Characterization and optical properties of gold nanoparticles dispersed in nylon 11 thin films

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We have prepared nylon 11 thin films containing individually isolated Au particles with various volume fractions ranging from 1.7 to 8.3% by means of a consecutive evaporation followed by heat treatment. The films obtained were characterized by TEM, XPS and UV–VIS absorption spectroscopy. Au particles were homogeneously distributed in the whole of the film after heat treatment at 100 °C for 10 min. The mean size of the Au particles increased from 3.2 to 5.2 nm in diameter upon increasing the volume fraction of Au particles. UV–VIS spectroscopy revealed that a peak position due to the surface plasmon resonance absorption of the Au particles shifted to longer wavelength as the volume fraction of the Au particles increased, accompanied by an increase of its peak intensity.

Solid dielectric materials such as polymers doped with nanometer-sized metal particles are of considerable interest because such materials exhibit unusual physical and chemical properties, and possess exciting possibilities for potential applications. The properties of such composites are usually affected by the nature, size and shape of the dispersed metal particles and the volume fraction of the metal phase. Several properties which depend on film microstructure have been observed in previous studies, *e.g.*, the optical absorption band due to the surface plasmon resonance of fine metal particles,[1] the change of the electrical conductivity from insulating to metallic behaviour at the percolation threshold[2] and the third-order non-linear optical susceptibility, which strongly depends on the dopant concentration.[3] For the experimental and theoretical description of these effects on physical properties, it is important to determine the size, shape and also the spatial distribution of the dispersed metal particles in the composite film.

Various methods to prepare metal-doped polymer films have been developed and the characteristics of these films have been studied by many researchers.[4–9] For materials to be utilized in electrical and optical devices, it is important to ensure a thin film process such as layer or circuit pattern and to manipulate the size and the concentration of dispersed metal particles to give desired properties for the obtained materials.

We have previously developed and reported a novel process to prepare polymer films containing metal nanoparticles by a thermal relaxation technique.[10,11] This technique relies on the consecutive evaporation of a polymer and a metal, and then heat treatment. It has been shown that heat treatment subsequent to film deposition leads to dispersion of metal particles owing to the structural relaxation of polymer matrix. By this method nylon 11 films containing dispersed metal particles such as Au or Ag can be readily prepared.[10] This technique has been available for the study of metal–polymer systems with metal particle sizes in the order of several nanometers.[12] Our previous studies have related mainly to the preparation of composite films with thicknesses of several micrometers.

Here, we report on the characterization and optical properties of Au nanoparticle/nylon 11 composite films with thicknesses of <100 nm having various Au volume fractions, prepared by the thermal relaxation technique. The microstructure and depth distributions of Au particles were characterized by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). We also discuss the relationship between the film microstructure and optical properties which are characteristic of the Au particles.

Experimental

Nylon 11 was used as a polymer matrix as employed in a previous paper.[10] The nylon 11 matrix film with a thickness of 60 nm was prepared on a glass substrate by vapour deposition of a nylon 11 pellet (Aldrich) using a resistance-heated molybdenum boat at a pressure of $<10^{-4}$ Torr. Au metal was then vapour deposited on the nylon 11 film at room temperature using an alumina-coated tungsten filament. The amount of deposited Au ranged from 5.90 to 29.5×10^{15} atom cm^{-2}. The deposition rate of Au was maintained at 0.5 Å s^{-1} as monitored by quartz-crystal microbalance.

The Au/nylon 11 films were then heat-treated at 100 °C for 10 min in an atmosphere of nitrogen. The thickness of the film was directly measured by atomic force microscopy. Since significant variations of the film thickness with the amount of deposited Au could not be observed, the thickness is assumed to be constant for the films with different Au volume fraction. Thus the Au volume fraction in the film was approximately calculated from the amount of deposited Au by using the density of Au bulk metal. After the heat treatment, optical absorption spectra were measured with a UVDEC 660 spectrophotometer (Japan Spectroscopic Co. Ltd.) over wavelengths ranging from 350 to 850 nm, and the samples were further prepared for TEM analysis.

