Surface Modification-Based Synthesis and Microstructural Tuning of Nanocomposite Layers: Monodispersed Copper Nanoparticles in Polyimide Resins

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Research into the preparation of nanocomposites containing metal and/or semiconductor nanoparticles dispersed in solid state dielectric materials has been triggered by the technologically important applications of these nanocomposites in optics, sensors, and nanoelectronics. In particular, such composite materials offer exciting possibilities for potential thin film device applications with novel functions arising from size-quantization effects.[1] The major limitation of these nanocomposite films is the difficulty in controlling their microstructure during synthetic processes. Relevant microstructural properties include the size, size distribution, and interparticle spacing of the dispersed nanoparticles, and thickness of the composites, which essentially determine the properties and performance of the nanocomposites. A technique that allows precise control over film microstructure is, therefore, indispensable for the preparation of composite thin films with desired properties.

Metal nanoparticles dispersed in polymeric matrixes have recently been the subject of intense study aiming to develop nanocomposite films.[2−8] The potential advantage of such metal/polymer systems is that the size and distribution of dispersed metal nanoparticles can be readily controlled, based on the thermoplastic properties of the host polymers.[9,10] Polyimides are one potential class of materials for this application. Polyimide is known to be a high-performance organic material that has been widely used in microelectronics device fabrication and packaging applications.[11−15] In particular, the metallization of polyimide has been the subject of intense study aiming to develop metallic circuits on the polyimide substrate.[16−19] Important characteristics of polyimide that make it attractive for microelectronics applications are its good thermal stability, chemical resistance, ease of planarization and patterning by lithographic techniques, and low dielectric constant. The development of synthetic methods for preparing polyimide-based nanocomposite films containing inorganic nanoparticles could generate a class of novel and versatile hybrid nanomaterials. However, despite the numerous studies on physical and chemical means of preparing metal/polymer nanocomposites and nanofabrication using these materials,[2−8] as of yet, there have been few studies on the use of polyimides as host materials. Conventional ion implantation applied to polyimide substrates causes significant surface damage due to irradiation-induced carbonization.[20,21] A simple process for the preparation of polyimide-based nanocomposites remains to be developed. The present report centers on a synthesis route for nanocomposites containing monodispersed copper nanoparticles. The technique involves a simple alkali treatment-based surface modification of the polyimide film and an ion exchange reaction, enabling fine-tuning of product microstructure. The polyimide resin surface is chemically modified using potassium hydroxide (KOH) to form carboxylic acid groups in the modified layer through imide ring-cleavage reactions. The subsequent copper ion complexation achieved by ion exchange with the bound potassium ions is followed by reduction in a hydrogen atmosphere, yielding metallic nanoparticles (Scheme 1). The present method exploits the homogeneous distribution of cation exchange groups in the modified layer and the fact that hydrogen-induced reduction of copper ions is accompanied by a condensation reaction that forms heterocyclic imide rings (re-imidization). The primary goal of the study is to determine how processing conditions influ-

