Preparation, Characterization and Optical Properties of Nano-sized Bimetallic Particles Dispersed in Polymer Thin Films

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We have prepared nano-sized Au/Cu bimetallic particles with various compositions dispersed in nylon 11 thin films by means of vacuum evaporation technique followed by heat treatment. The particles produced were characterized by TEM, EDX, XPS and UV-vis absorption spectroscopy. The composition in the bimetallic particles could be varied over the entire composition range by controlling the initial deposition amount of constituent metals. It was found that the bimetallic particles were well isolated individually having narrow size distribution and the mean size of the particles were increased with increasing Au/Cu atomic ratio in the bimetallic particles. Optical absorption due to surface plasmon resonance absorption of the Au particles decreased with decreasing the Au/Cu ratio, which can be caused by the changes in the dielectric constant of the particles due to alloying.
Key words: bimetallic particles, thin film, polymer, surface plasmon

1. INTRODUCTION

Nano-sized metal particles have been of considerable interest both from fundamental point of view and for potential applications in novel photonics and electronics devices based on their unique properties which are generally very different from those of bulk material. Nano-sized bimetallic particles have also been the subject of intensive research of the surface chemistry and catalytic properties [1, 2], because physical and chemical properties of metal particles can be improved by adding the other component to the monometallic particles. Many studies related to the preparation and properties of bimetallic particles have been performed for a system consisting of bimetallic particles supported on solid surface and/or dispersed in organic solution [3-9]. However, the bimetallic particles embedded in solid dielectric materials such as polymers or glasses have been little investigated.

We have previously developed and reported a novel process to prepare polymer thin films containing nano-sized metal particles at relatively high concentration by a thermal relaxation technique [10, 11]. This technique relies on the conventional vacuum evaporation technique of a polymer and a metal, consecutively, and subsequent heat treatment above the glass transition temperature (Tg) of the polymer matrix. By the heat treatment, upper metal layer deposited on the polymer surface can penetrate into the bulk phase of the polymer matrix as nano-sized particles through the structural rearrangement of polymer molecules. We have previously succeeded in preparing nano-sized Au, Ag, Pd and Cu$_2$O particles dispersed in nylon 11 thin films by using the thermal relaxation technique [12-14]. It seems that this technique can also be applied to prepare bimetallic particles dispersed in polymer matrix, because the vacuum evaporation technique is often applied

to prepare metallic alloy thin films [15,16].

In this paper, we report on the preparation and characterization of nano-sized Au/Cu bimetallic particles dispersed in nylon 11 thin films by using the thermal relaxation technique. We show that the composition of the bimetallic particles can be readily varied by controlling the deposition amount of constituent metals, since gold and copper are completely miscible [17]. The obtained composite thin films were characterized by transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS), and visible (VIS) absorption spectroscopy.

2. EXPERIMENTAL

The composite films were prepared by a conventional 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 4.0×10^{-4} Torr, and the thickness of the nylon 11 film was set to 100 nm as monitored by a quartz-crystal microbalance. The Au/Cu bimetallic particles were prepared by a co-evaporation technique. Gold and copper were simultaneously vapor deposited on the nylon 11 film from two separate alumina-coated tungsten filament under the control of two quartz oscillator. 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/cm^2). These films were deposited on Si wafer for XPS measurement, thin carbon films supported on nickel mesh grids for TEM ob-

servation, and a quartz substrate for VIS absorption spectroscopy. The obtained metal(s)/nylon 11 laminated films were then heat-treated at 100 °C for 10 min in N_2.

The core level binding energy for Au 4f and Cu 2p photoelectrons and kinetic energy of Cu LMM Auger electrons were measured by a X-ray photoelectron spectrometer, ESCA 750 (Shimadzu), using Mg-Kα X-ray source. The size and size distribution of dispersed particles were observed by using a JEOL JEM-2010 transmission electron microscope operating at 200 kV, equipped with EDX analyzer (NORAN Instrument, Inc.). Optical absorption spectra were measured with a UVDEC 660 spectrophotometer (Japan Spectroscopic Co. Ltd) over the wavelength range 350-850 nm.