The particle size, size distribution and crystalline character of dispersed Au particles were observed by using a JEM-2010 (JEOL) transmission electron microscope operating at 200 kV, which provided a 0.19 nm point resolution. The samples for TEM observation were prepared as follows. A thin carbon layer was coated on the composite film formed on the glass substrates for the purpose of preventing charging up effects by the electron beam during the TEM observation. The samples were then exposured to hydrogen fluoride vapour for 30 s. These films were separated from the substrate by floating onto a water bath and put on holey triafol films supported on TEM copper grids.

The depth profile of Au in the film was measured by a X-ray photoelectron spectrometer, ESCA 750 (Shimadzu), using an Mg-Kα X-ray source. Depth profiling was carried out by argon ion sputtering at an acceleration voltage of 2 kV, 5–10 mA ion beam current and 30° incidence angle.

Results and Discussion

After heat treatment, the colour of the film visibly changed from transparent purple to transparent ruby red, which could be due to dispersion of the Au particles. Fig. 1 shows the effect of heat treatment on the Au depth distribution obtained by XPS measurements. The intensity of Au $4f_{7/2}$ photoelectrons was measured for the specimen with a deposition of 29.5×10^{15} Au atom cm^{-2}. For the as-deposited film the photoelectron intensity for Au was localized at the surface. However, the intensity was smaller than that expected for a continuous Au film. This indicates that the deposited Au film is not uniform but discontinuous and island-like at the surface. After heat treatment at 100 °C for 10 min, the photoelectron intensity for Au was remarkably reduced at the surface and emission of Au 4f photoelectrons could be detected in the entire film. From this drastic change in the depth profile, it is clear that the Au has penetrated into the nylon 11 upon heat treatment. This behaviour is consistent with the previous result of the depth profile measured by electron-probe X-ray microanalysis for thick nylon 11 films (*ca.* 200 μm).[11] Based on this result, the films heat-treated at 100 °C for 10 min were employed for the following measurements.

Fig. 2 shows the depth profiles of Au in the films with various Au volume fractions after heat treatment. Since the sputtering rate of the film by the Ar ion was considered to be different for specimens with different Au volume fractions during the depth profiling, the depth scales were corrected so that the position where the emission of Si 2p photoelectrons from the glass substrate could be detected corresponds to a depth of 60 nm. The removed film depth was then proportional to the sputtering time at a constant Ar ion current. For all samples the binding energy of the Au $4f_{7/2}$ photoelectrons was 83.9 ± 0.05 eV corresponding to that of bulk metallic gold. The filled circles in Fig. 2 shows a magnified depth profile for the sample containing the lowest amount of deposited Au. As can be seen, the profiles for films containing the lowest and highest amounts of Au are very similar. This indicates that the depth distribution of Au after heat treatment is independent of the initial amount of deposited Au, and also suggests that the Au volume fraction can be controlled by varying the amount of Au deposition and the thickness of the nylon 11 matrix.

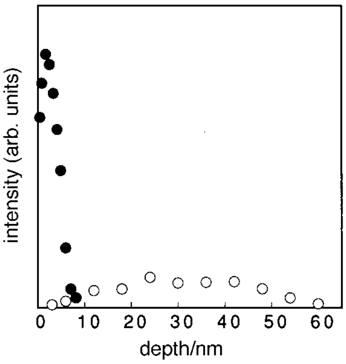

Fig. 1 XPS depth profile of Au in the film after vapour deposition of Au at room temperature (●) and after subsequent heat treatment at 100 °C for 10 min (○). Amount of deposition: 29.5×10^{15} atom cm^{-2}.

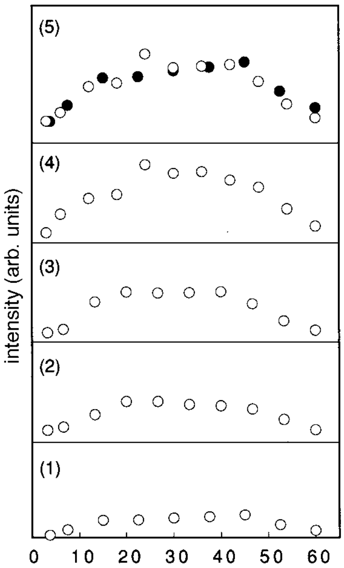

Fig. 2 XPS depth profiles of Au in the film heat-treated at 100 °C for 10 min. The amount of deposited Au is equal to (1) 5.90, (2) 11.8, (3) 17.7, (4) 23.6 and (5) 29.5×10^{15} atom cm^{-2}. The filled circles in (5) show a magnified intensity of the lowest amount of deposition, indicating that the shape of the depth profile of Au in the film does not change with the amount of deposited Au.

