Eur. Phys. J. D **24**, 377–380 (2003)
DOI: 10.1140/epjd/e2003-00116-7

THE EUROPEAN PHYSICAL JOURNAL D

Fabrication and structural characterization of nanocomposites consisting of Ni nanoparticles dispersed in polyimide films

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Received 10 September 2002

Abstract. Formation and structure of composite layer consisting of polyimide films containing Ni nanoparticles were investigated. The preparation method relies on KOH treatment on polyimide film to form carboxyl acid groups and adsorption of Ni ions by ion exchange followed by hydrogen reduction. The amount of Ni ions adsorbed in polyimide films were found to be systematically controlled by changing initial KOH concentration, subsequent ion exchange time, pH and temperature. Cross-sectional TEM observation revealed that Ni nanoparticles with 3-5 nm in diameter were homogeneously dispersed in the surface modified polyimide layer after heat treatment above 250 °C in H_2 atmosphere. The size and distribution of the Ni nanoparticles were strongly dependent on the heat treatment temperature, indicating that this method allows microstructural tuning of metal/polymer nanocomposites.

PACS. 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 68.35.Fx Diffusion; interface formation

1 Introduction

The preparation of nanocomposites consisting of solid state materials containing metal and/or semiconductor nanoparticles has attracted much attention because they exhibit unusual physical and chemical properties originated from the nanoscale structures. In particular, such composite materials can offer exciting possibilities for potential thin film device applications with novel functions arising from quantum size effects. The properties of these nanocomposites are known to be dependent on various structural factors, *e.g.*, size, concentration, and special distribution of the guest nanoparticles as well as dielectric properties of host matrices [1–3]. Therefore, the method which allows manipulation of the film microstructure is indispensable to prepare composite thin films with desired properties.

Metal nanoparticles dispersed in polymeric matrices have recently been the subject of intense study aiming to develop the nanoelectronics devices. The thermoplastic properties of the host polymers is the potential advantage for fabrication of the nanocomposites because the size and distribution of dispersed metal nanoparticles can be readily controlled. A wide variety for fabrication of metal polymer composite has thus been developed, including physical and chemical techniques [4–12]. Among these, polyimide is known to be a high performance organic material that has been used extensively in microelectronics device fabrication and packaging because of its good thermal stability, chemical resistance, and low dielectric constant [13–15]. However, there have been as yet few studies on the use of polyimide as host materials.

In this study, we report a method for preparing the polyimide thin films containing Ni nanoparticles, which relies on the incorporation of Ni ions in surface modified polyimide films and subsequent thermally-induced hydrogen reduction. The films obtained were characterized by FT-IR, ICP, GD-OES, TEM and electron diffraction. It has been shown that the thickness of modified polyimide layer as well as the amount of adsorbed Ni ions, both of which are closely related to the subsequent formation of Ni nanoparticles/polyimide nanocomposites, can be systematically controlled by the experimental conditions.

2 Experimental

Typical PMDA-ODA type polyimide film (Kapton 200-H, Toray-DuPont) was used in this study as host polymeric materials. The procedure employed for fabrication of nanocomposites involves several steps: (i) surface

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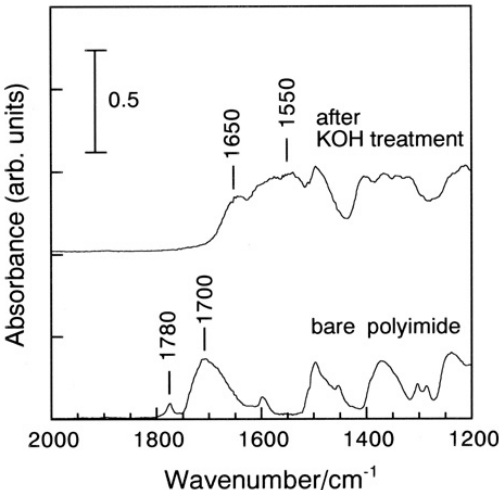

Fig. 1. ATR FT-IR spectra of bare polyimide and surface modified polyimide films with 5 M KOH aqueous solution at 50 °C for 5 min.