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(1) Klabunde, K. J. *Nanoscale Materials in Chemistry*; John Wiley & Sons, Inc.: New York, 2001.
(2) Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P. *Nature* **1994**, *370*, 354.
(3) Dabbousi, B. O.; Bawendi, M. G.; Onitsuka, O.; Rubner, M. F. *Appl. Phys. Lett.* **1995**, *66*, 1316.
(4) Lamber, R.; Wetjen, S.; Schulz-Ekloff, G.; Baalmann, A. *J. Phys. Chem.* **1995**, *99*, 13834.
(5) Beecroft, L. L.; Ober, C. K. *Chem. Mater.* **1997**, *9*, 1302.
(6) Akamatsu, K.; Tsuboi, N.; Hatakenaka, Y.; Deki, S. *J. Phys. Chem. B* **2000**, *104*, 10168.
(7) Breimer, M. A.; Yevgeny, G.; Sy, S.; Sadik O. A. *Nano Lett.* **2001**, *1*, 305.
(8) Wang, T. C.; Rubner, M. F.; Cohen, R. E. *Langmuir* **2002**, *18*, 3370.
(9) Shull, K. R.; Kellock, A. J. *J. Polym Sci. B: Polym. Phys.* **1995**, *33*, 1417.
(10) Cole, D. H.; Shull, K. R.; Baldo, P.; Rehn, L. *Macromolecules* **1999**, *32*, 771.
(11) Bhansali, S.; Sood, D. K. *Sensors Actuators A* **1996**, *52*, 126.
(12) Faupel, F.; Willecke, R.; Thran, A. *Mater. Sci. Eng. R* **1998**, *22*, 1.
(13) Kiene, M.; Strunskus, T.; Peter, R.; Faupel, F. *Adv. Mater.* **1998**, *10*, 16.
(14) Inagaki, N.; Tasaka, S.; Narushima, K.; Mochizuki, K. *Macromolecules* **1999**, *32*, 8566.
(15) Park, I. S.; Ahn, E. C.; Yu, J.; Lee, H. Y. *Mater. Sci. Eng. A* **2000**, *282*, 137.
(16) Kiang, M. H.; Lieberman, M. A.; Cheung, N. W.; Qian, X. Y. *Appl. Phys. Lett.* **1992**, *60*, 2767.
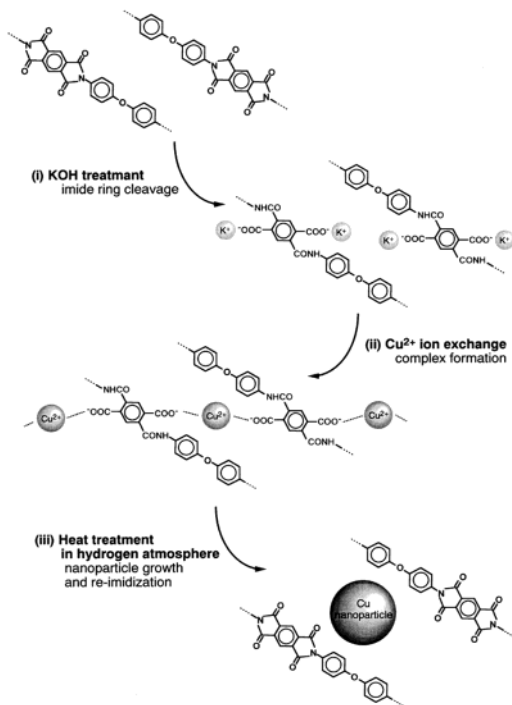(17) Murphy, M. M.; Van herle, J.; McEvoy, A. J.; Thampi, K. R. *J. Electrochem. Soc.* **1994**, *141*, L94.
(18) Shafeev, G. A.; Themlin, J. M.; Bellard, L.; Marine, W.; Cros, A. *J. Vac. Sci. Technol. A* **1996**, *14*, 319.
(19) Kordas, K.; Nanai, L.; Galbacs, G.; Uusimaki, A.; Leppavuori, S.; Bali, K. *Appl. Surf. Sci.* **2000**, *158*, 127.
(20) Das, J. H.; Morris, J. E. *J. Appl. Phys.* **1989**, *66*, 5816.
(21) Kobayashi, T.; Iwata, T.; Doi, Y.; Iwaki, M. *Nucl. Instr. Methods B* **2001**, *175*, 548.
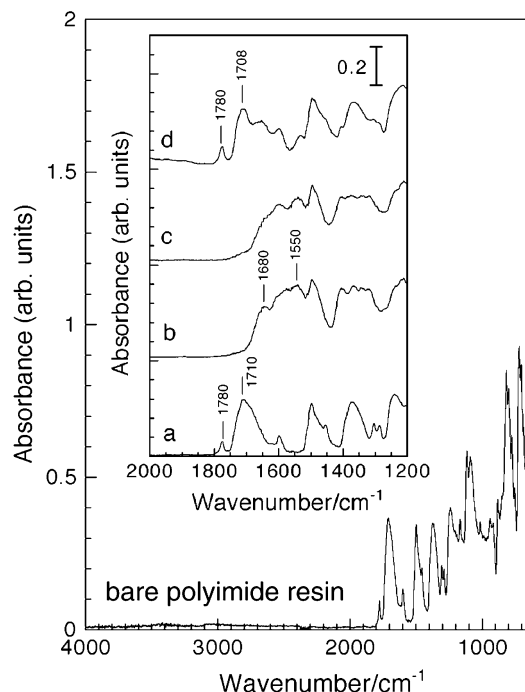
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Scheme 1. Schematic Diagram of the Present Synthesis Process for Composite Polyimide Layers Containing Monodispersed Copper Nanoparticles

