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Synthesis and Structural Control of Metal-Containing Polyimide Nanocomposite

Hiroyuki Shinkai, Shingo Ikeda, Kensuke Akamatsu,
Hidemi Nawafune and Satoshi Tomita
Faculty of Science and Engineering, Konan University, 8-9-1 Okamoto, Higashinada, Kobe 658-8501, Japan, and
PRESTO, Japan Science and Technology Agency (JST), Wako, Saitama 351-0198, Japan
Fax: +81-78-435-2539, e-mail: akamatsu@center.konan-u.ac.jp

We describe a novel approach for synthesis of polyimide films containing monodispersed Ni nanoparticles via surface chemical modification of polyimide using KOH solution and subsequent incorporation of Ni^{2+} ions through ion exchange reaction followed by heat treatment in a hydrogen atmosphere. The effect of heat treatment in a hydrogen atmosphere on microstructure of the composite film was investigated by ICP, ATR FT-IR measurements and cross-sectional TEM observations. Upon increasing in annealing temperature, the amount of unreduced Ni^{2+} ions was abruptly decreased, and mean diameter of Ni nanoparticle was increased simultaneously. In addition, surface modified layers transferred to polyimide through dehydration reaction during heat treatment. These results revealed that there is a strong correlation between the reduction of Ni^{2+} ions and thermal re-imidization of initially hydrolyzed polyimide layer.

Key words: Ni nanoparticle, polyimide, surface modification, nanocomposite

1. INTRODUCTION

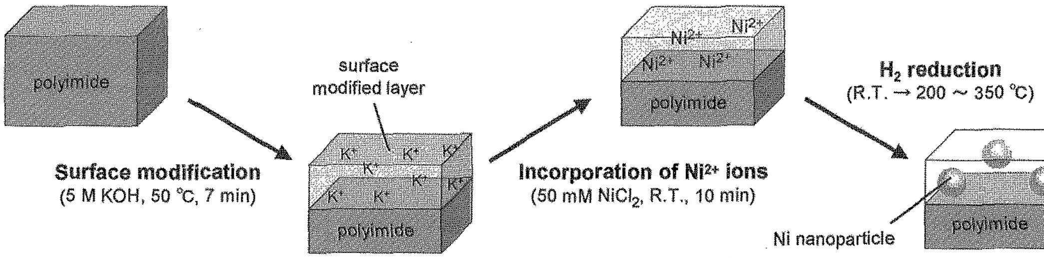
Metal-insulator nanocomposite materials have attractive physical and chemical properties resulted from embedded metal nanoparticles, which are quite different from those of bulk materials. In particular, magnetic nanoparticles are well known to exhibit unusual properties involving single domain nature and enhanced coercivity. These nanoparticles embedded in dielectric matrixes also show an enhanced magnetoresistance [1-3]. Therefore, these nanocomposite materials can be widely studied and expected as excellent candidates for applications in ultrahigh density magnetic storage media [4,5] and advanced magnetic device [6]. At this point, it is noted that the magnetic properties of these nanocomposites are known to be largely dependent on various microstructures including particle size, concentration, composition, dispersability, as well as on physical properties of surrounding matrix materials. Therefore, to apply such nanocomposites in terms of practical applications, there is a need for novel approaches to precise control over microstructural parameter of the composite films. In this point of view, polymeric materials can be suitable for the matrix materials because of thermal plasticity available for microstructural tuning [7,8].

Recently, we have reported a novel synthetic route for metallic nanoparticles dispersed in a polyimide matrix having numerous outstanding properties, such as low permittivity, high thermal and chemical resistance [9,10]. This process involves surface chemical modification of polyimide films using KOH solution, and incorporation of metallic ions through ion exchange reaction followed by heat treatment in a hydrogen atmosphere. Herein, we report on synthesis and structural control of magnetic (Ni) nanoparticle dispersed in polyimide films. In addition, we investigated annealing condition affect the reduction behavior of Ni^{2+} ions, Ni nanoparticle growth, and the changes in chemical structure of matrix material. The resulting Ni/polyimide nanocomposites were characterized by inductivity coupled plasma (ICP) atomic emission spectroscopy, Fourier transform infrared spectroscopy (FTIR) employing the attenuated total reflection (ATR) configuration, and transmission electron microscopy (TEM).