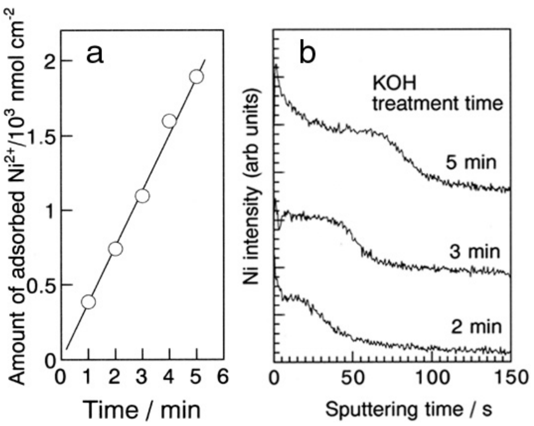

Fig. 2. (a) Relationship between amount of adsorbed Ni ions and KOH treatment time (5 M, 50 °C). (b) GD-OES depth profiles of Ni component in the surface modified film after ion exchange reaction.

modification of polyimide film by immersing into KOH solution (5 M, 50 °C, 5 min), (ii) adsorption of nickel (II) ions on the modified polyimide surface by ion exchange reaction (5 mM, $NiCl_2$ aq., 5 min at room temperature), (iii) heat treatment of these ion-exchanged films in hydrogen atmosphere (30 min). Structural change of polyimide film was studied with Fourier transform infrared (FT-IR) spectroscopy employing attenuated total reflection (ATR) configuration (FT/IR 615R, Japan Spectroscopic Co.). The amount of adsorbed Ni ions was measured by inductively-coupled plasma (ICP) atomic emission spectrometer (SPS7700, Seiko Instruments). Depth profile of Ni in the films was measured with glow discharge optical emission spectroscopy (GD-OES, JY500RF, Horiba). Microstructure of the composite films was observed using cross-sectional transmission electron microscopy (TEM) operating at 100 kV (Hitachi 7100). The samples for cross-sectional TEM observation were prepared by curing the epoxy resin containing the films and subsequent sectioning (*ca.* 60 nm) using ultramicrotome (Ultracut R, Leica).

3 Results and discussion

Figure 1 shows ATR FT-IR spectra obtained from bare polyimide and surface modified films that were treated by 5 M KOH at 50 °C for 5 min. The spectrum of bare polyimide is well characterized by a band attributed to characteristic vibration mode for both the backbone PMDA and ODA part of the polymer. The bands which are observed at 1780 cm^{-1} and 1700 cm^{-1} arise from carbonyl vibrations in in-phase and out-of-phase modes, respectively. The treatment with KOH solution results in significant change in the IR spectra. The band assigned to carbonyl stretching band of imide ring disappeared completely, while new bands are observed at 1680 cm^{-1} and 1550 cm^{-1}, corresponding to the amide I (carbonyl stretching) and amide II (N-H bending) modes of the amide bond, respectively [16]. Several peaks also appear around 1500-1600 cm^{-1}, which can be assigned to ionized carboxyl groups complexed with pottasium ions. Formation of carboxyl groups was also confirmed by X-ray photoelectron spectroscopic measurements (results not shown). These results demonstrate that present KOH treatment gives rise to the formation of carboxyl groups and amide bonds through cleavage of imide rings in the PMDA part of the polyimide [17]. These carboxyl groups formed act as ion exchange component and can adsorb Ni ions on immersing the modified film into $NiCl_2$ aqueous solution.

Figure 2a shows effect of initial treatment time on the amount of subsequently adsorbed Ni ions in the modified polyimide film (KOH concentration: 5 M, temperature: 50 °C for 5 min). As the KOH treatment time increases, the amount of Ni ions adsorbed increases in linear fashion, indicating that the amount of Ni ions incorporated in the polyimide film can be controlled over the wide range. No potassium ions could be detected by ICP measurement after ion exchange process. At fixed KOH concentration and treatment time, the amount of adsorbed Ni ions was half as large as that of initial potassium ions, indicating that the incorporation of Ni ions into polyimide film can be achieved through exchange of monovalent potassium ions to divalent Ni ions, both of which are bound to carboxylic anion formed by cleavage of imide rings. The linear dependence observed in Figure 2a can be caused by the changes in thickness of polyimide film modified by KOH, which can be controlled by diffusion of KOH solution into polyimide film. This consideration is supported by GD-OES depth profiles obtained for the polyimide films modified by 5 M KOH solution at 50 °C for various times, as shown in Figure 2b. The intensity was corrected for all the samples by taking into account total signals originated from constructed component in the film and ion current during measurement. In the figure, we can see that the region in which the Ni component can be detected increases as the KOH treatment time increases. This indicates that the thickness of modified layer increases with increasing

