

Effect of composition and structure of gold/copper bimetallic nanoparticles on dispersion in polymer thin films

Kensuke Akamatsu,^{a,†} Takeshi Kawamura,^b Hideki Nabika,^a Shigehito Deki,^{*,a,b} Thomas Strunskus^{c,‡} and Franz Faupel^c

^aDivision of Molecular Science, Graduate School of Science & Technology, Kobe University, Rokkodai, Nada, Kobe 657-8501, Japan

^bDepartment of Chemical Science & Engineering, Faculty of Engineering, Kobe University, Rokkodai, Nada, Kobe 657-8501, Japan. E-mail: deki@kobe-u.ac.jp

^cLehrstuhl für Materialverbunde, Technische Fakultät der Universität Kiel, Kaiserstrasse 2, 24143 Kiel, Germany

Received 16th May 2002, Accepted 2nd September 2002

First published as an Advance Article on the web 7th October 2002

The effect of composition on the dispersion of $\text{Au}_x\text{Cu}_{1-x}$ bimetallic nanoparticles into a nylon 11 matrix has been investigated. TEM, UV-VIS, EDX, and XPS depth profiling were used for characterizing the changes in the composition of the bimetallic particles and the depth distribution of the particles in the nylon 11 layer caused by annealing in an N_2 atmosphere. TEM observation and EDX analysis revealed that island-like bimetallic particles were formed on the nylon 11 surface before annealing, the composition of which was systematically controlled. Upon annealing in an N_2 atmosphere, the $\text{Au}_x\text{Cu}_{1-x}$ 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 a critical composition for penetration of the bimetallic particles. By comparing the composition and structure of the bimetallic particles, the cause of these findings is discussed in terms of the surface free energy of the particles, which can be varied with their composition by the effect of alloying.

Introduction

Metal and semiconductor nanoparticles dispersed in polymeric matrices have recently been the subject of intense study in 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 of considerable interest and are attractive owing to their surface chemistry and catalytic properties, because the physical and chemical properties of the metal particles can be improved by adding the other component to the monometallic particles.^{1,2} The properties of such composite films are known to depend on the microstructure of the films and the interaction between the metal and the polymer.³⁻⁵ A wide variety of fabrication methods for polymer films containing small metal particles have been developed, including physical and chemical processes, *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 previously studied the formation and structure of polymer thin films containing metal nanoparticles, which were prepared by successive vacuum vapor deposition of a polymer and a metal followed by thermal annealing.^{17,18} The dispersion of the deposited metals can be achieved when the films are annealed at a temperature above the glass transition temperature (T_g) of the polymer. The structural relaxation of the polymer matrix caused by the heat treatment has proven to be responsible for the dispersion of the metal nanoparticles.¹⁹ In

previous work, it has been shown that Au particles can penetrate into nylon 11 films upon annealing in an inert atmosphere whereas Cu particles cannot.²⁰ In this paper, in order to investigate the cause of these findings, we have studied the effect of the composition and atmosphere on the dispersion of Au/Cu bimetallic nanoparticles, as well as their monometallic particles, induced by annealing in an N_2 atmosphere. Films with different compositions of particles 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 the bulk phase of the nylon 11 film, and discuss the dispersion mechanism in terms of the surface free energy of the particles.

Experimental procedure

$\text{Au}_x\text{Cu}_{1-x}$ 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) was then vapor deposited from a resistance-heated molybdenum boat. The deposition of the nylon 11 was performed at a pressure below 5.0×10^{-4} Torr at room temperature. The deposition rate was 2.0 nm s^{-1} , and the thickness of the nylon 11 film was 100 nm. The Au/Cu bimetallic particles were prepared by a co-evaporation technique. Gold and copper (both 99.99%) were simultaneously vapor deposited onto the nylon 11 film from two separate alumina-coated tungsten filaments under the control of two quartz crystal microbalances. The deposition rate of both components was controlled independently by the temperature of the evaporation source. Thus the molar ratio of the constituent metals could be varied while maintaining the total amount of metal deposition (23.6×10^{15} atoms cm^{-2}).