Figure 1. ATR-FTIR spectrum of bare polyimide resin (Kapton 200-H). Inset: ATR-FTIR spectra in the 1200–2000-cm^{-1} region of polyimide resin before (a) and after KOH treatment (b), and after subsequent ion exchange (c) followed by heat treatment in a hydrogen atmosphere at 250 °C for 30 min (d). Bars indicate characteristic peaks attributable to carbonyl and amide bond vibrations. See text for details.
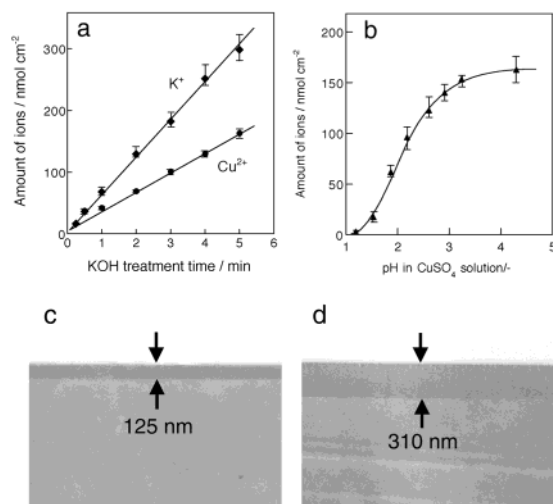
ence the composites' microstructural properties, such as thickness of composite layer, nanoparticle size, and moleculer structure of the matrix.

In a typical experiment, pyromellitic dianhydride-oxydianiline (PMDA-ODA) type polyimide films (Kapton 200-H, Toray-DuPont) were first immersed in aqueous KOH for appropriate reaction times and then washed with distilled water (step (i) in Scheme 1). Subsequently, they were immersed in aqueous copper(II) sulfate ($CuSO_4$) (50 mM) to exchange potassium ions with copper ions, washed with copious amounts of water, and then dried (step (ii)). The resultant films were annealed at various temperatures in a furnace under hydrogen gas flow for 30 min (step (iii)). The adsorption of K^+ and Cu^{2+} ions was confirmed by inductively coupled plasma (ICP) atomic emission spectroscopic measurements (SPS7700, Seiko Instruments). Structural change in the polyimide film upon each processing step was studied with Fourier transform infrared (FT-IR) spectroscopy (FT/IR 615R, Japan Spectroscopic Co.) employing the attenuated total reflection (ATR) configuration.

Figure 1 shows ATR FT-IR spectra of bare polyimide and surface-modified films that were treated by KOH and subsequent ion exchange reaction followed by heat treatment at 250 °C for 30 min. The spectrum of bare polyimide is well-characterized by a band attributed to the characteristic vibration mode for both the backbone PMDA and ODA part of the polymer. We concentrate our attention on the carbonyl stretching band in an imide ring vibration because our KOH treatment gives rise to the cleavage of imide rings,[22] with associated bands at 1780 and 1710 cm^{-1} arising from symmetric and antisymmetric carbonyl stretching vibrations, re-