2. EXPERIMENTAL

Synthesis of Ni/polyimide composite films

In this study, the polyimide films used were pyromellitic dianhydride oxydianiline (PMDA-ODA) type (50-μm thick, Kapton 200-H, Toray-Du Pont Co., Ltd.). The scheme in Figure 1 illustrates the procedure that was used for synthesis of Ni nanoparticles /polyimide composite films. The polyimide films were immersed in aqueous KOH (5 M) solution at 50 ℃ for 7 min followed by rinsing with ion-exchanged water. This KOH treatment formed potassium salts of poly(amic acid) with ion-exchange capability through imide ring cleavage reaction [11-13]. To exchange K^+



Scheme 1. Schematic illustration of present process for synthesis of Ni-containing polyimide nanocomposites.

ions with Ni^{2+} ions, the films were then immersed into an aqueous $NiCl_2$ solution (50 mM) at room temperature for 10 min, which resulted in the formation of Ni^{2+} ion-doped polyimide films. After rinsing, this film was heated in a tube furnace under H_2 gas flow at the rate of 10 ℃ min^{-1} up to target temperature to reduce Ni^{2+} ions to metallic Ni.

Characterization

Amount of Ni^{2+} ions incorporated in polyimide resin was measured by ICP (SPS7700 plasma spectrometer, Seiko Instruments). To extract only unreduced Ni^{2+} ions from the films, they were immersed in CH_3COOH solution (10 vol %) at room temperature for 2 h. Structural changes in films upon each heating condition were studied with FTIR-ATR. The IR spectra were obtained using FT / IR 670PLUS (Japan Spectroscopic Co.). The microstructures of the composite films were confirmed by cross-sectional TEM observations, using a JEM-2000EX (JEOL) electron microscope operating at 200 kV. Thin cross-sections (ca. 100 nm in thickness) were prepared by conventional microtome technique using an ultramicrotome (Leica Ultracut R) with a diamond knife.

3. RESULTS AND DISCUSSION

Formation and growth of Ni nanoparticles in polyimide films.

Figure 1 shows cross-sectional TEM images of Ni^{2+} ion-doped polyimide films after heat treatment. In all cases, Ni nanoparticles are homogeneously dispersed in surface modified layer of polyimide films. Electron diffraction patterns obtained from these particles were indexed as fcc metallic Ni (inset in Figure 1). Mean diameter of the particles and their standard deviation in the annealed films at 270 ℃, 290 ℃ and 310 ℃ are estimated to be 3.4 ± 0.46 , 4.3 ± 0.51, and 7.6 ± 1.0 nm, respectively (Figure 1a-c). Average Ni nanoparticle size increases with increasing annealing temperature.

To better understand the formation and growth mechanism of Ni nanoparticle in polyimide resin, we explored how annealing condition influence the amount of unreduced (residual) Ni^{2+} ions and average Ni nanoparticle size (Figure 2). Amount of unreduced Ni^{2+} ions show a constant value up to 250 ℃, and abruptly

