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# Preparation and characterization of copper(I) oxide nanoparticles dispersed in a polymer matrix

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Nano-sized copper(I) oxide particles dispersed in nylon 11 thin films have been prepared by a thermal relaxation technique. The obtained composite films were characterized by XRD, HRTEM, XPS, AES and UV–VIS absorption spectroscopy. Upon heat treatment under air, metallic copper initially deposited on the nylon 11 surface penetrates into the bulk phase of the nylon 11 as $Cu_2O$ particles. The mean size of the $Cu_2O$ particles increased from 3.2 to 6.3 nm in diameter upon increasing the amount of Cu deposition. UV–VIS spectroscopy revealed that the absorption increased from as low as 600 nm with increasing the size and the concentration of the dispersed $Cu_2O$ particles.

## Introduction

In recent years, nano-sized semiconductor and metal particles embedded in solid dielectric matrices have attracted increasing interest because of novel applications as photonics and electronics devices based on quantum size effects and their high third-order non-linear susceptibility.[1–3] Among these composites, polymer films containing such nano-sized particles form one type of material that has been widely studied. For the preparation of these polymer composite films, various kinds of fabrication methods have been developed: plasma polymerization of monomers with simultaneous or alternating metal evaporation[4–9] and spinning or drying of solutions including polymers and metal ions or metal colloids.[10–13] Using these methods, composites prepared from mixed solutions contain several kinds of by-product, such as ions. On the other hand, the vacuum evaporation technique is known to produce highly pure composite materials because the film formation process is usually carried out under relatively high vacuum.

We have previously developed and reported a novel method to prepare composite films by a thermal relaxation technique,[14,15] in which nano-sized metal particles dispersed uniformly in a polymer matrix. This technique relies on consecutive evaporation of a polymer and a metal, to form a metal/polymer laminated film, following heat treatment at a temperature above the glass transition temperature of the polymer matrix. Our previous studies suggested that vacuum deposited polyamide films with a low molecular weight are effective for stabilizing dispersed metal particles owing to the strong interaction between the metal particles and the polyamide molecules. There are some advantages in this method. The volume fraction of the metal particles can be easily controlled and raised by several percent, and the size of the particles, with relatively narrow size distribution, can be manipulated by controlling the amount of metal deposition.[16] This technique has become available for other systems, such as size-controlled nano-sized particles dispersed in polymer thin films.[17]

We have also reported previously that, by means of the thermal relaxation technique, Cu metal deposited on a nylon 11 film could be dispersed as copper(I) oxide, $Cu_2O$, particles.[14] Copper(I) oxide is known to exhibit characteristic optical properties at relatively low temperature due to an exciton absorption[18] and its interaction with various phonon modes.[19,20] Although the absorption characteristics of the various exciton series for copper(I) oxide have been studied by many researchers,[21–25] the samples studied have been limited to bulk or platelet samples. To our knowledge, there are few studies related to the preparation of copper(I) oxide particles.[26,27] Therefore, it is of fundamental interest to prepare nano-sized copper(I) oxide particles and to characterize their optical properties as a function of particle size.

Here, we report on the preparation and characterization of nano-sized $Cu_2O$ particles dispersed in nylon 11 thin films by using the thermal relaxation technique. For the characterization of the obtained composite films, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and high-resolution transmission electron microscopy (HRTEM) were used. Optical properties of the composite films measured by UV–VIS absorption spectroscopy are also discussed.

## Experimental

Nylon 11 thin film with a thickness of 100 nm was prepared by the vacuum vapour deposition technique using a molybdenum boat at a pressure of $<5.0\times10^{-5}$ Torr. Cu metal (99.99%) was then vapour deposited from a tungsten filament on the nylon 11 film at a pressure of $<2.0\times10^{-5}$ Torr with a deposition rate of 0.2 $\text{Å}\ s^{-1}$ as monitored by a quartz-crystal microbalance. The films were deposited on a glass substrate for XRD and UV–VIS spectroscopy, Si wafer for XPS and AES, and thin carbon films supported on copper mesh grids for TEM observation. The Cu/nylon 11 laminated films were heat-treated at 100 °C for 30 min in $N_2$ and in air.