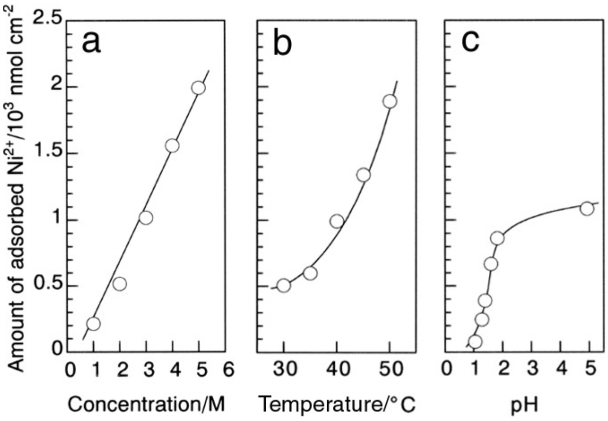

Fig. 3. Effect of (a) initial KOH concentration (50 °C, 5 min), (b) temperature during surface modification (5 M, 5 min), and (c) pH during subsequent ion exchange reaction (5 M, 50 °C for initial KOH treatment) on the amount of adsorbed Ni ions.

treatment time, leading that the larger amount of adsorbed Ni ions can be incorporated into the film treated by KOH solution for longer treatment time, as observed in Figure 2a.

This surface modification could also be promoted by the increase in KOH concentration, temperature during KOH treatment, and pH during ion exchange reaction (Fig. 3). The amount of adsorbed Ni ions increases linearly with KOH concentration (Fig. 3a), and also increases exponentially with increasing temperature (Fig. 3b). The decrease in pH (<2) during ion exchange reaction (adjusted using HCl) results in significant decrease in amount of adsorbed Ni ions (Fig. 3c), implying the ability to control the amount of Ni ions adsorbed in modified layer with constant thickness that was pre-determined by initial KOH concentration. Although the maximum amount of adsorbed Ni ions is essentially dependent on the number of carboxyl groups formed, these results demonstrate that the loading amount of Ni ions in the film can be systematically controlled by the experimental conditions, *i.e.*, temperature, concentration, and pH during surface modification and ion exchange reaction.

Cross-sectional TEM image of Ni-adsorbed modified polyimide films after heat treatment in H_2 atmosphere is shown in Figure 4. Heat treatment at 300 °C results in formation of Ni nanoparticles inside the modified layer, in which the nanoparticles disperse uniformly and isolated individually. Selected-area electron diffraction pattern exhibites Debye-Sherrer rings of Ni fcc phase, as shown inset in Figure 4b. This thermally- and hydrogen-induced formation was accelerated with an elevation of temperature as well as with increasing adsorbed Ni ions, *i.e.*, further high temperature treatment (350 °C) caused the growth of the Ni nanoparticles. No particles or clusters were detected inside the modified layer after heat treatment below 200 °C. We suggest that, during initial stage of heat treatment, formation of Ni clusters (nuclei) can lead decrease in local concentration of Ni ions bound to carboxylic acid anions. The concentration gradient near the Ni clusters formed may be driving force for further diffusion of remaining Ni ions toward the Ni clusters, resulting in growth of the clusters. Further experimental study is necessary in order to elucidate the growth mechanism, which are currently under way and results will be published elsewhere.

