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Formation of metal thin nanocomposite layer from precursor polyimide containing metal complex

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Herein, we report on fabrication of nickel nanocomposite on polyimide resin via a direct metallization process using nickel complexes as the nickel precursor. The process relies on synthesis of poly(amic acid) solutions containing nickel complex formed from 4,4'-biphthalic anhydride (BPDA)/2,2'-Bis[4-(4-aminophenoxy)phenyl]propane (BAPP) and formation of poly(amic acid) films containing nickel complex followed by chemical reduction. Nickel nanoparticles could be seen to form on the surface and into the precursor polyimide film. The thin nickel nanocomposite films could be used as precursors for copper clad on polyimide films; the copper clad on polyimide films were obtained by electroless nickel deposition and copper electrodeposition. The metal films were highly adhesive; the films readily pass the Scotch-tape test. These results suggest that the nanocomposite layer at the interfacial region acts as a glue between the deposited metal and polymer via a nanoscale interlocking effect.

Key words: Nickel nanocomposite, Nickel complex, Poly(amic acid), Copper clad on polyimide film

1. INTRODUCTION

Nanocomposite materials containing metal nanoparticles are of intense current interest for potential applications as magnetic, photonic and electronic materials. Especially, metal nanoparticles dispersed in polymeric matrixes have recently been the subject of intense study aiming to develop nanocomposite films [1-3]. The polymer-based materials containing metal nanoparticles have traditionally been prepared by a variety of chemical and physical methods including mixing metal particles with polymer solution [4], simultaneous or alternate plasma polymerization of monomer and metal sputtering or vacuum evaporation [5-8]. Recently, preparation of metal nanoparticle/polymer composites by the process of dissolution and reduction of metal salts or complexes within polyimide precursor films has been proposed [9-12]. Polyimides have found numerous applications in industries such as aerospace and electronics, where excellent dielectric properties, high-temperature stability, and chemical inertness are required [13-15]. Therefore, polyimide is an attractive matrix for composite materials for future device generation in which chemical and thermal stability is required.

In this paper, we report on the synthesis of 4,4'-biphthalic anhydride (BPDA)/2,2'-Bis[4-(4-aminophenoxy)phenyl]propane (BAPP) poly(amic acid) containing nickel complex and characterization of Ni nanoparticle-BPDA/BAPP composite films formed by wet chemical reduction. This work aims at fabricating metallized polyimide films with more desirable performances for copper-based advanced interconnection, because there has been substantial interest in the use of nickel seed layers on polyimide surfaces to anchor a second metal, particularly copper, for circuitry applications. The structural characteristics of the films were determined by Fourier transform infrared attenuated total reflectance method (FTIR-ATR), and morphology of the nickel nanocomposite films was determined by field emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM). We also report the formation of copper clad on polymer substrate using the nickel nanocomposite films.

2. EXPERIMENTAL

Film preparation.

The following procedure was used to prepare films containing nickel (II) acetylacetonate complexes. 2,2'-Bis[4-(4-aminophenoxy)phenyl]propane (BAPP) (2.05 g, 5 mmol) and *N*-methyl 2-pyrrolidinone (NMP) (40 ml) were placed into flask equipped with a

Table 1 Composition and characteristics of poly(amic acid) solutions containing nickel complex.

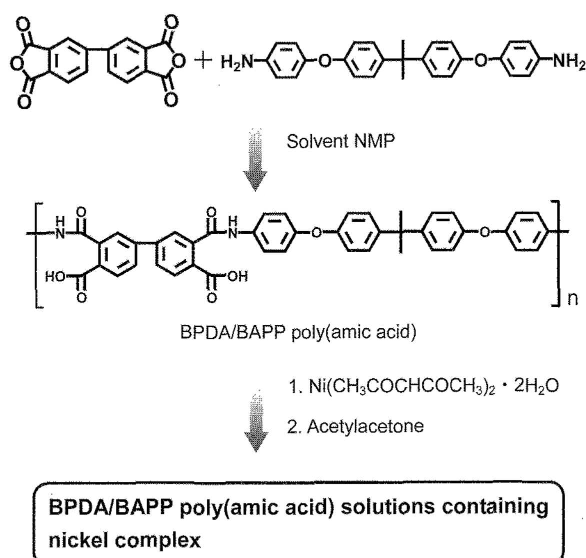
Entry	Nickel (II) acetylacetonate (mmol)	Acetylacetone (mmol)	Appearance	Viscosity a) (cP)
1	2.5	0	gel	-
2	2.5	2.5	sol	3405
3	2.5	5.0	sol	1613
4	5.0	0	gel	-
5	5.0	3.0	gel	-
6	5.0	5.0	sol	1510
7	5.0	8.0	sol	1140
8	7.5	0	gel	-
9	7.5	4.0	gel	-
10	7.5	7.5	sol	608
11	7.5	10.0	sol	475

a)Viscosity of poly(amic acid) solution was measured using E type viscometer.

mechanical stirrer. After dissolution of BAPP, 4,4'-biphthalic anhydride (BPDA) (1.47 g, 5 mmol) was added into the flask. The reaction mixture was stirred at room temperature for 4 h. Nickel (II) acetylacetonate and acetylacetone in NMP (15 ml) were then added in small portion and the reaction mixture was stirred at room temperature for 1 h. Addition of the nickel (II) acetylacetonate complex and acetylacetone to the poly(amic acid) solution gave a green homogeneous nickel (II)-doped resin. Nickel complex-doped poly(amic acid) solutions were spin-coated onto polyimide films using spin-coater, followed by heat treatment at 130 ℃ for 20 min to obtain 3.5 μm thick films. The nickel (II) complex-doped poly(amic acid) films were immersed into a 50 mM aqueous $NaBH_4$ solution at 50 ℃ for 3 min to reduce the doped nickel ions.

