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Dispersion of gold nanoparticles into a nylon 11 thin film during heat treatment: *in situ* optical transmission study

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Changes in the optical absorption spectra of Au/nylon 11 thin films during the dispersion of Au nanoparticles caused by heat treatment have been investigated by means of *in situ* optical transmission measurements using a multi-channel charge coupled device spectrophotometer attached to an integrating sphere. Temperature-dependent spectral changes of the surface plasmon resonance absorption of the Au nanoparticles were obtained by the measurement of total transmittance through the sample. It has been found that the peak wavelength of the plasmon band shifted to shorter wavelength and its intensity decreased in the temperature range 40–70 °C, corresponding to the temperature at which the nylon 11 matrix relaxed. In order to investigate the cause of this behaviour, we have measured the depth distribution of the Au particles in the film, crystallite size of the Au particles and refractive index of the nylon 11 matrix film by using XPS, XRD and ellipsometry, respectively. While the size of the Au particles and refractive index of the nylon 11 were nearly constant with heat treatment up to 100 °C, the Au particles have penetrated into the nylon 11 layer for the heat treatment at 50 °C and further dispersed more deeply above 70 °C. The change of the volume fraction of the Au particles caused by the penetration from the surface into the bulk phase of the nylon 11 matrix is suggested to be mainly responsible for the shift of the plasmon band. The dependence of the heating rate on the shift of the plasmon band was also observed.

Optical properties of solid dielectric materials such as polymers or glasses doped with nanometer-sized metal particles are currently the subject of intensive research fundamentally for potential applications. It is well known that metal nanoparticles exhibit characteristic optical properties due to the surface plasmon resonance of conduction electrons which results in an absorption band in the UV–VIS region.[1–3] In general, the plasmon band is very sensitive to the chemical composition of the particles, their size, shape, volume fraction, and also the surrounding medium because the electronic properties of the particles depend strongly on such parameters.[4–6] Therefore, spectral analysis of the optical absorption band provides useful information on the microstructural characteristics of such composite materials. In fact, the optical properties which depend on film microstructure have been reported and the characteristics of these films have been studied by many researchers.[7–10]

We have previously developed a process to produce composite films consisting of dispersed metal particles in polymer matrices by a thermal relaxation technique which relies on a consecutive evaporation followed by heat treatment.[11,12] In this technique, heat treatment subsequent to film deposition leads to the dispersion of metal nanoparticles from the effects of thermally induced structural relaxation of the polymer matrix. For the Au nanoparticles dispersed in nylon 11 thin films, we have shown that the volume fraction of Au nanoparticles in the film with a thickness of *ca.* 60 nm can be varied and the size of the particles was determined by controlling the amount of Au deposition.[13] It has been also found that the peak wavelength of the optical absorption band depend on both the size and the volume fraction of dispersed Au particles. In order to elucidate the cause of this dispersion phenomena, experimental data measured *in situ* during heat treatment is thought to be necessary.

Here, we report an *in situ* optical transmission measurement of the Au/nylon 11 system during heat treatment by using a high-sensitivity charge coupled device (CCD) analyzer attached to an integrating sphere. The integrating sphere is the ideal device for measuring the total power of optical radiation. The optical absorption spectra were calculated as temperature-dependent spectral changes, reflecting the microstructural changes of the films caused by the dispersion of Au particles. The relationship between optical spectral changes and the depth distribution of the Au nanoparticles in the film, analyzed by X-ray photoelectron spectroscopy, are also discussed.

Experimental

In situ optical transmission measurements

The experimental setup for transmission measurements is schematically shown in Fig. 1. Samples mounted, as shown, on the wall of the integrating sphere with 20 cm in diameter were irradiated with a AT-100HG halogen light source (Shimadzu) from outside the sphere. Radiation that is incident on the sample is partially reflected, partially transmitted and partially absorbed. The sphere effectively collects and spatially integrates the transmitted component, providing a uniform signal to a detector. The light transmitted through the sample was measured by means of a cooled-type photodetector placed on the sphere wall opposite to the sample port and baffled to prevent first strike radiation from reaching the detector. A twelve fiber optic cable connects the signal being measured to the multi-channel CCD spectrophotometer, PMA-11-C5966 (Hamamatsu Photonics K.K.), designed for real-time spectral analysis. To ensure high sphere efficiency, the total area of sample and detector port is $<5\%$ of the sphere surface area.