[†]Present address: Department of Chemistry, Faculty of Science and Engineering, Konan University, 8-9-1 Okamoto, Higashinada, Kobe 658-8501, Japan.

[‡]Present address: Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, Universitätsstr. 150, D-44780 Bochum, Germany.

The substrates used were an Si wafer for XPS measurement, and thin carbon films supported on copper mesh grids for TEM observation. After the deposition, the films were annealed at 100 °C for 10 min in an N₂ atmosphere.

Optical absorption spectra were measured with a UVDEC660 spectrophotometer (Japan Spectroscopic Co. Ltd.) over the wavelength range 350–800 nm. The depth distribution of Au and Cu in the films was measured by a X-ray photoelectron spectrometer, ESCA 850 (Shimadzu), using a Mg-K α X-ray source. Depth profiles were obtained by argon ion sputtering at a constant acceleration voltage of 2 kV, a 10–15 mA ion beam current and a 30° incidence angle. The mean size and composition of the particles were observed by using a JEM-2010 (JEOL) transmission electron microscope operating at 200 kV, equipped with an EDX analyzer (NORAN Instrument, Inc.). The samples for cross-sectional TEM observation were deposited on a cured epoxy resin, according to previous work.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 a water-bath were mounted on the carbon coated TEM copper grids. Before TEM observation, all the samples were again coated with a thin carbon layer in order to prevent electron charging effects during TEM observation.

Results and discussion

Deposition of bimetallic nanoparticles

Fig. 1 depicts the TEM image of a nylon 11 sample after simultaneous deposition of Au and Cu (Au_{0.70}Cu_{0.30}) at room temperature. Small metal particles of *ca.* 4 nm in diameter are seen on the TEM image. EDX elemental analysis of the individual particles with an electron beam spot 10 Å in diameter revealed that these particles are indeed bimetallic (monometallic particles were not observed), and some selected particles with slightly different sizes have nearly the same composition. We performed the TEM observation for all the samples with different compositions, and the characteristics of these particles are given in Table 1. Fairly good agreement for the compositions of AuCu bimetallic particles is observed between those calculated by the initial amount of metal deposition and those measured by EDX analysis. The mean size of the 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.*, the incorporation of Au into Cu results in an increase in particle size. Although the formation of small particles on the nylon 11 surface (island formation) at room temperature indicates a significant surface mobility of Au (and Cu) atoms or small clusters on nylon 11 surface during vapor deposition,²¹ the observed changes in particle size with composition can be caused by the different surface diffusion coefficients of the Au and Cu atoms on the nylon 11 surface, depending on the interaction between the deposited metal atoms and the nylon 11 molecules. Similar results for size-composition dependence

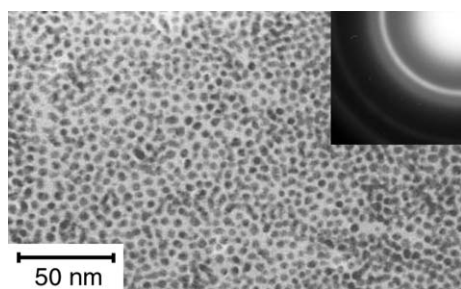


Fig. 1 TEM image and SAED pattern of as-deposited Au_{0.70}Cu_{0.30} nanoparticles deposited on the nylon 11 surface.

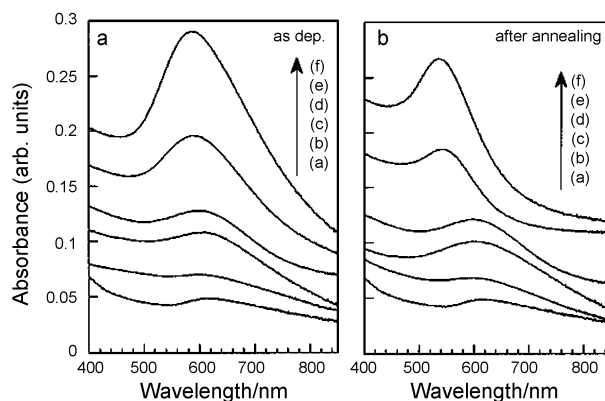


Fig. 2 Optical absorption spectra of the composite films: a, before; and b, after annealing at 100 °C for 10 min in an N₂ atmosphere. (a) Cu, (b) Au_{0.10}Cu_{0.90}, (c) Au_{0.43}Cu_{0.57}, (d) Au_{0.55}Cu_{0.45}, (e) Au_{0.70}Cu_{0.30}, (f) Au.