X-Ray diffraction studies of the films before and after heat treatment were carried out on a Rigaku RINT-2100 diffractometer with thin film attachment, using Cu-K$\alpha$ radiation (40 kV, 40 mA) with measurements made at an X-ray incidence angle of 1°. The diffraction patterns were obtained by step scanning at intervals of 0.1° with a fixed time of 15 s, and the crystallite sizes of Cu and $Cu_2O$ were calculated from the (111) diffraction line in accordance with Scherrer's formula. In order to calculate crystallite size accurately, the X-ray intensities were accumulated by repeating the measurement 10 times. The oxidation state of Cu in the films was investigated by XPS and AES with a X-ray photoelectron spectrometer, ESCA 750 (Shimadzu), using an Mg-K$\alpha$ X-ray source. Optical absorption spectra were measured with a UVDEC 660 spectrophotometer (Japan Spectroscopic Co. Ltd) over the wavelength range 300–850 nm. HRTEM observations were made on a

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JEM-2010 (JEOL) transmission electron microscope operated at 200 kV which provided a 0.19 nm point resolution.

## Results and Discussion

For the as-deposited film, a Cu thin film with a dark brown metallic luster was formed on the surface of the nylon 11 film. Upon heat treatment at 110 °C for 30 min under air, the film changed to transparent yellow. Fig. 1 shows optical absorption spectra of Cu/nylon 11 films before and after heat treatment under $N_2$ and air, and a Cu thin film deposited on a glass substrate prepared under the same conditions. The spectrum of the as-deposited film is very similar to that of the Cu thin film on glass, indicating that a metallic Cu thin film is initially formed on the nylon 11 surface, producing a Cu/nylon 11 laminated structure. The spectrum of the sample heated under $N_2$ was also found to remain unchanged. However, the spectrum of the sample heated under air changed drastically. These results indicate that the colour change of the Cu layer upon heat treatment may originate from the oxidation of Cu metal by air. This effect is confirmed by the XRD patterns as shown in Fig. 2. Owing to the very low amounts of Cu in the nylon 11 film, only the sample with the highest amount of Cu deposited was subjected to a series of XRD measurements. It can be seen in Fig. 2 that $Cu_2O$ is formed in the sample heated in air. For the as-deposited film and that heated in $N_2$, only the peaks originating from metallic Cu are observed, except for narrowing of the width of the Cu (111) diffraction line for the sample heated in $N_2$. This narrowing of the line width can be attributed to the growth of Cu crystallites within the deposited Cu film upon thermal annealing.

The oxidation state of Cu before and after heating in air was characterized by XPS and AES measurements. Although there was no significant shift of the Cu 2p peak upon heating in air, an indication of the oxidation state of Cu can be observed from the Cu LMM Auger peak, which occurs at a kinetic energy of 918.8 eV for bulk metallic Cu.[28] The corresponding Cu LMM Auger electron spectra are shown in Fig. 3. Whereas the kinetic energy of Cu for the as-deposited film was comparable to that of metallic copper, a shift in kinetic energy toward the lower energy side was observed for the sample heated in air. This peak was observed at 916.6 eV, which is very close to values observed for powder standards of copper(I) oxide measured in the same XPS apparatus, and that reported in the literature.[28] This result supports the XRD pattern as shown in Fig. 2, in which the $Cu_2O$ was formed by heating in air.

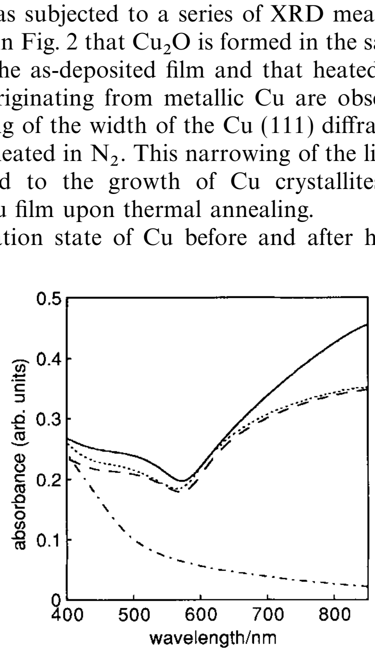

**Fig. 1** Optical absorption spectra of the Cu thin film on a glass substrate and Cu/nylon 11 laminated films heat-treated at 110 °C for 30 min. (—) Cu deposited on glass, (– – –) as-deposited film, (·····) heat-treated in $N_2$, (–·–·–) heat-treated in air. Amount of Cu deposition: $5.72 \times 10^{16}$ atom cm$^{-2}$.