3. RESULTS AND DISCUSSION

Figure 1 shows typical TEM image of the film with Au/Cu=76/24, heat-treated at 100 °C for 10 min. We can see that the nano-sized particles with mean size of *ca.* 4 nm in diameter were homogeneously distributed in the plane of the film. The selected area electron diffraction patterns of the dispersed particles with various Au/Cu ratios showed typical patterns for f.c.c. structure, with lattice parameters nearly corresponding to that of metallic gold. EDX analysis of the films with various Au/Cu ratios showed that these particles were bimetallic. Analysis of individual particles with an electron beam spot of 10 Å in diameter revealed that there are no monometallic particles and some selected particles with slight different size have the same composition. From these results, it seems very likely that the present Au/Cu bimetallic particles are characterized by a continuous solid solution phase and not by an ordered intermetallic compounds [18].

Table I summarizes characteristic parameters of dispersed bimetallic particles with various Au/Cu ratios and results of EDX quantitative analysis. The mean size of the particles decreased with the decrease of Au/Cu ratio. This behavior of particle size can be explained by the initial growth mode of metals on the nylon 11 surface, which are
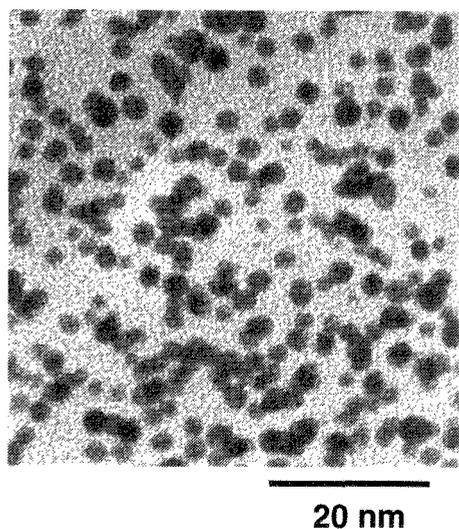
Table I Characteristic parameters of Au/Cu bimetallic particles dispersed in nylon 11 thin films heat-treated at 100 °C for 10 min

Sample	Au/Cu ratio by EDX	Mean size /nm	Std. deviation /nm
(a)	13/87	2.6	0.37
(b)	19/81	3.4	0.44
(c)	53/47	3.7	0.62
(d)	76/24	4.3	0.79
(e)	100/0	4.6	0.84

closely related to the interaction between atoms of a deposit and atoms of a substrate [19]. We have previously reported the different types of the initial growth mode of Au and Cu on the nylon 11 surface, *i.e.*, island growth for Au and layer growth for Cu [14]. In the case of vapor co-deposition, however, simultaneous alloying on the substrate surface at the initial stage of co-deposition can be expected [16]. By TEM observation and EDX analysis, it was found that the island particles were formed on the nylon 11 surface before heat treatment, and these islands were found to be already bimetallic. During co-deposition process, deposited Au and Cu atoms can be mixed and alloyed to be bimetallic islands at the nylon 11 surface, where the incorporation of Cu atoms may inhibit the growth of bimetallic islands due to their higher interaction energy with nylon 11 matrix than that of Au atoms [14]. These islands formed on the nylon 11 surface can penetrate into the bulk phase of the nylon 11 layer by the heat treatment above the T_g of the matrix (*ca.* 40°C), and thus the mean size of the dispersed bimetallic particles decreased as the amount of Cu deposition increases.

From these results, it was clearly demonstrated that the nylon 11 thin films containing Au/Cu bimetallic particles can be prepared by the thermal relaxation technique using the co-evaporation method, and the composition of the bimetallic particles can be readily varied by controlling the initial deposition amount of metals.