Characterization

The surface morphology and cross-sectional microstructure of the film were observed by field emission scanning electron microscopy (FESEM, JEOL, JSM-6340F) and transmission electron microscopy (TEM, JEOL, JEM-2000EX), respectively. For cross-sectional TEM observation, the samples were sectioned into ca. 100 nm thick slices with the conventional microtome technique using a diamond knife (Leica, Ultracut R). Structural change in the polyimide film was determined by Fourier transform infrared attenuated total reflectance method (FTIR-ATR, JASCO, FT/IR 620).



Scheme 1 Synthetic scheme for BPDA/BAPP poly(amic acid) solutions containing nickel complex.

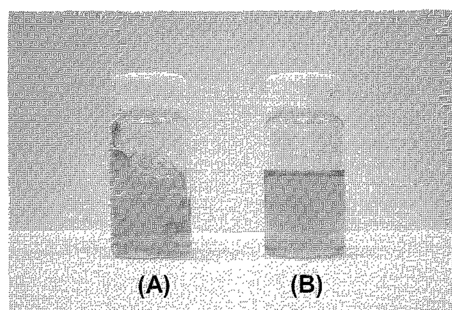


Figure 1 Photograph of poly(amic acid) solutions containing nickel complex before (entry 1 in Table 1) (A) and after addition of acetylacetone (entry 2 in Table 1) (B).

3. RESULTS AND DISCUSSION

Synthesis of poly(amic acid) solutions containing nickel complex

Poly(amic acid) solution containing nickel complex was synthesized by the pathway described in scheme 1. The polymerization was performed by dissolving BAPP in NMP and adding equivalent amount of BPDA into the solution. Finally, different amount of nickel (II) acetylacetonate complex and acetylacetone was mixed with the reaction mixture.

Table 1 displays characteristics of representative solutions. When only the nickel (II) acetylacetonate complex is added to the poly(amic acid) solution, immediate gelation of the polymer occurs (Figure 1 A), presumably due to coordination of polyamide carboxylate groups to nickel (II) ions. Gelation does not occur in the presence of equimolecular amount of

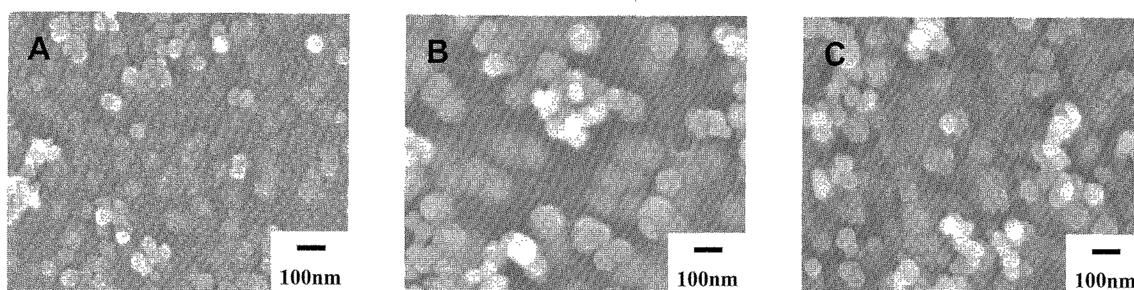


Figure 2 FE-SEM images of the surface structure for the BPDA/BAPP films containing nickel (Ⅱ) complex treated by 50 mM aqueous $NaBH_4$ solution at 50 ℃ for 3 min. The images were obtained from nickel (Ⅱ) doped poly(amic acid) films of (A) entry 3, (B) entry 7, and (C) entry 11 in Table 1.

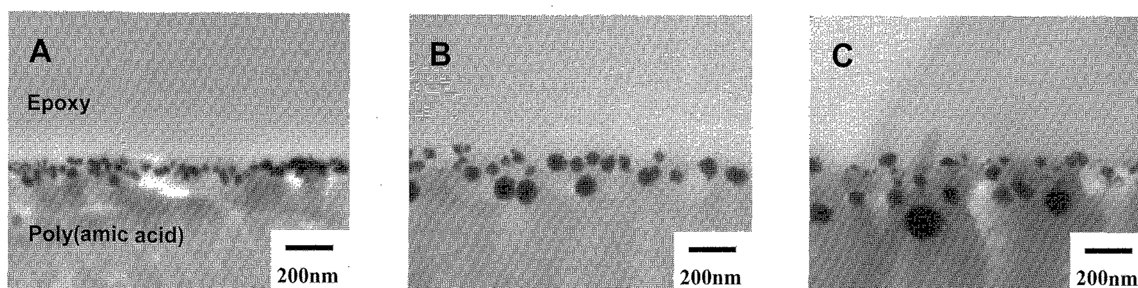


Figure 3 Cross-sectional TEM images of the BPDA/BAPP films containing nickel (Ⅱ) complex treated by 50 mM aqueous $NaBH_4$ solution at 50 ℃ for 3 min. The images were obtained from nickel (Ⅱ) doped poly(amic acid) films of (A) entry 3, (B) entry 7, and (C) entry 11 in Table 1.