have been obtained for Au/Pd bimetallic particles deposited on nylon 11 films.²² Upon annealing at 100 °C for 10 min in an N₂ atmosphere, no distinct change in the particle size is observed.

Changes in optical absorption spectra and depth distribution of the particles

Fig. 2 shows the optical absorption spectra for the samples with different compositions of particles after deposition at room temperature (Fig. 2a) and after subsequent annealing at 100 °C for 10 min in N₂ (Fig. 2b). For the as-deposited films all the spectra show broad absorption peaks around 600 nm, which correspond to the surface plasmon resonance (SPR) mode in metallic nanoparticles. As the Au content increases, these peaks are found to shift towards shorter wavelength, accompanied by an increase in the intensity. Since the SPR absorption energy of Au particles is higher than that of Cu particles, this observation could originate from the effect of alloying.²² Subsequent annealing at 100 °C gives rise to composition dependent changes in the absorption spectra (Fig. 2b); the spectra for the sample with $x \leq 0.55$ remains unchanged whereas those with $x = 0.70$ and 1.0 show shifts of the SPR peaks to shorter wavelength and sharpening as compared with the as-deposited samples.

The remarkable composition dependence was also observed in the particle distribution over the depth of the polymer matrix for the annealed samples. Fig. 3 shows the effect of particle composition on depth distribution of Au and Cu, obtained by XPS depth profiling measurement. The photoelectron intensity of the Au 4f_{7/2} and Cu 2p_{3/2} core levels in the annealed samples is plotted as a function of film depth. For all the particles containing Cu, no indication of oxidation state for Cu was observed in the Cu LMM Auger electron spectrum (not shown). For the Cu monometallic particles the Cu 2p photoelectron intensity is localized at the surface, indicating that the Cu particles cannot penetrate into the nylon 11 layer on annealing in an N₂ atmosphere, as observed in a previous study.²⁰ A photoelectron signal for Cu and Au in the Au_{*x*}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 spectra obtained, we quantitatively calculated the composition of the bimetallic particles using the integrated area of the Au 4f_{7/2} and Cu 2p_{3/2} peaks in the spectra. The inset in Fig. 3 shows the calculated Au contents in the bimetallic particles as a function of film depth. We can see that the composition of the particles is nearly constant over the depth of the matrix, and the average particle composition is consistent with those obtained by EDX analysis (Table 1).