Figure 2 and 3 shows XPS spectra of the Au/Cu bime-

20 nm

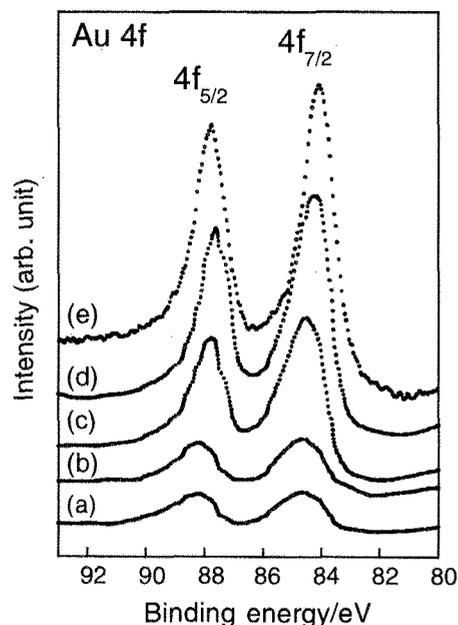Fig. 1 TEM image of Au/Cu bimetallic particles (Au/Cu=76/24) dispersed in nylon 11 thin films.

Fig. 2 Au 4f X-ray photoelectron spectra of Au/Cu bimetallic particles with various compositions. (a)-(e) corresponds to the sample listed in Table I.
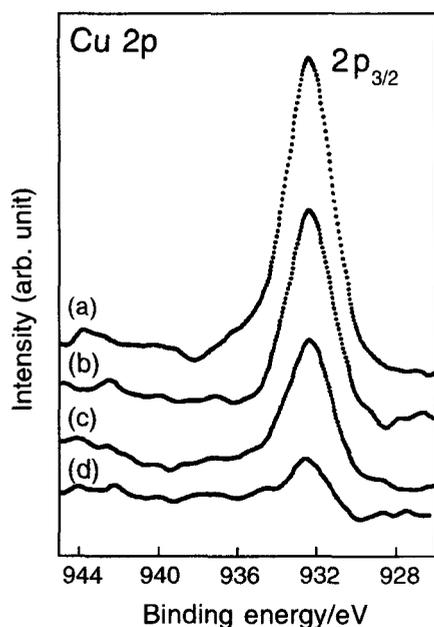
Fig. 3 Cu 2p X-ray photoelectron spectra of Au/Cu bimetallic particles with various compositions. (a)-(d) corresponds to the sample listed in Table I.

Fig. 5 Cu LMM Auger electron spectra of Au/Cu bimetallic particles dispersed in nylon 11 thin films. (a)-(d) corresponds to the sample listed in Table I.

tallic particles with various compositions dispersed in the nylon 11 thin films. The Au 4f and Cu 2p peak were measured and corrected using C 1s contamination peak (284.5 eV) as a reference. The results of the core-level binding energy shift were shown in Fig. 4, in which the measured values of binding energy were plotted as a function of the Cu content. We can see in the figure that, as the Cu content in the bimetallic particles increases, the binding energy of Au $4f_{7/2}$ photoelectrons shifted from the bulk value (84.0 eV) to higher energies. This indicates the alloy formation of the Au/Cu bimetallic particles [20, 21]. Although there was no significant shift for the Cu 2p photoelectrons, the oxidation state of Cu can be observed from the Cu LMM Auger peak, which occurs at 918.8 eV in kinetic energy for bulk metallic Cu. Corresponding Cu LMM
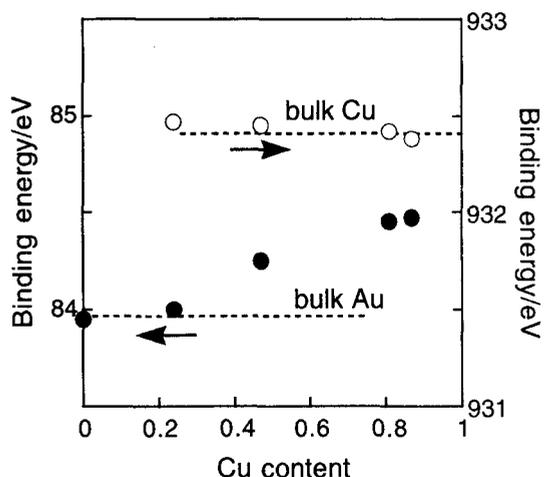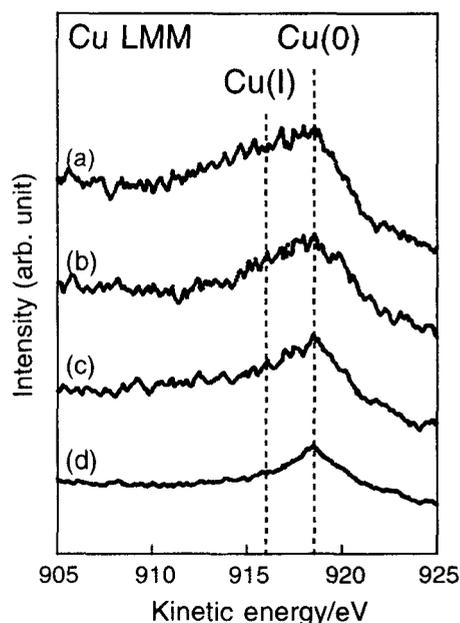
Auger electron spectra were shown in Fig. 5. Whereas the kinetic energy of Cu for the sample with lower Cu content was well comparable to that of metallic copper, an indication of the oxidation of copper was observed for the sample with higher Cu content. For sample with Cu content of > 0.5, broad shoulder was observed at around 916.6 eV which was close to that observed for Cu_2O powder standards measured in the same XPS apparatus and that reported in the literature [22]. Therefore, a fraction of the copper is thought to be in the form of an oxide, and it may be possible that the particles with higher Cu content consist of a Au/Cu alloy core surrounded by a Cu_2O shell, as is the case with Au/Cu bimetallic particles prepared by reverse micelles [9].