Fig. 3 shows TEM images of specimens heat-treated at 100 °C for 10 min. It was found that the Au particles were dispersed homogeneously in the plane of the film. The mean size of Au particles increased with increasing Au volume fraction and characteristic parameters of the Au particles are listed in Table 1. Selected area electron diffraction patterns of specimens containing >5% of Au volume fraction showed patterns typical of the gold fcc structure, with lattice parameters corresponding to those of bulk gold. Below 5% volume fraction, broad diffraction lines were observed, which may be due to the very small size of the particles (<4 nm). Particle size distributions were obtained by counting 200 particles on the TEM images. The corresponding size distributions are shown as histograms in Fig. 4. The histograms showed a fairly narrow peak distribution, but slight broadening was observed with increase of Au volume fraction.

The crystalline character of the Au particles could be observed by imaging of Au lattice owing to the amorphous nature of the nylon 11 matrix. High-resolution TEM images for specimens 1, 3 and 5 of Table 1 are shown in Fig. 5. By direct observation of the lattice planes, it is seen that smaller Au particles were mostly single crystals (specimen 1), and larger particles were twinned, having a common (111) plane (specimen 3 and 5). In some cases, multiply twinned particles such as decahedra or icosahedra were evident. As the Au volume fraction increases, single particles appear to coalesce, forming larger non-spherical particle. However, this is an effect of the overlapping of particles in the plane of the TEM image. This effect was confirmed by a tilting sequence of the sample in the TEM specimen holder. Since the heat treatment is performed at temperatures above the glass transition temperature (T_g) of nylon 11 (*ca.* 70 °C), the nylon 11 matrix can behave as a viscous fluid giving mobility towards the Au particles, which may allow a coalescence of the particles. The individual Au particles in the films were, however, well isolated after heat treatment. We suggest that this effective isolation could be attributed to the strong interaction between Au particles and nylon molecules. The dispersed Au nanoparticles are stable with no aggregation or coalescence occurring over six months under air.

The mechanism of metal dispersion caused by heat treatment is proposed as follows:[10] because the nylon 11 thin films on the glass substrate are fixed rapidly from the gaseous state to the solid state during the vapour deposition process, these films possess a thermodynamically metastable structure which can relax to a much more stable structure upon heat treatment, *i.e.*, a structural rearrangement of nylon molecules could occur during heat treatment at temperatures above T_g of nylon 11. With the effect of the thermally induced structural relaxation, a composite thin film in which the Au particles are uniformly dispersed and stably fixed with nylon molecules is obtained.

Fig. 6 shows the optical absorption spectra measured at room temperature for the Au/nylon 11 composite films heat-