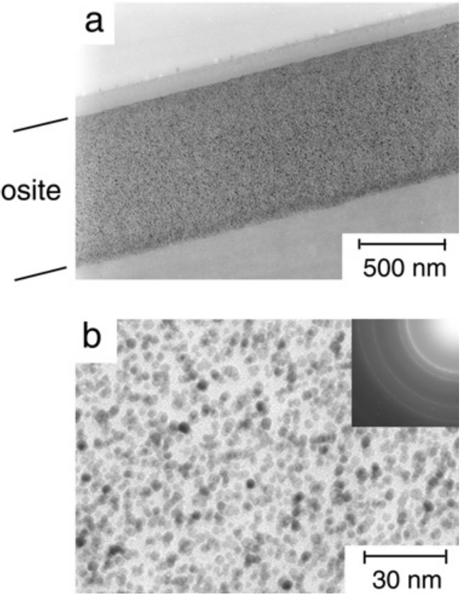

Fig. 4. Cross-sectional TEM image of Ni adsorbed surface modified polyimide film after heat treatment at 300 °C for 30 min in H_2 atmosphere (a). (b) Enlarged image of (a). Inset: selected area electron diffraction pattern of the film.

4 Conclusion

The present study has demonstrated a methodology to prepare Ni nanoparticle-based modified polyimide nanocomposites. Incorporation of large amount of Ni ions on modified layer were successfully achieved though ion exchange reaction from carboxylic acid anions formed by KOH treatment-induced ring-cleavage reaction of polyimide resin. It has been shown that the amount of adsorbed Ni ions could be systematically controlled over wide range by changing experimental conditions, *i.e.*, time, concentration, temperature, and pH during initial KOH treatment and subsequent ion exchange. Annealing in hydrogen atmosphere subsequent to incorporation of Ni ions into the modified polyimide surface leads to successful formation of Ni nanoparticles with the size range of 3–5 nm. This process can be applied for fabrication of polyimide-based hybrid nanocomposites containing a wide variety of metallic, semiconducting, and magnetic nanoparticles.

The authors acknowledge Prof. S. Deki for allowing us to use the FT-IR spectrometer. This work was supported by Grant-in-Aid of Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (No. 14750579).

References

1. A. Heilmann, G. Kampfrath, V. Hopfe, J. Phys. D: Appl. Phys. **21**, 986 (1988)
2. B. Laurent, E. Kay, J. Appl. Phys. **65**, 1717 (1989)
3. S. Ogawa, Y. Hayashi, N. Kobayashi, T. Tokizaki, A. Nakamura, Jpn J. Appl. Phys. **33**, L331 (1994)
4. E. Kay, M. Hecq, J. Appl. Phys. **55**, 370 (1984)
5. L. Martinu, H. Biederman, J. Zemek, Vacuum **35**, 171 (1985)
6. K. Kashiwagi, Y. Yoshida, Y. Murayama, Vac. Sci. Technol. A **5**, 1828 (1987)
7. M. Haruta, K. Saika, T. Kobayashi, S. Tsubota, Y. Nakahara, Chem. Expr. **3**, 159 (1988)
8. K. Esumi, T. Tano, K. Torigoe, K. Meguro, Chem. Mater. **2**, 564 (1990)
9. C. Reinhardt, A. Heilmann, W. Grunewald, C. Hamann, Thin Solid Films **246**, 77 (1993)
10. M. Moffitt, L. MacMahon, V. Pessel, A. Eisenberg, Chem. Mater. **7**, 1185 (1995)
11. R. Lamber, S. Wetjen, G. Schulz-Ekloff, A. Baalmann, J. Phys. Chem. **99**, 13834 (1995)
12. L. Chen, W. Yang, C. Yang, Macromol. Symp. **105**, 235 (1996)
13. C.C. Parks, J. Vac. Sci. Technol. A **15**, 1328 (1997)
14. C.K. Hu, J.M.E. Harper, Mater. Chem. Phys. **52**, 5 (1998)
15. F. Faupel, R. Willecke, A. Thran, Mater. Sci. Eng. R **22**, 1 (1998)
16. D.J. Skrovanek, S.E. Howe, P.C. Painter, M.M. Coleman, Macromolecules **19**, 699 (1986)
17. H. Nawafune, T. Nishioka, H. Tsuji, S. Mizumoto, M. Seita, M. Kusaka, J. Jap. Inst. Electron. Pack. **2**, 390 (1999)