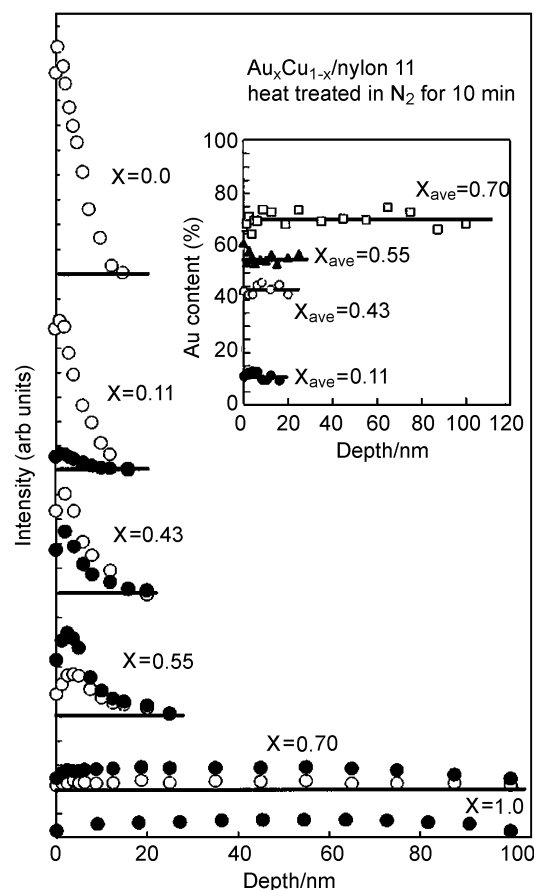


Fig. 3 Depth distribution of Au and Cu in the nylon 11 film annealed at 100 °C for 10 min in an N₂ atmosphere. Inset: Au contents in AuCu bimetallic nanoparticles as a function of depth into the nylon 11 matrix.

Cross-sectional TEM images for the samples with $x = 0.55$ and 0.70 after annealing in an N₂ atmosphere are shown in Fig. 4. The Au_{0.55}Cu_{0.45} particles are observed to be localized at the nylon 11 surface, which preserves the initial layered structure consisting of bimetallic islands deposited on the nylon 11 surface (as-deposited sample). On the other hand, a homogeneous distribution of the Au_{0.70}Cu_{0.30} particles in the nylon 11 phase is clearly observed. These results are also consistent with the depth distribution obtained by the XPS measurements (Fig. 3).

As shown in Fig. 2, the SPR peak shifts towards shorter wavelength upon annealing only for the samples for which the particles disperse into the nylon 11 layer, *i.e.*, Au_{0.70}Cu_{0.30} and Au monometallic particles. It is well known that the SPR absorption of a composite system consisting of metal particles and a dielectric matrix can be characterized by the effective relative permittivity of the composites, which depends on the size and shape of the particles, the volume fraction of the metal phase, and the relative permittivity (refractive index) of the matrix.^{23–25} Among these parameters, we suggest that the

Table 1 Characteristic parameters of Au_xCu_{1-x} particles deposited on the nylon 11 surface before and after annealing at 100 °C for 10 min in an N₂ atmosphere

Deposition amount (Au/Cu)/10 ⁵ atoms cm ⁻¹	Mean particle size (after annealing)/nm	Au : Cu ratio by EDX
23.6/0.00 ($x = 1.0$)	4.4 (4.3)	100 : 0
16.5/7.10 ($x = 0.70$)	3.2 (3.2)	70.8 : 28.2
13.0/10.6 ($x = 0.55$)	2.7 (2.9)	55.0 : 45.0
10.1/13.5 ($x = 0.43$)	2.5 (2.5)	43.2 : 56.8
2.60/21.0 ($x = 0.11$)	2.5 (2.6)	11.5 : 88.5
0.00/23.6 ($x = 0.0$)	2.4 (2.6)	0 : 100

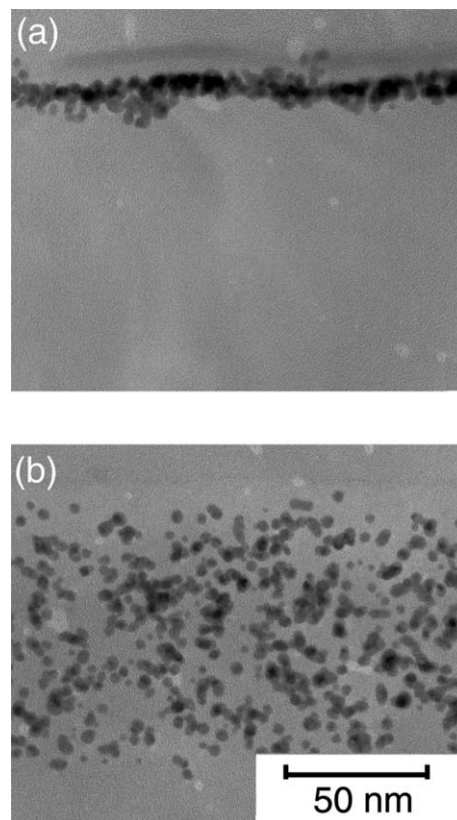


Fig. 4 Cross-sectional TEM images of: (a) Au_{0.55}Cu_{0.45} and (b) Au_{0.70}Cu_{0.30} nanoparticles.