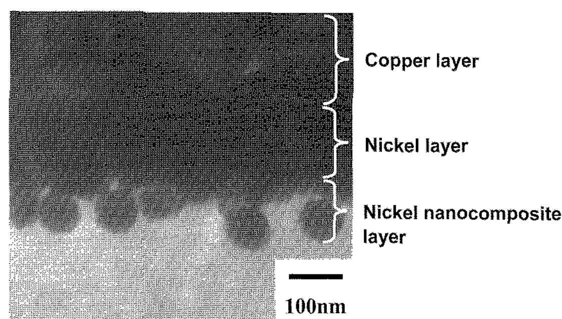


Figure 4 Cross-sectional TEM image of the copper clad on polyimide film.

acetylacetone as complex agent for nickel (Ⅱ) ions (Figure 1 B). This is solid evidence for formation of the nickel (Ⅱ) trisacetylacetonate complex.

Formation and morphology analyses of the nickel nanocomposite films

Poly(amic acid) films containing nickel (Ⅱ) complex were fabricated by spin-coating onto polyimide films from the solution of entry 3, 7, 11 in Table 1, and the films were then prebaked at 130 ℃ for 20 min. Nickel nanoparticle/poly(amic acid) composite films could be fabricated by wet chemical reduction of the precursor films. The chemical state of nickel nanoparticles was nickel (0), that was confirmed by X-ray photoelectron spectroscopic measurements (results not shown). To investigate the relationship between concentrations of nickel (Ⅱ) and film morphology, SEM and TEM analyses were carried out. Figure 2 shows the variation of the surface morphologies for the films obtained after aqueous $NaBH_4$ treatment. The SEM images in Figure 2A show that, at lower concentration of nickel (Ⅱ) complex in polymer, there are small spherical nickel particles with diameters of ca. 50 nm on film surfaces. The SEM images in Figure 2B and 2C demonstrate the increase of the nickel particle size on the film surface at higher concentration of nickel (Ⅱ) complex in polymer. The particle sizes are on the order of 50-150 nm in diameter. This is because nickel particle growth (size increase) is faster than particle formation (number increase) at higher concentration of nickel (Ⅱ) complex in polymer.

Figure 3 shows cross-sectional TEM images of the nanocomposite films obtained after $NaBH_4$ treatment. At the lower concentration of nickel (Ⅱ) complex in polymer, small nickel nanoparticles are located near the surface (Figure 3A). However, at the higher concentration of nickel (Ⅱ) complex, large nickel particles existed in the depth of ca. 400 nm (Figure 3C).

In all films there are only small nickel aggregates which do not appear to be in contact with one another, thereby all films are not conductive.

Fabrication of copper clad on polymer substrate from nickel/poly(amic acid) nanocomposite films

The thin nickel naocomposite films can be useful as precursors for copper clad on polyimide films. The copper clad on polyimide films are obtained by electroless nickel deposition and copper electrodeposition after deionization and imidization. First, the nickel nanoparticle/poly(amic acid) composite film is dipped into 10 wt% aqueous citric acid solution for 2 min to completely extract the metallic ions in the films. Subsequently, the poly(amic acid) was heated at 200 ℃ for 5 min and 300 ℃ for 5 min to achieve complete imidization. Imidization was confirmed with FTIR-ATR (result not shown). Then, immersion of the film into an electroless nickel deposition bath resulted in the formation of nickel thin layer, which can act as barrier layer for diffusion of copper into polymer substrate. Finally, copper thin layer was fabricated by copper electrodeposition (Figure 4). The good adhesion of the copper thin films to polyimide substrate was achieved, as verified by Scotch-tape test. We suggest that the nickel nanocomposite layer thus formed could act as a glue between the deposited metal and polyimide via a nanoscale interlocking effect.

4. CONCLUSION

We report on formation of nickel nanoparticle/polyimide composite films by direct metallization process using nickel complexes as the nickel precursor. The nanocomposites can be fabricated on a BPDA/BAPP polyimide film formed from homogeneous poly(amic acid) solutions containing nickel (II) acetylacetonate complex. The nanocomposite layer generated after reduction treatment catalyzes electroless nickel deposition, after which the microstructure of the interfacial composite layer between the underlying films and the deposited nickel remains unaltered. Therefore, the nanocomposite layers improved the adhesion between the polyimide and deposited metal layer, allowing one to obtain copper clad on polyimide films.

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