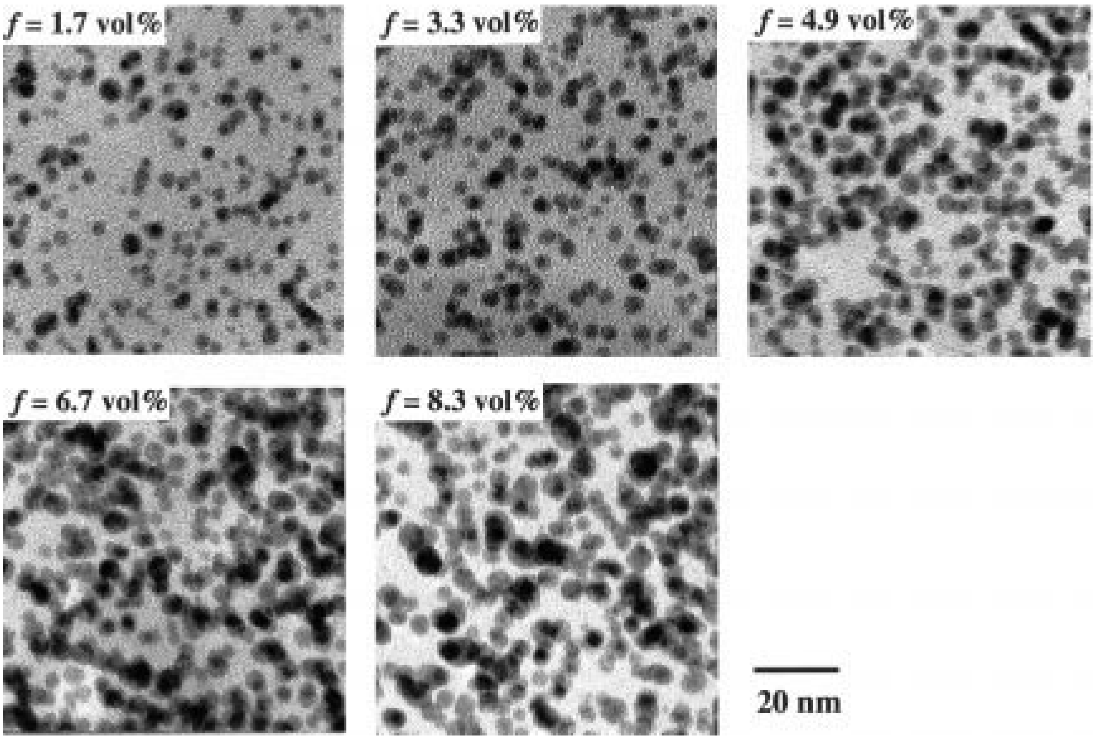

Fig. 3 TEM images of the Au-dispersed nylon 11 films heat-treated at 100 °C for 10 min. The Au volume fraction is equal to (1) 1.7, (2) 3.3, (3) 4.9, (4) 6.7 and (5) 8.3 vol%.

Table 1 Characteristic parameters of Au particles in the composite films containing various amounts of Au

specimen	amount of deposited Au/10^{15} atom cm^{-2}	volume fraction (%)	mean particle size/nm	standard deviation/nm
1	5.90	1.7	3.2	0.50
2	11.8	3.3	3.7	0.50
3	17.7	4.9	4.1	0.56
4	23.6	6.7	4.6	0.62
5	29.5	8.3	5.2	0.74

treated at 100 °C for 10 min. It is well known that small metal particles show characteristic optical properties due to surface plasmon resonance, which results in an absorption peak in the UV–VIS region.[1,13,14] The plasmon band of the Au particles in the present study was observed at *ca.* 520 nm. As the Au volume fraction increased, the intensity of the absorption peak was enhanced. The change of the absorption peak position of the plasmon band is shown in Fig. 7. The peak wavelength shifted continuously toward longer wavelengths with increase of Au volume fraction. Similar red shifts have been reported for other metal–polymer systems.[8,9] The plasmon band is affected by the dispersed metal particle size, the relative permittivity of the surrounding matrix and the volume fraction of metal phase.[1,13,14] The shift of the maximum absorption in the absorption spectra can be predicted by the Maxwell–Garnett (MG) theory for films with isolated spherical metal particles embedded in a dielectric medium.[15] When the metal particles are much smaller than the wavelength of light, the effective relative permittivity, ε, of such a composite system is expressed approximately by

$$\varepsilon=\varepsilon_{\mathrm{d}}\,\frac{\varepsilon_{\mathrm{m}}(1+2f)+2\varepsilon_{\mathrm{d}}(1-f)}{\varepsilon_{\mathrm{m}}(1-f)+\varepsilon_{\mathrm{d}}(2+f)} \qquad (1)$$

where $\varepsilon_{\mathrm{m}}(\omega)=\varepsilon'_{\mathrm{m}}+\varepsilon''_{\mathrm{m}}$, which is complex and frequency dependent, is the relative permittivity of the metal particle, ε_{d} is the relative permittivity of the surrounding medium and f is the volume fraction occupied by the metal particles. The maximum absorption is observed at the wavelength that satisfies the following condition,

$$\varepsilon'_{\mathrm{m}}+\frac{2+f}{1-f}\varepsilon_{\mathrm{d}}=0 \qquad (2)$$