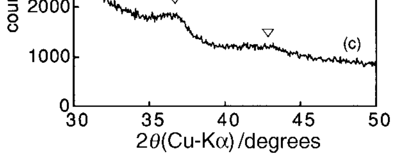

**Fig. 2** X-Ray diffraction patterns of the Cu/nylon 11 films heat-treated at 110 °C for 30 min. (a) As-deposited film, (b) heat-treated in $N_2$, (c) heat-treated in air. Assignment: ○, $Cu^0$, ▽; $Cu_2O$. Amount of Cu deposition: $5.72 \times 10^{16}$ atom cm$^{-2}$.

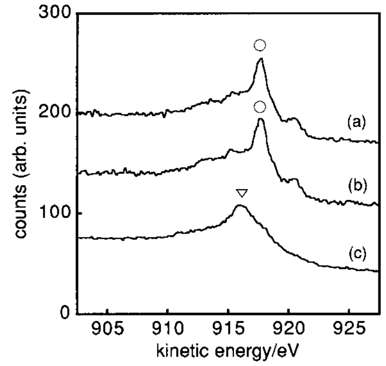

**Fig. 3** Cu LMM Auger electron spectra of Cu/nylon 11 films heat-treated at 110 °C for 30 min. (a) As-deposited film, (b) heat-treated in $N_2$, (c) heat-treated in air. Assignment: ○, $Cu^0$, ▽; $Cu^I$. Amount of Cu deposition: $5.72 \times 10^{16}$ atom cm$^{-2}$.

Fig. 4 shows HRTEM images of samples heated at 110 °C for 30 min in air. The $Cu_2O$ particles were dispersed homogeneously in the plane of the film, and lattice fringes were clearly observed. It was found that these $Cu_2O$ particles were mostly single crystals. Selected area electron diffraction patterns of these samples showed typical Debye–Scherrer rings assigned to the cubic $Cu_2O$ crystal, with lattice parameters corresponding to those of bulk $Cu_2O$. The mean size of the dispersed $Cu_2O$ particles increased with increasing the amount of Cu deposition. This tendency to increase in particle size is similar to that observed in the case of gold.[16] The characteristics of $Cu_2O$ particles are given in Table 1.

For the thermal relaxation technique, the following mechanism is proposed:[14,29] during the vapour deposition process the nylon 11 vapour solidifies to form a thin film on the substrate, with a thermodynamically metastable structure. Upon heat treatment, the metals, initially deposited on these metastably fixed polymer surfaces, penetrated into the bulk phase of the polymer layer using a relaxation of the polymer molecules into a much more stable structure as the driving force. Using this process, various kinds of metal particles such as Au, Ag and Pd can be readily produced. Masui *et al.*[30] have reported that, by using the thermal relaxation technique, cerium metal deposited on nylon 11 film dispersed as well characterized cerium(IV) oxide ultrafine particles. In their study, the Ce/nylon 11 laminated films were heated under vacuum. They suggested that the initially produced cerium metal particles were partially oxidized by the oxygen or water residue in the vacuum chamber and completely oxidized by air when the samples were taken out from the chamber, which is due to the nature of rare earth metals to be oxidized easily. In the case of Cu studied by us, however, although the samples were taken from the vacuum chamber and exposed to air after sample preparation, the Cu LMM Auger peaks for the as-deposited film and $N_2$-treated film were essentially assigned to metallic copper (Fig. 3). It was found that the upper Cu layer did not disperse as Cu