change in the volume fraction of the metal particles due to the dispersion of the particles is the most important for the observed shift of the SPR peaks, because the mean size of the particles presently studied is mostly unchanged after annealing, and the refractive index of the nylon 11 matrix did not significantly change upon annealing.²⁶ For the as-deposited samples, the higher local volume fraction of the particles in the surface region due to island formation leads to dipole interaction between neighboring islands, which results in a red shift of the SPR peak.²⁷ Upon penetration of the particles into the nylon 11 layer, as observed for Au_{0.70}Cu_{0.30} and the Au particles, the particle concentration per unit volume (local volume fraction of the particles) decreases, because of the simultaneous increase in the interparticle distance. The decrease in the local volume fraction of particles results in a blue shift of the SPR peak due to a reduction of the dipole interaction effect between neighboring particles, which is related to the effective relative permittivity of the composite film. Therefore, the observed blue shift of the SPR peak upon annealing, shown in Fig. 2, can be qualitatively explained by the changes in the effective relative permittivity of the composite film, which is caused by a decrease in the average local volume fraction of the particles due to the dispersion of the particles. The present dispersion-induced change in the SPR absorption has also been observed for Au²⁶ and Ag²⁸ nanoparticles during annealing.

Electron diffraction analysis

Fig. 5 shows an intensity distribution curve obtained from the electron diffraction patterns of the as-deposited samples. The diffraction patterns are completely assigned to a typical fcc structure. The gradual shift of the (111) peak can clearly be seen, indicating the formation of a solid solution in the bimetallic particles. Using the d-spacing of a single-crystalline Au thin film for the calibration of the diffraction patterns, we calculated the lattice constant of the bimetallic particles from the (111) diffraction peak. The calculation was carried out for

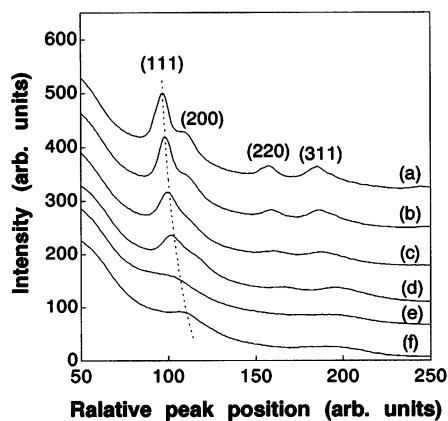


Fig. 5 Intensity distribution curve taken from the SAED patterns of the bimetallic nanoparticles deposited on the nylon 11 surface. Assignment for the diffraction line is indicated.

the samples before and after annealing, and the results obtained are given in Table 2. For the as-deposited samples, the lattice constants were found to be smaller than those of the bulk metals and corresponding alloys,²⁹ *i.e.*, lattice contraction occurs for the particles deposited on the surface of the nylon 11 films. Upon annealing in an N₂ atmosphere, the lattice constant increases slightly but still less than that of bulk materials.

Dispersion process of the particles

The results of depth profiling and cross-sectional TEM observation clearly indicate the existence of a critical composition for penetration of the Au_xCu_{1-x} bimetallic particles into the 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 embedded in the polymer must be lower than that of the isolated particle at the nylon 11 surface. If the surface tension of the particle, γ_{particle} , exceeds the sum of the interfacial tension, $\gamma_{\text{particle-nylon}}$, and the surface tension of the nylon 11, γ_{nylon} , there must be a driving force for penetration of the particles into the nylon 11 matrix,^{30,31}

$$\gamma_{\text{particle}} > \gamma_{\text{particle-nylon}} + \gamma_{\text{nylon}}$$

i.e., the particles can be completely embedded into the nylon 11 matrix. In previous work, we have shown that the inequality [eqn. (1)] is obeyed for the Au particles/nylon 11 system.¹⁹ Since the monometallic Cu particles were not dispersed upon annealing, we suggest that the inequality [eqn. (1)] is obeyed when the surface energy of the bimetallic particles is varied by doping of Au atoms into Cu particles up to a certain composition, *i.e.*, $x \geq 0.70$.