This equation predicts that the band maximum shifts to longer wavelength with an increase of the metal volume fraction, as determined by the factor $(2+f)/(1-f)$, and with the relative permittivity of the surrounding medium. The relative permittivity of metals depends on particle size, which is attributed to the interactions of conduction electrons.[16] When the particle size falls below the mean free path of conduction electrons in the bulk metal, the effective mean free path becomes that of the dimensions of the particle. This effect leads to the additional size dependence of the relative permittivity of the metal, and can also be, therefore, responsible for the shift of the plasmon band. Fig. 8 shows the relationship between the real part of relative permittivity of gold and the factor $(2+f)/(1-f)$, according to eqn. (2). For the calculation of $\varepsilon'_{\mathrm{m}}$, the size effect caused by the free path limitation is introduced into ε_{m},[17] and the experimental data of optical constants by Otter is employed for the bulk relative permittivity of gold.[18] A linear relationship was observed in the present experimental region of the Au volume fraction. The concentration of the Au nanoparticles in the present study is expected to be high owing to small particle

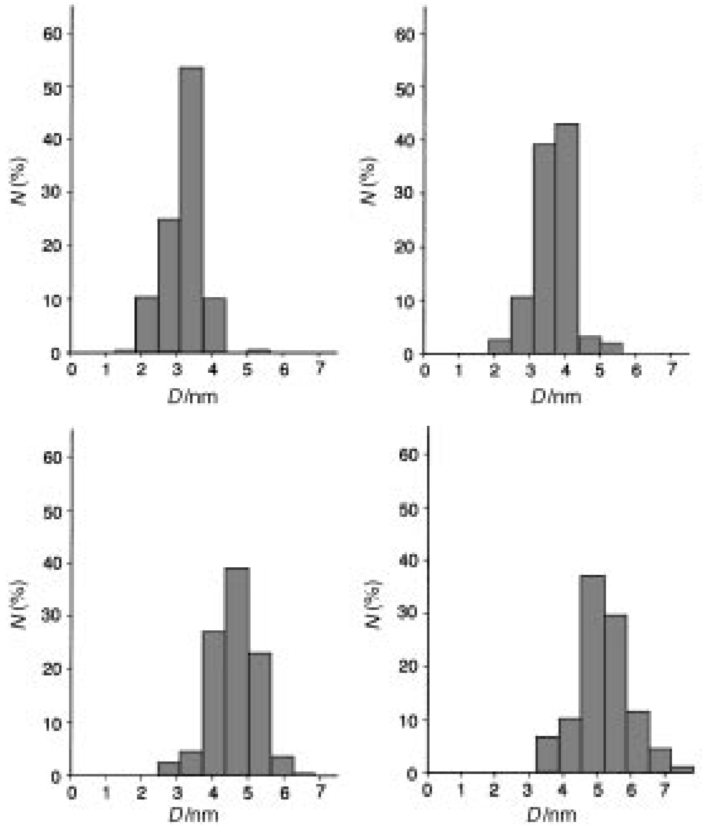

Fig. 4 Particle size distributions of dispersed Au particles in the films heat-treated at 100 °C for 10 min. The histograms were obtained from TEM images of the specimens (1)–(5) of Table 1. Mean particle size (D_m) is equal to (1) 3.2, (2) 3.7, (3) 4.1, (4) 4.6 and (5) 5.2 nm.

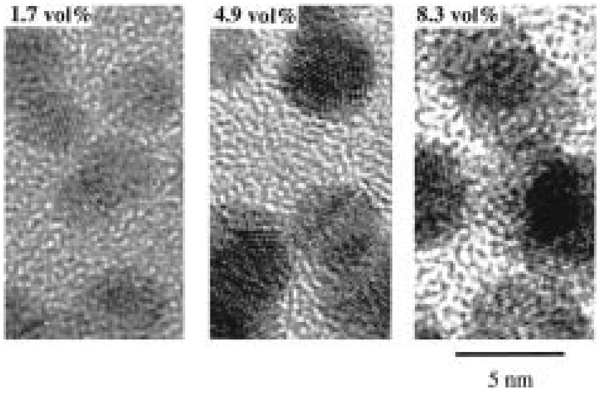

Fig. 5 High-resolution TEM images of dispersed Au particles in the film heat-treated at 100 °C for 10 min, showing the crystalline character of the Au particles. The specimens (a), (b) and (c) correspond to the specimens (1), (3) and (5) of Fig. 1, respectively. Mean size of the Au particles is equal to (a) 3.2, (b) 4.1 and (c) 5.2 nm.