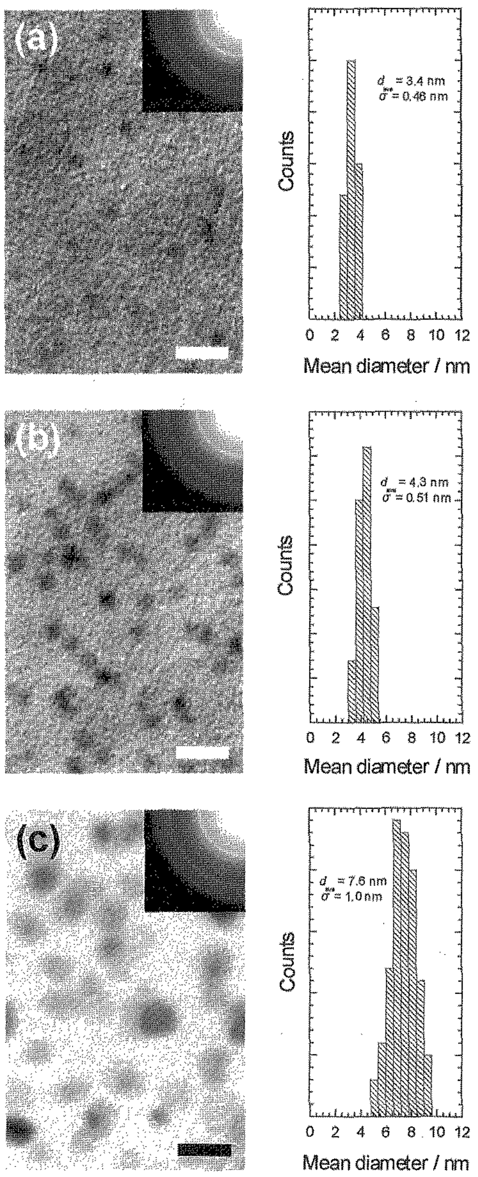


Figure 1. Cross-sectional TEM images of Ni^{2+} doped polyimide films after heat treatment at (a) 270 ℃, (b) 290 ℃ and (c) 310 ℃. Scale bar : 10 nm. The inset show the electron diffraction pattern.

decreases at 260-310 ℃. Above 310 ℃, Ni signals are no longer evident. On the other hand, average Ni nanoparticle size increases at 270-310 ℃ (No particle could be observed below 270 ℃.). Above 310 ℃, it is found that Ni nanoparticles with mean diameter of ca. 8 nm are formed, the value of which is constant upon further increasing in annealing temperatures. These results suggest that diffusion of Ni^{2+} ions plays a very important role for Ni nanoparticle growth.

Changes in chemical structure of polyimide matrix.

To gain further insight into the detailed relationship between reduction behavior of Ni^{2+} ions and changes in chemical structure of polyimide matrix surrounding Ni nanoparicles, ATR-FTIR measurements were performed for films heat-treated at various temperatures. The representative results are shown in Figure 3. Ni^{2+} ion-doped film obtained before annealing shows absorption band which can be assigned to the amide I (carboxyl C=O stretching) at 1680 cm^{-1} and amide II (N-H bending) at 1550 cm^{-1} , indicating that as-Ni^{2+} ion-doped polyimide film is assigned to Ni polyamate structure [14,15]. Upon increasing in annealing temperature, intensities of amide I and II modes, arising from amide groups and carboxyl groups, completely disappear and new band of imide are clearly visible at 1780 and 1710 cm^{-1}, which can be assigned to symmetric and asymmetric stretching vibration of carbonyl groups coupled through the five-membered imide ring, respectively [14,15]. These spectra agreed well with the spectrum of bare polyimide films (results not shown). These results indicate that a ring closure reaction forming imide rings (re-imidization) from the surface modified layer proceeds. In addition, it is noted that the degree of re-imidization with increasing annealing temperature is in good agreement with reduction behavior of Ni^{2+} ions. For example, for Ni-containing polyimide films obtained after annealing at 250 ℃, all of the Ni^{2+} ions are reduced (Figure 2) and the matrix is simultaneously completely converted into polyimide. These results imply that changes in chemical structure of polyimide matrix are closely associated with

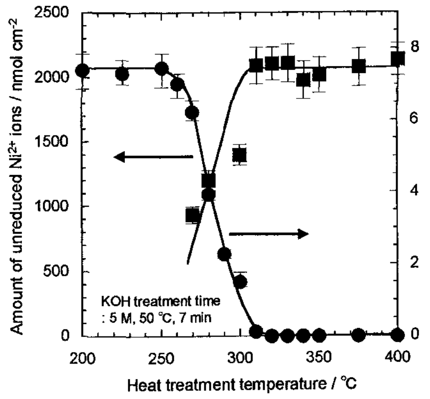


Figure 2. Effect of heat treatment temperature on amount of unreduced Ni^{2+} ions and average Ni nanoparticle size in composite layer.