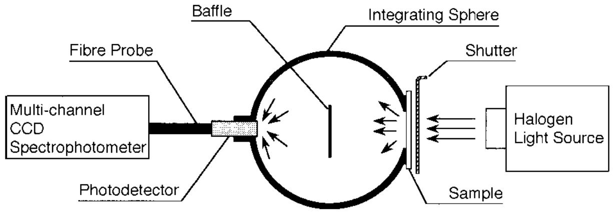

Fig. 1 Experimental setup of the optical transmission measurement using a multi-channel charge coupled device (CCD) spectrophotometer attached to an integrating sphere

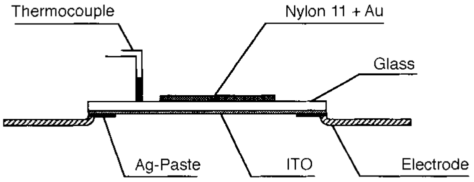

Fig. 2 Schematic diagram of the sample used for optical transmission measurement. The Au/nylon 11 thin film is heated by a resistively heated indium tin oxide (ITO) thin film coated on a glass substrate.

The schematic diagram of the sample apparatus is shown in Fig. 2. The nylon 11 matrix film with a thickness of 110 nm was vapour deposited on a glass substrate coated with an indium tin oxide (ITO) thin film which acts as a semiconductor heater. Au metal was vapour deposited on the nylon 11 film at room temperature with a deposition level of 17.0×10^{15} atoms cm^{-2}.

The experimental details for sample deposition were described in a previous paper.[13] The sample prepared on the ITO glass substrate was mounted on the sphere wall and heated at a constant rate under irradiation with the light source. The spectra were recorded at an appropriate temperature interval. Exposure time of the photodetector is 5 ms and the number of integrations is 30. The time required for each measurement is thus 150 ms and temperature rise during this is negligible ($<0.005\,°\mathrm{C}$) under the present heating conditions. Thus we can carry out *in situ* optical transmission measurements, in which the obtained spectra can be studied as a function of temperature.

By running a measurement using an ITO glass specimen with no sample deposition, the total transmitted component through the sample is derived. After measuring the total transmittance, the optical absorption spectra of the sample can be calculated by the simple relation, $A = -\log(I/I_0)$, where A is the absorbance, I is the transmitted intensity through the sample and I_0 is that through the ITO glass substrate as a reference.

Characterization of films

The properties of the films after the heat treatment at various temperature were characterized by using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and ellipsometry. The samples were deposited on glass plates for XRD, and Si wafers for XPS and ellipsometric measurements. XRD measurements were carried out using a RINT 2100 diffractometer (Rigaku) with thin film attachment and crystallite sizes of Au were calculated from the Au(111) diffraction peak in accordance with Scherrer's formula. In order to accurately calculate the crystallite size, intensities were accumulated by repeating the measurement 15 times. XPS analysis for obtaining the depth distribution of Au in the film was carried out on a ESCA 750 (Shimadzu) instrument. Depth profiles were obtained by argon ion sputtering at an acceleration voltage of 2 kV and 5–10 mA ion current. The refractive index of deposited nylon 11 films heat treated at various temperatures were determined by ellipsometric measurements using an He–Ne laser (632.8 nm).

Results and Discussion

During the heat treatment from room temperature up to 100 °C at a constant heating rate, the colour of the film changed gradually from purple to transparent ruby red. Fig. 3 shows the results of *in situ* transmission measurements for the Au/nylon 11 film during heat treatment under air; $-\log(I/I_0)$ is plotted as a function of the wavelength and the temperature. Generally, the transmittance contains information about the absorption as well as the scattering of light. The term $-\log(I/I_0)$ is therefore termed extinction. However, the extinction spectra were practically equivalent to the absorption spectra because the scattering effect is not important when the particle size is <10 nm. The ordinate of Fig. 3 thus represents the absorbance. The spectra were measured for the specimen with a deposition of 17.0×10^{15} atoms cm^{-2} and heating rate was $0.5\,°\mathrm{C\,min}^{-1}$. As the temperature increased, the spectra changed significantly. The peak wavelength due to the surface plasmon resonance absorption of the Au particles shifted from *ca.* 600 nm (at room temperature) to *ca.* 535 nm (at 100 °C) with increasing temperature, accompanied by a decrease of its peak intensity. The change of the peak wavelength and absorbance of the plasmon band during the heating process is shown in Fig. 4. The shift of the plasmon band occurred in the temperature range 40–70 °C, which corresponds to the glass transition temperature (T_g) of nylon 11 matrix (*ca.* 40 °C) and, in this temperature region, the absorbance decreased simultaneously.