It is well known that small metallic particles show the

Fig. 4 Core-level binding energy shift of Au 4f7/2 and Cu 2p3/2 photoelectrons of Au/Cu bimetallic particles dispersed in nylon 11 thin films as a function of Cu content in the particles. (●) : Au $4f_{7/2}$, (○) : Cu $2p_{3/2}$
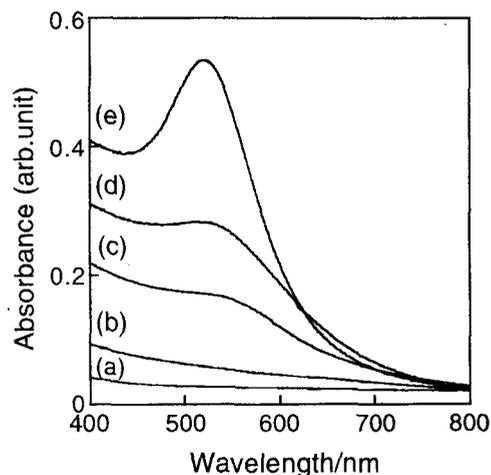

Fig. 6 Optical absorption spectra of Au/Cu bimetallic particles dispersed in nylon 11 thin films. (a)-(e) corresponds to the sample listed in Table I.

optical absorption in the ultraviolet-visible region due to the excitation of the surface plasmon resonance (SPR) of free electrons [23]. The SPR absorption peak of small Au and Cu particles can be generally observed in the visible region. Figure 6 shows optical absorption spectra of the nylon 11 thin films containing Au/Cu bimetallic particles with various compositions as well as Au monometallic particles, after the heat treatment at 100 °C for 10 min. For pure Au particles, the SPR absorption band was observed at around 530 nm. The absorption in the short wavelength region of < 500 nm was due to 5d - 6sp interband transition of gold [23]. As the Cu content in the particles increased, the absorbance of the SPR band and interband transition decreased, accompanied by the shift of the SPR peak to longer wavelength ((c) and (d)). The spectra for the bimetallic particles with Cu content of > 0.5 ((a) and (b)) are monotonous and no SPR peak was observed. Since the SPR absorption of small metal particles is originated from the collective motion of the conduction electrons interacted with external electromagnetic field of the incident radiation, which are closely related with the dielectric constant of the particles, the shift of the SPR peak can be caused by the change in the dielectric constant of the particles due to alloying. Further theoretical study is, however, required in order to quantitatively understand the changes of the absorption spectra which depend on composition in the bimetallic particles. Damping of the SPR peak for the sample (a) and (b) may be due to the formation of oxide shell in the particles as can be observed in the Cu LMM Auger spectra.