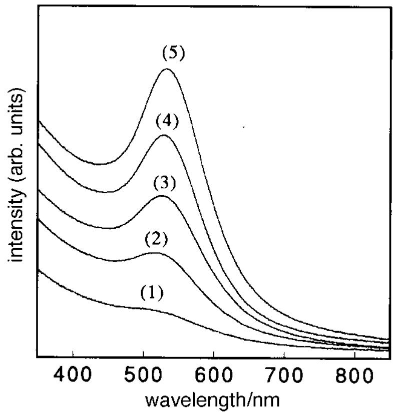

Fig. 6 Optical absorption spectra of the Au-dispersed nylon 11 composite films heat-treated at 100 °C for 10 min. The Au volume fraction is equal to (1) 1.7, (2) 3.3, (3) 4.9, (4) 6.7 and (5) 8.3 vol%.

sizes, as can be observed in Fig. 3. Increase of particle concentration leads to a relative decrease of interparticle distance. Under such conditions a electromagnetic interaction between each dispersed particle polarized by the external electromagnetic field of incident light may become more important for optical properties, which effect is approximately taken into account in the MG equation as the Lorentz local field relation.[15] Since all the nylon 11 matrices were prepared and heat-treated under the same conditions, the relative permittivity of the nylon 11 will not vary with Au volume fraction. Therefore, the shift of plasmon band toward longer wavelengths as shown in Fig. 7 is caused by the increase of both the size and the volume fraction of dispersed Au particles.

Conclusion

Nylon 11 thin films containing nanometer-sized Au particles of various volume fractions have been reproducibly prepared using a thermal relaxation technique. After heat treatment the Au particles were distributed homogeneously in the whole of the film and were well isolated, owing to the strong interaction between the Au particles and nylon molecules. We have shown that it is possible to control the volume fraction of the Au particles in films of fixed thickness by varying the initial amount of deposited Au. The mean size of the Au particles increased simultaneously with increasing Au volume fraction. The absorption peak due to the surface plasmon resonance of

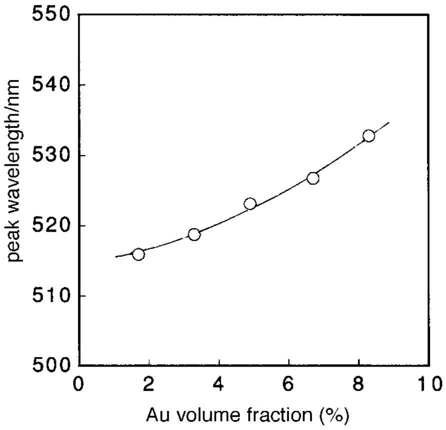

Fig. 7 Relationship between the peak wavelength of the surface plasmon band of Au particles and the volume fraction of Au particles in the film heat-treated at 100 °C for 10 min

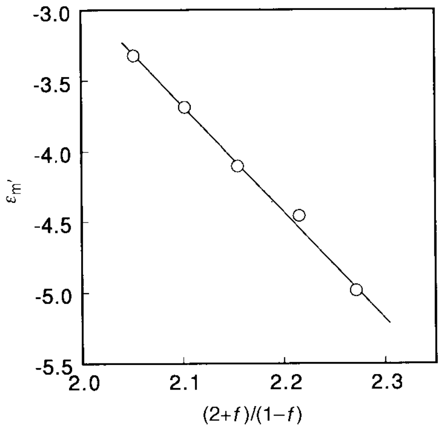

Fig. 8 Relationship between the real part of the relative permittivity of gold at the peak wavelength of the plasmon band and the factor $(2+f)/(1-f)$

Au particles shifted toward longer wavelengths as the Au volume fraction was increased. This behaviour is mainly a characteristic of the films having increasing particle size and volume fraction of dispersed Au particles.

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