Table 2 Lattice constants and surface stress coefficients of Au_xCu_{1-x} particles before and after annealing

x in Au _x Cu _{1-x}	Lattice constant/Å	Surface stress coefficient/N m ⁻¹
As-deposited		
1.0	4.66326	1.59 ± 0.2
0.70	3.94871	1.14 ± 0.3
0.55	3.88233	0.84 ± 0.2
0.43	3.82583	0.79 ± 0.2
0.11	3.67427	0.71 ± 0.2
0.0	3.60741	0.64 ± 0.2
After annealing		
1.0	4.70828	0.98 ± 0.2
0.70	4.01731	0.82 ± 0.1
0.55	3.87901	0.76 ± 0.2
0.43	3.83472	0.73 ± 0.2
0.11	3.68132	0.65 ± 0.2
0.0	3.61021	0.60 ± 0.2

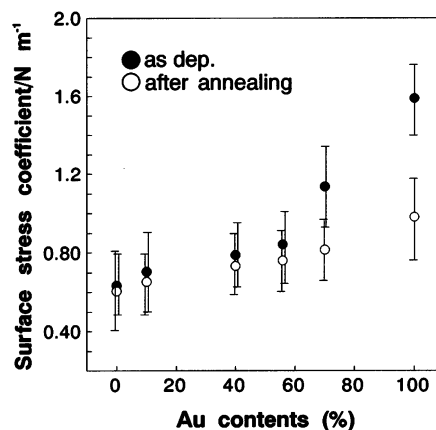


Fig. 6 Variation of surface stress coefficient of Au_xCu_{1-x} nanoparticles with Au content in the particles before and after annealing at 100 °C for 10 min in an N₂ atmosphere.

From these considerations, we calculated the average surface stress of the particles from the lattice constant obtained by the electron diffraction patterns. According to Mays *et al.*,³² for spherical particles with a cubic structure, the surface stress coefficient, f , can be expressed as follows:

$$f = -\frac{3\Delta a D}{4aK}$$

where a is the bulk lattice constant of the corresponding material, Δa is the change in lattice constant, K is the bulk compressibility, and D is the mean particle size. We used the values of the bulk materials for a and K ,^{29,33,34} and the mean particle size for D obtained by TEM observation. For the bimetallic particles, a linear relationship between the compressibility and the composition was assumed for the calculation of K . The results obtained for as-deposited and annealed samples are also given in Table 2 and shown in Fig. 6. The f values for the Au_xCu_{1-x} particles with $x \leq 0.55$ are mostly unchanged upon annealing and in the range 0.6–0.8 N m⁻¹. On the other hand, for the Au particles ($x = 1.0$) and the Au_{0.70}Cu_{0.30} bimetallic particles, thermal annealing causes decreases of f from 1.6 to 1.0 N m⁻¹ and from 1.15 to 0.8 N m⁻¹, respectively. If the anisotropic effect is neglected, the surface stress is related to the surface tension as follows:

$$f = \gamma + \frac{d\gamma}{de}$$

where $d\gamma/de$ gives the dependence of γ on the elastic strain e . In previous work, on Au particles, $d\gamma/de$ was found to be negative since the surface tension of gold was estimated as 1.9 J m⁻² by extrapolation of the value for the melting temperature to room temperature by using Eötvös's rule,³⁵ and the surface stress coefficient decreased gradually as the particles dispersed in the matrix. In the case of copper, the extrapolated value for the surface stress was estimated to be 0.30 J m⁻².³⁴ This low value implies that the surface stress of copper is very small as compared with gold, which is consistent with the present results. Although it is difficult to calculate the surface tension of the Au_xCu_{1-x} alloys because no data is available for surface tension of the alloys at the melting temperature, $d\gamma/de$ may be intrinsically negative for crystalline materials as found experimentally for Au and Ag particles dispersed in nylon 11 films.^{19,28} If this consideration is evident, the stress at the surface for the particles is one of compression. For the Au_{0.70}Cu_{0.30} particles, the decrease of surface stress coefficient is mainly caused by an increase of lattice constant because the mean particle sizes did not change after annealing. The increase of lattice constant due to hydrostatic pressure indicates a decrease of surface tension, as theoretically reported.³⁶ From