spectively (inset, Figure 1a).[23] The KOH treatment results in a significant change in the IR spectra as seen in Figure 1b. The band assigned to the carbonyl stretching of imide rings disappears completely, while new bands are observed at 1500–1700 cm^{-1}. These peaks can arise from the superposition of the ionized carboxyl vibration mode of carboxyl groups complexed with K^+ ions (1500–1600 cm^{-1}), and amide I (carbonyl stretching, 1680 cm^{-1}) and amide II (N–H bending, 1550 cm^{-1}) modes of the amide bond.[6,24] Formation of carboxyl groups was also confirmed by X-ray photoelectron spectroscopic measurements (results not shown). These results demonstrate that the present KOH treatment yields poly(amic acid) through a hydration reaction,[25] which is usually utilized as a precursor for polyimide resin. After ion exchange, although the spectrum is mostly similar in form (Figure 1c) as compared to that of the KOH-treated film (Figure 1b), a slight decrease in intensity at 1680 cm^{-1} and complex features around 1500–1600 cm^{-1} suggest that a number of coordination states coexist within the Cu^{2+} complexes.

(22) Seita, M.; Nawafune, H.; Kanai, T.; Nishioka, T.; Mizumoto, S. *Electron. Circuits World Conv.* **1999**, *8*, 1.

(23) Strunskus, T.; Grunze, M.; Kochendoerfer, G.; Wöll, Ch. *Langmuir* **1996**, *12*, 2712.

(24) Skrovanek, D. J.; Howe, S. E.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1986**, *19*, 699.

(25) Actual number density of cleaved imide groups and unreacted imide groups after KOH treatment should be determined to precisely calculate chemical conversion of imide groups since the volume of reacted film can be changed after KOH treatment due to hydrolysis and insertion of K^+ ions. Adsorption of water molecules may result in swelling of the modified film and should be taken into account. We believe, at present, most of the imide rings (95% or higher) can be converted into poly(amic acid) under the present experimental conditions since the vibration band of imide rings is not observed after KOH treatment in the IR spectra shown in Figure 1. More data are required to evaluate the conversion efficiency and this is now in progress.

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Figure 2. (a) Plots of the amount of adsorbed K⁺ ions in polyimide resin after KOH treatment (1 M, 50 °C) and of Cu²⁺ ions after subsequent ion exchange using CuSO₄ solution (50 mM) as a function of immersion time. (b) Effect of pH of the CuSO₄ solution used during the ion exchange reaction on the amount of adsorbed Cu²⁺ ions. (c, d) Cross-sectional TEM images of polyimide resins after KOH treatment (1 M) at 50 °C for 2 and 5 min, respectively.

The present alkali treatment-promoted reaction allows precise control of the modified thickness of the polyimide film and the amount of adsorbed ions. In Figure 2a, insertion of the polyimide film into a 1 M KOH solution at 50 °C is followed by the linear increase in the amount of potassium ions with treatment time.[26] This linear dependence is caused by the conformal diffusion of the KOH solution into the film, increasing the thickness of the KOH-modified section of the polyimide film linearly with immersion time. This is confirmed by cross-sectional transmission electron microscopy (TEM) images of polyimide films immersed in KOH at 50 °C for 2 min (Figure 2c) and 5 min (Figure 2d).[27] The slightly dark region corresponds to the modified layer. The images reveal a thin modified section for 2 min of KOH treatment and a thicker section for 5 min of KOH treatment; the thickness is measured to be proportional to the treatment time. The extent of surface modification also depends on the KOH concentration and temperature: higher KOH concentrations and elevated temperatures promote the surface modification. After ion exchange, the same linear dependence of adsorbed Cu²⁺ ions with respect to initial KOH treatment time are observed (Figure 2a), and no potassium ions can be detected. Most importantly, at a fixed KOH (1 M) immersion time, the amount of adsorbed Cu²⁺ ions is half that of K⁺ ions adsorbed initially, indicating that the incorporation of copper ions into polyimide film can be achieved through exchange of monovalent potassium ions with divalent copper ions in a 2:1 ratio, where the two cation species are both bound to carboxylic anions formed by cleavage of imide rings. The depth profile of Cu in the modified layer after ion exchange reveals uniform distribution of Cu in the film (Supporting