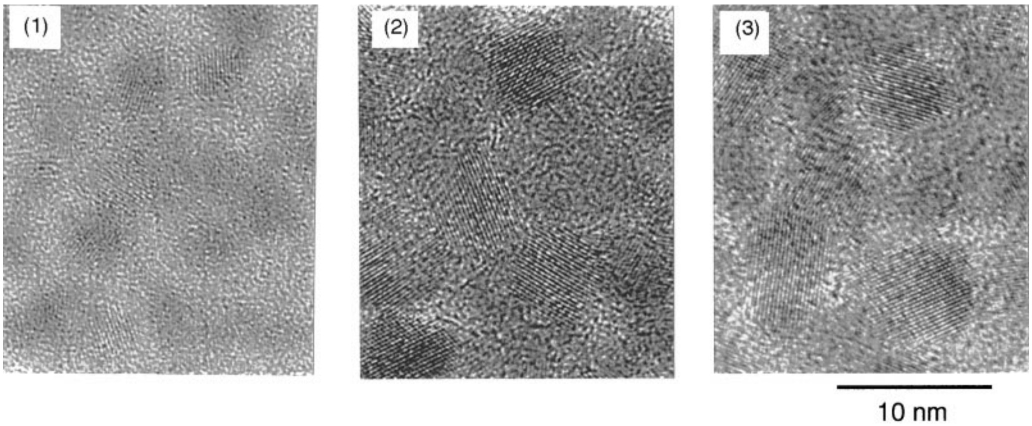

**Fig. 4** High-resolution TEM images of dispersed $Cu_2O$ particles in the nylon 11 film heat-treated at 110 °C for 30 min. Amount of Cu deposition: (1) 1.72, (2) 3.43, (3) $5.72 \times 10^{16}$ atom $cm^{-2}$.

**Table 1** Summary of the effect of heat treatment atmosphere and characteristics of $Cu_2O$ particles in the composite films containing various amounts of Cu

| specimen | amount of deposited $Cu/10^{16}$ atom $cm^{-2}$ | heat treatment atmosphere | crystallite size/nm | mean particle size/nm | standard deviation/nm | colour of the films |
|---|---|---|---|---|---|---|
| 1 | 5.72 | No | 4.9(Cu) | | | dark brown |
| 2 | 5.72 | $N_2$ | 12.2(Cu) | | | dark brown |
| 3 | 1.72 | air | —[a] | 3.7 | 0.64 | yellow |
| 4 | 3.43 | air | —[a] | 5.2 | 0.78 | yellow |
| 5 | 5.72 | air | 5.6($Cu_2O$) | 6.4 | 1.02 | yellow |

[a] No distinct diffraction peak was observed due to the low amounts of Cu.

metallic particles when the Cu/nylon 11 laminated samples were heated under an inert gas like $N_2$, but only the growth of Cu crystallites was observed (Fig. 2). We have measured the depth profiles of Cu in the film by XPS attached with an argon ion etching apparatus: the photoelectron intensity from Cu 2p electrons for an $N_2$-treated sample was localized at the surface, showing depth profiles similar to that for an as-deposited film. On the other hand, the photoelectrons of Cu could be detected throughout the entire film for an air-treated sample, *i.e.*, dispersion of Cu into the nylon 11 layer could occur when the film was heated under air, indicating that oxidation plays an important role in the formation and dispersion of $Cu_2O$ particles. In addition, when the amount of Cu deposited is very small (corresponding to three monolayers of Cu for a continuous film), no photoelectron signal for C, N or O in the nylon 11 underlayer was observed in the XPS spectrum for the as-deposited film. This indicates that the Cu atoms grow as continuous thin films (layer growth) and not as islands, which may be due to the strong interaction between evaporated Cu atoms and the nylon 11 substrate.[31]

From these results, one possible dispersion mechanism is proposed as follows: during the heat treatment of the Cu/nylon 11 laminated film under air, Cu—Cu metallic bonds can be broken by reaction with oxygen, resulting in the formation of $Cu_2O$, and at the same time the metal layer is divided into nano-sized $Cu_2O$ particles through the effect of thermally induced structural relaxation of the nylon 11 matrix. Then the $Cu_2O$ particles can penetrate into the nylon 11 layer, where the $Cu_2O$ particles have sufficient mobility to disperse from the surface into the bulk phase of the polymer because the nylon 11 matrix can behave as a viscous fluid at temperatures above its glass transition temperature.