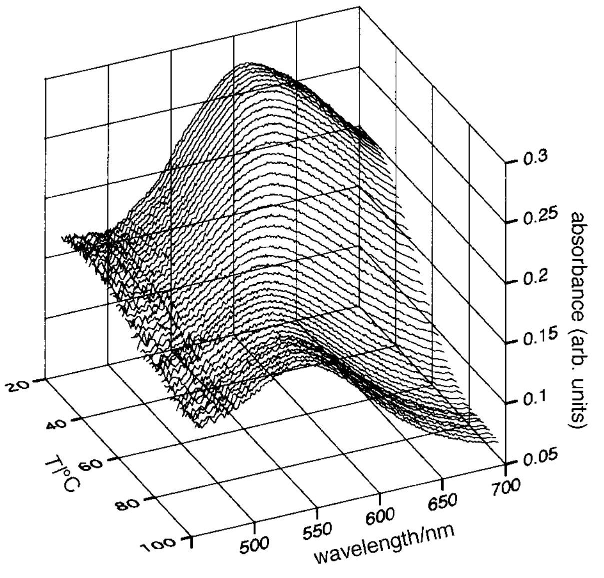

Fig. 3 Changes in the optical absorption spectra calculated from the total transmittance through the sample. The peak wavelength of the surface plasmon band of the Au nanoparticles shifted continuously from 600 nm (at 25 °C) to 535 nm (at 100 °C) during heat treatment. Amount of initial Au deposition: 17.0×10^{15} atoms cm^{-2}.

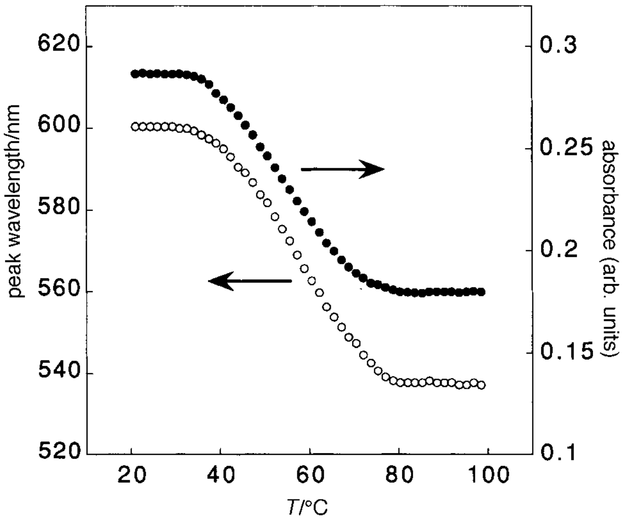

Fig. 4 Variations for the peak wavelength of the Au plasmon band and for the absorbance at the peak wavelength with temperature, obtained from the absorption spectra shown in Fig. 3

Fig. 5 shows the depth distribution obtained by XPS measurements for Au/nylon 11 films heat treated at various

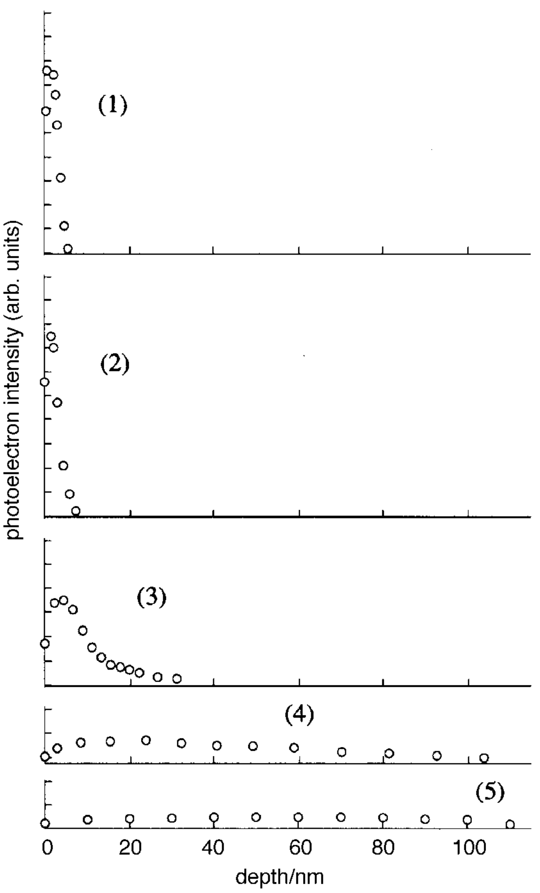

Fig. 5 XPS depth profiles of Au in the nylon 11 film heat-treated at various temperatures. The heat treatment temperature: (1) as-deposition, (2) 35 °C, (3) 50 °C, (4) 70 °C, (5) 100 °C.