Information, Figure S1), supporting conformal diffusion of KOH and thus uniform reaction of alkali-induced cleavage of the imide rings during initial KOH treatment. Typically, the amount of adsorbed Cu²⁺ ions reaches ca. 160 nmol cm⁻² for the film initially modified by KOH solution (1 M) for 5 min.

Copper ion loading can also be controlled by changing the pH of the CuSO₄ solution (Figure 2b). A decrease in pH during the ion exchange reaction (adjusted using dilute H₂SO₄) results in a significant decrease in Cu²⁺ adsorption, suggesting that pH can be varied to control the amount of copper ions adsorbed in a modified layer of a given thickness determined by initial KOH treatment. Although the maximum amount of adsorbed Cu²⁺ ions is essentially dependent on the number of carboxyl groups formed, our results demonstrate that the Cu²⁺ ion loading in the film can be systematically controlled by varying experimental conditions, that is, temperature, concentration, and pH, during surface modification and ion exchange. These play an important role in determining the subsequent formation and microstructure of copper/polyimide nanocomposites.

Heat treatment of these ion-exchanged films in a hydrogen atmosphere yielded copper nanoparticles, which caused an absorption peak to emerge at ca. 580 nm in UV–vis absorption spectra due to surface plasmon resonance absorption of copper particles.[28] The effect of heat treatment in a H₂ atmosphere on a composite film microstructure was characterized by cross-sectional TEM observation. Figure 3 depicts typical cross-sectional TEM images of copper-adsorbed modified polyimide films after heat treatment in a H₂ atmosphere and corresponding size histograms of the dispersed nanoparticles. In Figure 3a, heat treatment at 250 °C yields a homogeneous dispersion of copper nanoparticles within the modified layer of uniform thickness. Electron diffraction patterns of these nanoparticles were indexed as consisting entirely of metallic Cu with a fcc structure. This thermally induced and hydrogen-induced formation is accelerated with increasing temperature; that is, heat treatment at higher temperature (350 °C) results in the increase of the nanoparticle size (Figure 3b). The mean particle size ranges from 3.5 nm for the film heat-treated at 250 °C to 8.0 nm for that heat-treated at 350 °C; both values show a standard deviation to within 10% of the mean particle size. The mean size could be reproducibly controlled in the 2–10-nm range with a narrow size distribution by heat treatment from 200 to 380 °C. No particles or clusters were detected inside the modified layer upon heat treatment below 200 °C. Assuming that the density of Cu nanoparticles is identical to that of the bulk value, the volume fraction of Cu nanoparticles in the composite layer could be calculated from Cu loading and thickness of the composite, the value of which was estimated to be 3.7% for both films shown in Figure 3. The volume fraction may be controlled by varying the initial Cu²⁺ ion loading into the modified layer of a given thickness through pH-dependent ion exchange reaction (Figure 2b). Heat treatment also causes structural changes within the modified polyimide layers. As shown in Figure 1d, the FTIR spectrum of

(26) ICP measurements were performed for dilute HNO₃ solution after immersion of surface-modified and ion-exchanged polyimide films.

(27) The samples for TEM observation were obtained by sectioning the films in the direction perpendicular to the film surface with ultramicrotome (Leica Ultrcut UCT) using a diamond knife. Thickness of the thin sections was ca. 90 nm.