For the case of the sample heated under $N_2$, however, although the nylon 11 matrix relaxed during the heat treatment, the Cu film was not finely divided and remained as a thin film. For the case of the gold/nylon 11 system previously studied, small Au islands were initially formed on the nylon 11 surface, and the island particles could be dispersed into the nylon 11 layer even when the samples were heated under an inert atmosphere. The difference observed between the Cu/nylon 11 and Au/nylon 11 system may be caused by the different types of the initial growth mode, *i.e.*, layer growth for Cu and island growth for Au on the nylon 11 surface. The layer growth mode implies a large interaction energy between atoms of the deposit and atoms of the substrate (adhesion).[31] This strong interaction may be the reason why the Cu thin film did not disperse as Cu metallic particles. Further studies are required to fully account for the cause of this phenomenon. Nevertheless, the present results demonstrate the applicability of the thermal relaxation technique to the preparation of other copper compound particles by treatment under a reactive gas atmosphere. For example, we have succeeded in the preparation of CuS particles dispersed in nylon 11 films by heat treatment under $H_2S$ gas flow, and the results will be reported elsewhere.

Fig. 5 shows optical absorption spectra of $Cu_2O$ particles dispersed in the nylon 11 film after the heat treatment, using the nylon 11 film without Cu deposition and heat-treated under same condition as a reference. The spectra were nor-

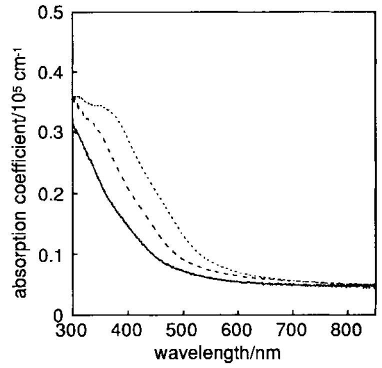

**Fig. 5** Optical absorption spectra of $Cu_2O$ particles dispersed in the nylon 11 film. The spectra were normalized to the unit amount of Cu deposition. Mean particle size: (—) 3.2, (– – –) 5.4, (·····) 6.7 nm.

malized to the unit amount of Cu deposition (weight film thickness) and at 850 nm. A broad shoulder was observed at around 350 nm for the largest particles, but the absorption for smaller particle sizes monotonically increased at as low as 600 nm. In addition, the absorption edge evaluated from the spectrum for $Cu_2O$ particles was not clear due to long tails in the 500–600 nm region. Since electronic transitions of $Cu_2O$ from valence bands of copper d orbitals to the s-like conduction bands are parity forbidden, $Cu_2O$ is thus classified as a direct forbidden semiconductor material.[32] This direct band gap of bulk $Cu_2O$ is known to be 2.17 eV at room temperature,[33] and thus bulk $Cu_2O$ crystals are strongly absorbing in the visible region as low as 600 nm. In Fig. 5, the spectra were red-shifted and the absorption tail increased with increasing the particle size, which is probably due to light scattering by agglomerated particles, because the particle size and concentration in the sample with the higher amount of Cu deposition should be much larger than that in the sample with lower amount of Cu deposition (Fig. 4). We tried to estimate the values of optical band gap energy from absorption data by using the $(\alpha h\nu)^{2/3}$ *vs.* $h\nu$ relation which is applied to the direct forbidden transition system.[34] However, we could not obtain the values, since the absorption data did not obey the above simple relation. Generally, optical properties of nano-sized particles are very different from those of the bulk material. Therefore, it is not evident that the absorption data of nano-sized particles obey the above relation. Since a quantitative discussion related to the size-dependent changes in the absorption spectra is difficult at present because of the difficulty in obtaining the optical band gap energy, further detailed experimental and theoretical studies are required. In particular, further information related to the optical properties of the $Cu_2O$ particles may be obtained from the measurement of the exciton absorption characteristics at low temperatures, which are now under investigation.

## Conclusion

Using a thermal relaxation technique, nylon 11 thin films containing nano-sized crystalline $Cu_2O$ particles were reproducibly prepared. XRD and AES studies revealed that the $Cu_2O$ particles were formed only when the Cu/nylon 11 laminated film was heat-treated under air, suggesting that during heat treatment the Cu thin film deposited on the nylon 11 surface was oxidized to form $Cu_2O$ and finely divided into nano-sized particles with the effect of the molecular rearrangement caused by the structural relaxation of the nylon 11 matrix. The dispersed $Cu_2O$ particles were relatively homogeneous in size, and the mean size of the particles increased simultaneously with increasing amount of initial Cu deposition. In the optical absorption spectra, the absorption increased with increasing amount of Cu deposition, due to the increase in the particle size and the concentration of the $Cu_2O$ particles. This technique can also be applied for the preparation of other kinds of copper compound particles, *e.g.*, CuS particles.

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