temperatures. These films were deposited on an Si wafer substrate to prevent charging up effects during XPS measurement and argon ion sputtering process. The depth scales were corrected for the specimens heat treated at various temperature by taking into account for the sputtering time and Ar ion current.[13] The profiles for the film heat-treated at 35 °C are very similar to that for as-deposited film, indicating that the Au is localized at the surface of the nylon 11 for the heat treatment below 35 °C. However, their intensity was smaller than that expected for a pure continuous Au thin film. It is considered that the Au is deposited to form islands and thus results in very broad plasmon absorption for as-deposited. The Au has penetrated into the nylon 11 layer upon heat treatment at 50 °C and penetrated more deeply at 70 °C, showing a concentration gradient in the profile as shown in Fig. 5. After heat treatment at 100 °C, Au was dispersed homogeneously in the depth scales of the nylon 11 layer.

We note here that the thickness of the nylon 11 film used in the present study is about twice that used in the previous paper (*ca.* 60 nm).[13] If the total amount of the Au is constant and composite films in which the Au particles dispersed homogeneously in the entire film are produced, a thicker film has low volume fraction of Au and a thinner film has high volume fraction. It is clear that the volume fraction of the Au particles in the film can be controlled by varying not only the amount of Au deposition but also the thickness of the nylon 11 matrix layer.

Table 1 summarizes the crystallite sizes of Au particles calculated using Scherrer's method and the refractive index of the nylon 11 matrix film determined by means of ellipsometric measurements. Both the size and the refractive index appear to be essentially unchanged upon heat treatment up to 100 °C.

Table 1 Crystallite sizes of the Au nanoparticles in the film and refractive index of the nylon 11 matrix film heat-treated at various temperature

heat treatment temperature/°C	crystallite size/nm	refractive index
no	3.8	1.53
35	3.8	1.53
50	3.7	1.53
70	3.7	1.54
100	3.7	1.55

We have proposed previously that the Au deposited on the nylon 11 surface could be dispersed into the bulk phase of the nylon 11 upon structural relaxation of the nylon 11 matrix induced by heat treatment. Since the nylon molecules are quenched from the gaseous phase into the solid phase, to form a thin film, during the vapour deposition process, the nylon 11 films produced are in a metastable state which relaxes upon thermal annealing. We have observed by differential scanning calorimetry that a relaxation of vapour deposited nylon 11 was observed during the heating cycle with a threshold at *ca.* 45 °C. At the temperature which the relaxation of the nylon 11 matrix occurred, the Au particles, having island-like structures at the surface for the as-deposited film, penetrated and dispersed into the nylon 11 layer (Fig. 5). Unfortunately, the microscopic structures of the present composite films having different dispersion states of the Au particles are not well characterized. However, it seems likely that the Au particles have sufficient mobility to disperse into the nylon 11 matrix because the nylon 11 can behave as a viscous fluid at temperatures above the T_g of nylon 11. Fig. 6 shows the effect of the heating rate on the shift of the Au plasmon peak position. As can be clearly seen, the temperature at which the peak wavelength shifts to shorter wavelengths is raised as the heating rate is increased. It seems that this behavior reflects thermal effects in the relaxation of nylon 11 matrix.

The temperature-dependent spectral changes reflects reasonably the changes of the film microstructure during dispersion of the Au nanoparticles, *i.e.*, the effect of the dispersion of the Au nanoparticles caused by heat treatment. The plasmon band is usually affected by the dispersed metal particle size, the relative permittivity of the surrounding medium and volume fraction of metal phase. The shift of maximum absorption can be well explained qualitatively by the Maxwell–Garnett (MG) theory for films with metal particles dispersed in a dielectric medium.[14] The MG theory is applicable for samples with any

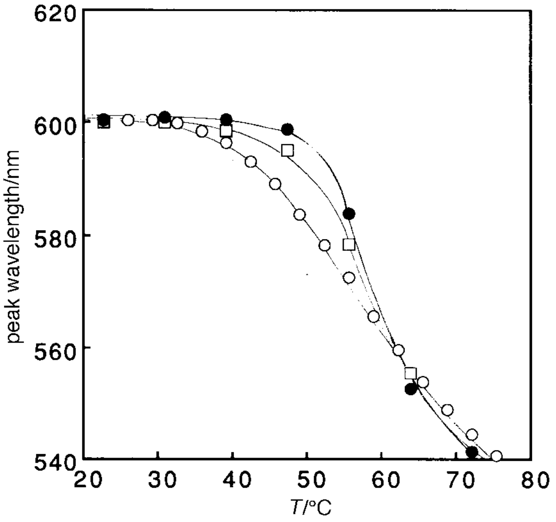

Fig. 6 Effect of the heating rate for the shift of the plasmon peak wavelength, indicating that the dispersion of the Au particles has a close relation to the thermal behaviour of the nylon 11 matrix. Heating rate: (○) 0.5, (□) 3.3, (●) 13.0 °C min^{-1}.