these considerations, it seems likely that the difference of the surface free energy between the particles localized at the nylon 11 surface and those embedded in the nylon 11 matrix is the driving force for penetration of the particles, *i.e.*, the dispersion of the Au_{0.70}Cu_{0.30} and Au particles can be attributed to a reduction of the high surface free energy of the particles by embedding them into the nylon 11 matrix. Particles with $x \leq 0.55$ may already be stable when deposited at the nylon 11 surface because the surface stress coefficient of these particles is relatively small as compared with those obtained for the Au_{0.70}Cu_{0.30} and Au particles. We suggest that the surface free energy of the deposited bimetallic particles, which is different for their compositions (due to the alloying effect), determines whether the particles can penetrate into the nylon 11 layer. Further theoretical study is in progress to verify these considerations and the results will be published elsewhere. It is noted that, even if the inequality [eqn. (1)] is obeyed, 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 molecular chains become mobile so as to provide sufficient mobility toward the particles.

Conclusion

We have studied the changes in the dispersion state of vapor deposited Au_xCu_{1-x} bimetallic nanoparticles of various compositions into nylon 11 thin films caused by thermal annealing. In the optical absorption spectra, broad SPR peaks were observed for the as-deposited samples, of which the position depends on their compositions, due to alloying. Thermal annealing in an N₂ atmosphere caused a blue shift of the SPR peak only for the particles with $x = 0.70$ and 1.0 , and the particles were observed to penetrate homogeneously into the nylon 11 matrix, whereas those with $x \leq 0.55$ were still localized at the surface. The critical composition that determines whether or not the particles can be embedded into the nylon 11 layer was found to be around $x = 0.55-0.70$. The detailed analysis of the lattice constant of the particles revealed that, before annealing, the surface stress coefficient of the particles with $x = 0.70$ and 1.0 was much higher than that of the particles with $x \leq 0.55$ and decreased upon embedding in the nylon 11 matrix through annealing. The penetration of the particles is suggested to be attributed to a reduction of the high surface free energy of the particles by embedding them into the nylon 11 matrix, while the particles with $x \leq 0.55$ are stable at the nylon 11 surface due to their relatively low surface free energy. The present study demonstrates that there is a strong correlation between the structure and dispersibility of particles in a polymer matrix, providing insight into the formation, structure and stability of metal/polymer composite systems.

Acknowledgements

This study was supported by the Joint Research Project between Japan and Germany by JSPS and DFG in FY2000-2001, and CREST of JST (Japan Science and Technology).