(28) Doremus, R.; Kao, S.; Garcia, R. *Appl. Opt.* **1992**, *31*, 5773.
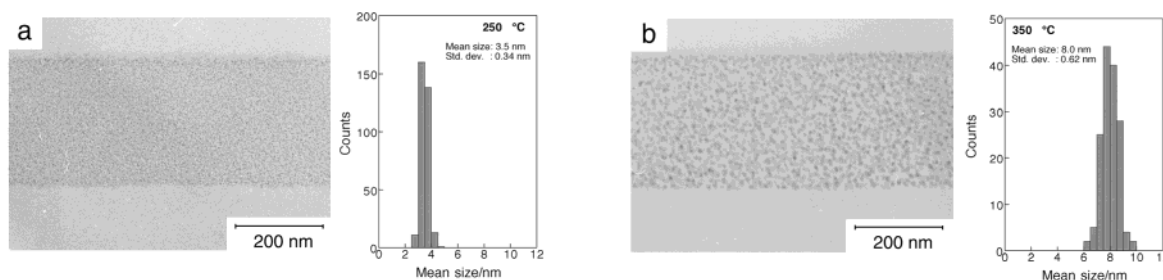
Figure 3. Cross-sectional TEM images of polyimide films containing Cu nanoparticles and the corresponding size histograms of Cu nanoparticles. Samples were prepared by heat treatment of Cu^{2+}-adsorbed resins at 250 °C (a) and 350 °C (b) for 30 min in a hydrogen atmosphere.

the film obtained by heat treatment of the ion-exchanged sample in a H_2 atmosphere is very similar to that of a bare polyimide film (Figure 1a), indicating complete re-imidization of the modified layer due to elimination of water molecules from carboxyl groups and amide bonds to form heterocyclic imide rings. Thus, the present composites are defined as copper/polyimide nanocomposites, with monodispersed copper nanoparticles homogeneously dispersed in high-performance polyimide matrixes.

The formation of copper nanoparticles in polyimide films was previously reported in the case of vacuum evaporation of copper onto a fully cured polyimide substrate at an elevated temperature and very low deposition rate.[12,13] In this case, the growth of copper nanoparticles within the polyimide film indicates the mobility of copper atoms and/or clusters, high enough to form nanoparticles in the polyimide under high temperature. In the present study, however, when the film obtained after heat treatment at 250 °C was again treated at 350 °C, no particle growth was observed. This observation indicates that the particle size can be determined during initial reduction stages, at which diffusion of copper ions may play a more important role in nanoparticle growth. Although diffusion of copper carboxylate was observed at the interface between the poly(amic acid) precursor and copper substrate,[29,30] a detailed experimental study is necessary to elucidate the formation mechanism of monodispersed copper nanoparticles in the film.

The additional advantage of the uniform incorporation of copper nanoparticles into polyimide film presented here is that they can initiate subsequent electroless copper plating. In this process, the copper nanoparticles can act as deposition seeds as well as adhesion promoters through a nanoscale mechanical interlocking effect, which may be suitable for further miniaturization of electronics devices to achieve large-scale integration. A study is currently underway and results will be published in a forthcoming article.

In conclusion, the present study has demonstrated a new methodology for preparing copper nanoparticle-based polyimide nanocomposites where the film microstructure, for example, particle size, volume fraction, and film thickness, is well-defined and can be systematically controlled. In addition to providing a powerful method for controlling the microstructures of metal/polymer nanocomposites, the method described here also allows one to evaluate the size-, thickness-, and concentration-dependent optical, electrical, and mechanical properties of these nanocomposites. Furthermore, patterned microstructures constructed of polyimide-based hybrid nanocomposites containing a wide variety of metallic, semiconducting, and magnetic nanoparticles are now available, potential applications of which are currently being investigated.

Supporting Information Available: Figure showing depth profile of Cu in the film after ion exchange (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Kowalczyk, S. P.; Kim, Y. H.; Walker, G. F.; Kim, J. *Appl. Phys. Lett.* **1988**, *52*, 375.
(30) Nagai, N.; Hironaka, T.; Imai, T.; Harada, T.; Nishimura, M.; Mimori, R.; Ishida, H. *Appl. Surf. Sci.* **2001**, *171*, 101.