value of metal volume fraction. The absorption coefficient, α, of the plasmon band of isolated metal particles is expressed as:

$$\alpha = \frac{18\pi f \varepsilon_d^{3/2}}{\lambda(1-f)} \cdot \frac{\varepsilon''_m}{\{\varepsilon'_m + [(2+f)/(1-f)\varepsilon_d]\} + \varepsilon''^{2}_m} \qquad (1)$$

Where $\varepsilon_m\ (\omega) = \varepsilon'_m + i\varepsilon''_m$, which is complex and frequency dependent, is the relative permittivity of the metal particle, $\varepsilon_d = n^2$, with n being the refractive index of the matrix, is the relative permitivity of the surrounding medium, λ is the wavelength of light and f is the volume fraction occupied by the metal particles. The maximum absorption is given by

$$\varepsilon'_m + \frac{2+f}{1-f}\varepsilon_d = 0 \qquad (2)$$

Eqn. (1) and (2) predicts that the band maximum shifts to shorter wavelength and absorption intensity decreases with the decrease of the metal volume fraction and with the relative permittivity of the surrounding medium.

The crystalline size of the Au particles did not vary with heat treatment temperature and the refractive index of the nylon 11 matrix is only slightly changed upon heat treatment even at temperatures above 70 °C (Table 1). Although no diffraction peaks were observed from the XRD pattern of the nylon 11 film with no metal deposition (X-ray amorphous), the slight increase of n may be attributed to the relaxation of the nylon 11 matrix caused by heat treatment, because the crystallinity of the relaxed films is considered to be relatively larger than that of the unrelaxed films which have metastable structures. The variation of refractive index only amounts to 0.02. This small change of refractive index appears not to influence the absorption spectra. From these results, the shift of the plasmon band seems to mainly be caused by the changes in the depth distribution of the Au nanoparticles in the film. The penetration of the Au particles from the surface into the nylon 11 matrix film leads to a relative decrease of particle concentration per unit volume. As a result, the local volume fraction of the Au particles in the film decreases gradually with heat treatment, resulting in both the shift of the absorption peak position toward shorter wavelength and the decrease of the absorbance, as predicted by the MG theory. This volume fraction effect is explained by the dipole interaction between dispersed particles. When the volume fraction of the Au particles is high, *i.e.* interparticle distance is small, dipoles induced in the particles by the external electromagnetic field of incident radiation affects their neighboring particles. The dipole interaction is reduced by dispersion of the Au particles from the surface into the bulk layer of the nylon 11, since distances between Au particles increases. The plasmon peak intensity of metal particles is damped by the superposition of the peak corresponding to the absorption threshold of the interband transition which occurs at *ca.* 500 nm for gold.[15] This effect may also be responsible for the decrease of the absorbance.

In order to quantitatively understand the experimental results, it may be necessary to take into account the concentration gradient for the depth distribution of the Au nanoparticles, which are not easily treated theoretically. Further detailed experimental and theoretical studies are required to fully understand the changes in the absorption spectra which depend significantly on temperature. Further information in particular, could be obtained from microscopic characterization with respect to the depth distribution of the particles *via* cross-sectional transmission electron microscopy observations.

Conclusion

By means of *in situ* transmission measurements, temperature-dependent changes in the optical absorption spectra, showing a close relationship to the film microstructure, have been successfully measured for a dispersion of Au nanoparticles during heat treatment. It was found that the peak wavelength of the plasmon band shifted toward shorter wavelengths in the temperature range near the glass transition temperature of the nylon 11 matrix film. This shift of the maximum absorption is mainly caused by the decrease of the Au volume fraction owing to the penetration of the Au particles from the surface into the nylon 11 matrix. The shift of the plasmon band also depends on the heating rate, *i.e.* the temperature, at which the peak wavelength shifted to longer wavelength occurred, shifted to higher temperature with increasing heating rate. From these results, it is very likely that thermal behaviour of the nylon 11 matrix film plays an important rule for the dispersion of the Au particles into the matrix layer. This method is suitable for the elucidation of the dispersion mechanisms of metal nanoparticles as a consequence of thermal relaxation of the polymer matrix.

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