}_{0.45}$ particles are not dispersed into the nylon 11 matrix, whereas the homogeneous distribution of the $\mathrm{Au}_{0.70}\mathrm{Cu}_{0.30}$ particles in the matrix is clearly observed. These results were also consistent with the depth distribution obtained by the XPS measurements (Fig. 2).

The above results indicate the existence of critical composition for penetration of the AuCu bimetallic particles into nylon 11 layer. In order for the penetration of the particles into the nylon 11 film to be energetically favorable, the Gibbs free energy of a metal particle must be lower than that of the isolated particle at the nylon 11 surface. If the surface tension of the particle $\gamma_{particle}$ exceeds the sum of the interfacial tension $\gamma_{particle-nylon}$ and the surface tension of the nylon 11 γ_{nylon}, embedding of the metal particle is energetically favorable [22,23],

$$\gamma_{particle} > \gamma_{particle-nylon} + \gamma_{nylon} \tag{1}$$

i.e., nylon 11 matrix can wet completely the surface of the particles. In the previous work, we have shown that the inequality (1) is obeyed for the Au/nylon 11 system [19]. Since the monometallic Cu particles were not dispersed by the heat treatment, we suggest that the inequality (1) can be obeyed when the surface energy of the bimetallic particles may be varied by doping of Au atoms into Cu particles up to a certain composition, *i.e.*, $x > 0.55$. In addition, the penetration of the particles can only be achieved when the temperature rises above the T_g of the nylon 11 matrix (*ca.* 40 °C), at which the nylon 11 matrix begin to behave as a viscous fluid. Further experimental study is, however, necessary to verify this assumption. In particular, more detailed information associated with the surface tension of the particles can be obtained from the analysis of surface stress coefficient of the particles with

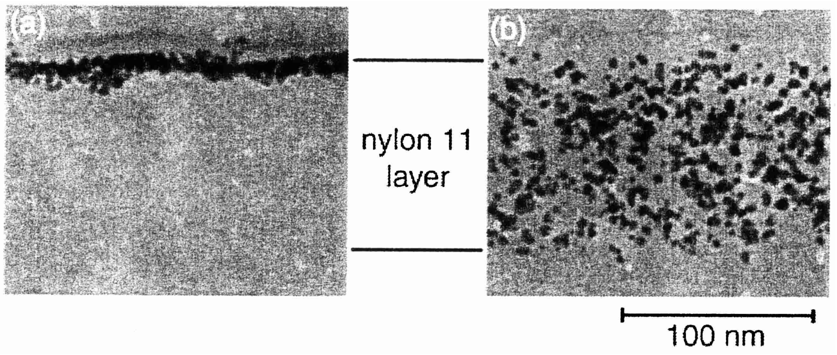

Fig. 4. Cross-sectional TEM images of (a) $Au_{0.55}Cu_{0.45}$ and (b) $Au_{0.70}Cu_{0.30}$ nanoparticles.

different composition, which is now underway in our group and results will be presented in the forthcoming article.

4 Conclusion

We have studied the dispersion of vapor deposited Au_xCu_{1-x} bimetallic nanoparticles with various compositions into nylon 11 thin films by means of depth profiling technique and quantitative composition analysis. After the heat treatment in N_2, the particles with $x = 0.70$ and 1.0 were observed to penetrate homogeneously into the nylon 11 matrix whereas those with $x = 0.0$, 0.11, 0.43, 0.55 were localized at the surface. The surface energy of the bimetallic particles, which may be different with their compositions, was suggested to be responsible for dispersion of the particles; the critical composition that determines whether or not the particles can be embedded into the nylon 11 layer was around $x = 0.55$-0.70.

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