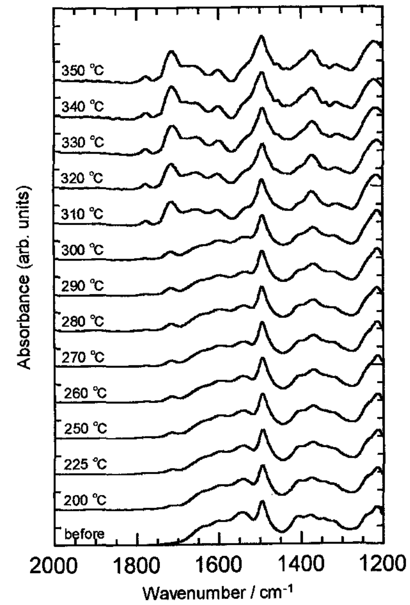
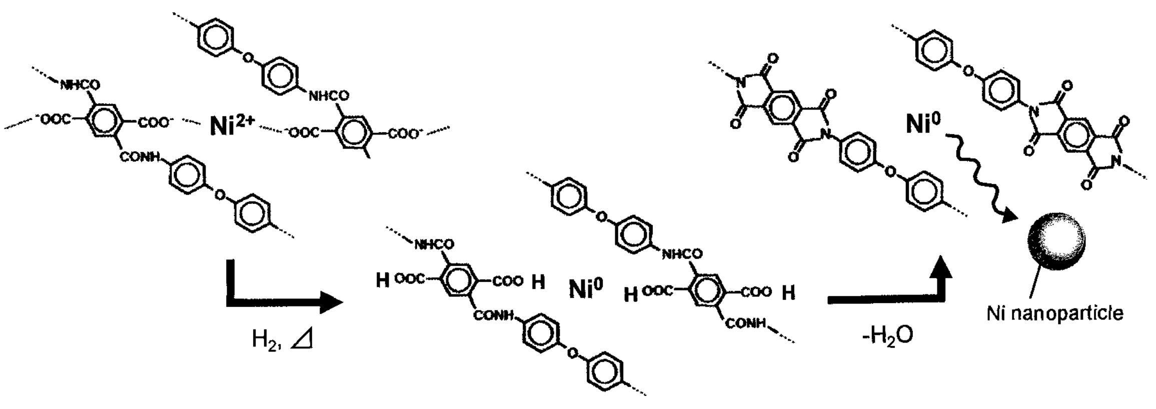


Figure 3. Changes in ATR-FTIR spectra of Ni^{2+}-doped polyimide with heat treatment under H_2 atmosphere.



Scheme 2. Schematic diagram of proposed mechanism for formation of Ni nanoparticles in polyimide films.

reduction of Ni nanoparticles.

Discussion.

A possible formation and growth mechanism of Ni nanoparticles within the polyimide-based matrix is suggested as follows. Reduction of Ni^{2+} ions is triggered by accepting electrons from hydrogen molecules, which results in dissociation of Ni^{2+} ions from carboxylate anions. The protonation of carboxylate anions then immediately occurs to form carboxylic acids, followed by re-imidization process via a dehydration / condensation reaction between carboxylic acid and neighboring amide bond. Subsequent diffusion and agglomeration of Ni atoms produces nano-sized Ni particles (Scheme 2). Therefore, in the present system, resulting nanocomposite films are constructed from magnetic Ni nanoparticles dispersed in the high -performance polyimide matrix.

4. CONCLUSION

We have described a simple chemical process for fabrication of Ni nanoparticles/polyimide nanocomposite via surface modification approach. After annealing in a hydrogen atmosphere, uniformly dispersed Ni nanoparticles are formed in surface modified polyimide layer. It has been shown that average Ni nanoparticle size can be controlled by annealing temperature. Furthermore, analytical, vibrational, and microscopic characterization revealed that there was a strong correlation between growth behavior of Ni nanoparticles and changes in chemical structure of surrounding matrix, that is, degree of re-imidization with increasing in annealing temperature. This novel strategy for synthesis of metal/polyimide nanocomposites can be available for preparing other nanocomposites constructed from many other metal and/or semiconductor nanoparticles, which could be find a wide range applications.

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