4. CONCLUSION

The composite thin films consisting of nano-sized Au/Cu alloy particles dispersed in nylon 11 films have been prepared by thermal relaxation technique combined with co-evaporation method. The Au/Cu molar ratio could be varied by controlling the initial deposition amount of constituent metals, and mean size of the dispersed particles decreased with decreasing the Au/Cu ratio. Optical absorption due to surface plasmon resonance absorption of the Au particles decreased with decreasing the Au/Cu ratio and disappeared for the particles composed of more than 50 % copper, which can be due to the change in the dielectric constant of the particles and formation of copper oxide in the particle surface.

ACKNOWLEDGMENT

REFERENCES

[1]   F. J. C. M. Toolenaar, D. Reinalda and V. Ponec, *J. Catal.*, **64**, 110-115 (1980).

[2]   H. A. C. M. Hendrickx and V. Ponec, *Surf. Sci.*, **192**, 234-240 (1987).

[3]   M. Haruta, K. Saika, T. Kobayashi, S. Tsubota and Y. Nakahara, *Chemistry Express*, **3**, 159-162 (1988).

[4]   K.Esimi, T. Tano, K. Torigoe and K. Meguro, *Chem. Mater.*, **2**, 564-571 (1990).

[5]   H. Liu, G. Mao and S. Meng, *J. Mol. Catal.*, **74**, 275-282 (1992).

[6]   N. Toshima, M. Harada, Y. Yamazaki and K. Asakura, *J. Phys. Chem.*, **96**, 9927-9933 (1992).

[7]   M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, J. M. Genet and B. Delmon, J. Catal., **144**, 175-192 (1993).

[8]   J. S. Bradley, E. W. Hill, C. Klein, B. Chaudret and A. Duteil, *Chem. Mater.*, **5**, 254-260 (1993).

[9]   C. Sangregorio, M. Galeotti, U. Bardi and P. Baglioni, *Langmuir*, **12**, 5800 (1996).

[10] T. Noguchi, K. Gotoh, Y. Yamaguchi and S. Deki, *J. Mater. Sci. Lett.*, **10**, 477-479 (1991).

[11] T. Noguchi, K. Gotoh, Y. Yamaguchi and S. Deki, *J. Mater. Sci. Lett.*, **10**, 648-649 (1991).

[12] K. Akamatsu and S. Deki, *J. Mater. Chem.*, **7**, 1773-1777 (1997).

[13] K. Akamatsu and S. Deki, *Nanostruct. Mater.*, **8**, 1121-1129 (1997).

[14] S. Deki, K. Akamatsu, T. Yano, M. Mizuhata and A. Kajinami, *J. Mater. Chem.*, **8**, 1865-1868 (1998).

[15] R. Anton, *Thin Solid Films*, **125**, 305-311 (1985).

[16] R. Anton and A. A. Schmidt, *Surf. Sci.*, **357**, 835-839 (1996).

[17] G. Meitzner, G. H. Via, F. W. Lytle and J. H. Sinfelt, *J. Chem. Phys.*, **83**, 4793-4799 (1985).

[18] H. Okamoto, D. J. Chakrabarti, D. E. Laughlin and T. B. Massalski, "Binary Alloy Phase Diagrams", 2nd ed., Eds. by T. B. Massalski, H. Okamoto, P. R. Subramanian and L. Kacprzak, ASM Int., Ohio (1990), vol. 1, pp. 358-362.

[19] K. Reichelt, *Vacuum*, **38**, 1083-1099 (1988).

[20] W. Eberhardt, S. C. Wu, R. Garrett, D. Sondericker and F. Jona, *Phys. Rev.*, **B31**, 8285-8287 (1985).

[21] S. B. DiCenzo, P. H. Citrin, E. H. Hartford Jr. and G. K. Wertheim, *Phys. Rev.*, **B34**, 1343-1345 (1986).

[22] G. Schön, *Surf. Sci.*, 35, 96-108 (1973).

[23] U. Kreibig and M. Vollmer, "Optical Properties of Metal Clusters" Springer-Verlag, Berlin, Heidelberg (1995), p. 13.