References

- 1 F. J. C. M. Toolenaar, D. Reinalda and V. Ponec, *J. Catal.*, 1980, **64**, 110.
- 2 H. A. C. M. Hendrickx and V. Ponec, *Surf. Sci.*, 1987, **192**, 234.
- 3 A. Heilmann, G. Kampfrath and V. Hopfe, *J. Phys. D: Appl. Phys.*, 1988, **21**, 986.
- 4 C. Laurent and E. Kay, *J. Appl. Phys.*, 1989, **65**, 1717.
- 5 S. Ogawa, Y. Hayashi, N. Kobayashi, T. Tokizaki and A. Nakamura, *Jpn. J. Appl. Phys.*, 1994, **33**, L331.
- 6 E. Kay and M. Hecq, *J. Appl. Phys.*, 1984, **55**, 370.
- 7 L. Martinu, H. Biederman and J. Zemek, *Vacuum*, 1985, **35**, 171.
- 8 K. Kashiwagi, Y. Yoshida and Y. Murayama, *J. Vac. Sci. Technol., A*, 1987, **5**, 1828.
- 9 C. Reinhardt, A. Heilmann, W. Grünwald and C. Hamann, *Thin Solid Films*, 1993, **246**, 77.
- 10 A. Heilmann, J. Werner, D. Schwarzenberg, S. Henkel, P. Grosse and W. Theiß, *Thin Solid Films*, 1995, **270**, 103.
- 11 R. Lamber, S. Wetjen, G. Schulz-Ekloff and A. Baalman, *J. Phys. Chem.*, 1995, **99**, 13834.
- 12 M. Haruta, K. Saika, T. Kobayashi, S. Tsubota and Y. Nakahara, *Chem. Express*, 1988, **3**, 159.
- 13 K. Esimi, T. Tano, K. Torigoe and K. Meguro, *Chem. Mater.*, 1990, **2**, 564.
- 14 M. Moffitt, L. MacMahon, V. Pessel and A. Eisenberg, *Chem. Mater.*, 1995, **7**, 1185.
- 15 L. Chen, W. Yang and C. Yang, *Macromol. Symp.*, 1996, **105**, 235.
- 16 G. B. Sergeev, I. A. Gromchenko and M. A. Petrukina, *Macromol. Symp.*, 1996, **106**, 311.
- 17 T. Noguchi, K. Gotoh, Y. Yamaguchi and S. Deki, *J. Mater. Sci. Lett.*, 1991, **10**, 477.
- 18 T. Noguchi, K. Gotoh, Y. Yamaguchi and S. Deki, *J. Mater. Sci. Lett.*, 1991, **10**, 648.
- 19 K. Akamatsu and S. Deki, *J. Colloid Interface Sci.*, 1999, **214**, 353.
- 20 S. Deki, K. Akamatsu, T. Yano, M. Mizuhata and A. Kajinami, *J. Mater. Chem.*, 1998, **8**, 1865.
- 21 K. Reichelt, *Vacuum*, 1988, **38**, 1083.
- 22 S. Deki, K. Akamatsu, Y. Hatakenaka, M. Mizuhata and A. Kajinami, *Nanostruct. Mater.*, 1999, **11**, 59.
- 23 U. Kreibitz and L. Ganzel, *Surf. Sci.*, 1985, **156**, 678.
- 24 Y. Takeuchi, T. Ida and K. Kimura, *J. Phys. Chem.*, 1997, **101**, 1322.
- 25 P. Palpant, B. Prével, J. Lermé, E. Cottancin, M. Pellarin, M. Treilleux, A. Perez, J. L. Vialle and M. Broyer, *Phys. Rev. B*, 1998, **57**, 1963.
- 26 K. Akamatsu and S. Deki, *J. Mater. Chem.*, 1998, **8**, 637.
- 27 U. Kreibitz and M. Vollmer, in *Optical Properties of Metal Clusters*, Springer-Verlag, Berlin, 1995, p. 13.
- 28 K. Akamatsu, N. Tsuboi, Y. Hatakenaka and S. Deki, *J. Phys. Chem. B*, 2000, **104**, 10168.
- 29 *Phase Diagrams of Binary Gold Alloys*, ed. H. Okamoto and T. B. Massalski, ASM Int., T. M. Metals Park, OH, 1987.
- 30 F. Faupel, *Phys. Status Solidi A*, 1992, **134**, 9.
- 31 T. Strunski, M. Kiene, R. Willecke, A. Thran, C. V. Bechtolsheim and F. Faupel, *Mater. Corros.*, 1998, **49**, 180.
- 32 C. W. Mays, J. S. Vermaak and D. Kuhlmann-Wilsdorf, *Surf. Sci.*, 1968, **12**, 134.
- 33 J. S. Vermaak and D. Kuhlmann-Wilsdorf, *J. Phys. Chem.*, 1968, **72**, 134.
- 34 H. J. Wasserman and J. S. Vermaak, *Surf. Sci.*, 1972, **32**, 168.
- 35 N. K. Adam, *Physics and Chemistry of Surfaces*, Dover, New York, 1968, p. 158.
- 36 M. Drechsler and J. F. Nicholas, *J. Phys. Chem. Solids*, 1967, **28**, 2609.