

Preparation and Properties of Polyimide Films Codoped with Barium and Titanium Oxides

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ABSTRACT: Polyimide hybrid films containing bimetallic compounds were obtained by codoping poly(amic acid) with a barium and titanium precursor prepared from BaCO₃, Ti(OBu)₄, and lactic acid followed by casting and thermal curing. FTIR, WAXD, and XPS measurements showed that barium and titanium precursor could be transformed to BaTiO₃ at a temperature above 650°C, while the mixed oxides were only found in hybrid films. The measurements of TEM and AFM indicated a homogeneous distribution of inorganic phase with particle sizes less than 50 nm. The hybrid films exhibited fairly high thermal stability, good optical transparency, and promising mechanical properties. The incorporation of 10 wt % barium and titanium oxide lowered surface and volume electrical resistivity by 2 and 5 orders, respectively, increasing dielectric constant from 3.5 to 4.2 and piezoelectric constant from 3.8 to 5.2×10^{-12} c/N, relative to the nondoped polyimide film. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1810–1816, 2002

Key words: polyimides; hybrid films; nanometric composite

INTRODUCTION

Polyimides are well known for their outstanding stability, excellent chemical resistivity, and favorable mechanical strength. They have widely been used in aerospace and electric industries.^{1–3} However, in some case, the properties of a polyimide do not always meet the requirements for optimum performance. For example, the high resistivity of polyimide, which is useful in a lot of electrical applications, provides no benefit in static charge

dissipation and in the production of thin-film resistive heaters. For these specific applications a great deal of researches have been devoted to the synthesis of modified polyimides and polyimide composite materials that exhibit unique physical properties. The incorporation of various metallic additives, such as TiO₂, into polyimides by doping procedure has been reported to improve mechanical, electrical, and optical properties.^{4–9} In most cases, however, a heterogeneous distribution of the oxide particles with markedly high concentration on or near the polymer surface was often observed.^{6–8} Meanwhile, large particles with sizes large than 100 nm were also formed. Taylor's works indicated that polyimide hybrid films can be prepared by codoping by using bimetallic dopants such as Li₂PdCl₄, and the polyimide hy-

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brid films had uniform properties.^{10, 11} Whether the polyimide hybrid films prepared from other bimetallic dopants also possess uniform properties promoted us to study newly codoped system by using bimetallic dopant and to investigate the properties of correspondingly hybrid polyimide films. In this article, the polyimide hybrid films containing barium and titanium oxides were described.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) were available commercially. They were purified by sublimation or recrystallization before use. Poly(amic ester) based on PMDA and ODA was prepared according to the procedure described previously.¹¹ Barium oxide (BaO), titanium dioxide (TiO₂), barium carbonate (BaCO₃), titanium butoxide [Ti(OBu)₄], and lactic acid were used as received. Anhydrous *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and *N*-methyl-2-pyrrolidinone (NMP) were distilled under reduced pressure over calcium hydride and stored under nitrogen atmosphere. Pyridine was dried with potassium hydroxide and distilled under nitrogen.

Preparation of Barium and Titanium Precursor

Ti(OBu)₄ (4 mmol) and lactic acid (30 mmol) were mixed and allowed to react for 2 h under stirring. BaCO₃ (4 mmol) was then added in stoichiometric amount to this solution in portions. The slurry was stirred vigorously at room temperature for 4 h to form a clear solution. The excess lactic acid and butyl alcohol produced during reaction were removed by distillation under reduced pressure. Result solid product was dried at room temperature under vacuum for another 24 h. Herein after this mixture was called barium and titanium precursor (abbreviated as BTL) to distinguish it from other compound containing barium and titanium.

Preparation of Polyimide Hybrid

Barium and titanium precursors with various ratios of BTL/polymer were added to poly(amic acid) or poly(amic ester) solution within 0.5 h. After stirring for 12 h, BTL dissolved completely in

polymer solution and the mixtures became transparent. The supplemental water was added under vigorous stirring for another 6 h followed by filtering with 0.5- μ m filters and casting onto clean glass plates to obtain films. The films were dried at 40°C for 12 h, and then were imidized and gelled in a nitrogen atmosphere at 100, 200, and 300°C each for 1 h and finally 400°C for 2 h. Finally, the hybrid films were removed from the glass plates.

Measurement

Intrinsic viscosities were determined at 0.5 g/dL in DMAc with an Ostwald viscometer at 30 \pm 0.1°C. Ba and Ti contents were determined by ICP according to the procedure described by Farinas and Barba¹² using a TJA POEMS spectrometer. FTIR spectra were obtained with a Bio-Rad Digilab Division FTS-80 spectrometer. Thermogravimetric analyses (TGA) were obtained with Perkin-Elmer TGA-2 thermogravimetric analyzer. The wide angle X-ray diffraction measurements were undertaken on a Rigaku D/May-IIB X-ray diffractometer with Cu K _{α 1} radiation (λ = 1.5405 Å 40 kV, 30 mA). X-ray photoelectric spectra were obtained with a VG ESCALAB-MKII photoelectron spectrometer system. Transmission electron microscopy (TEM) was performed on JEM-2010 transmission electron microscopy. Morphologies of thin films were examined by atomic force microscopy on Digital Nanoscope IIIA. Room-temperature surface and volume direct current electrical resistivities of 75-mm diameter samples were determined using CGZ-17B super high-insulate resistivities and DJX-p-1 three-electrode system after electrification of the sample with +100 V DC for 5 min. Piezoelectric constants were measured using Model ZJ-2 piezo d₃₃ meter under a frequency of 100 Hz.

RESULTS AND DISCUSSION

Barium and Titanium Precursor

It is very important that a qualified dopant has good solubility in the solution of polyimide precursor and good compatibility with other components in doping system.^{9, 10} In this study, much attention has been paid to the selection of barium and the titanium precursor. Some baric com-

pounds such as $\text{Ba}(\text{Ac})_2$, BaCO_3 , BaO , barium stearate, and barium citrate cannot dissolve in organic solvent used in the synthesis of poly(amic acid) or poly(amic ester), and were rejected to be used as the barium precursor. Titanium alkoxide is widely used as a titanium precursor in sol-gel reaction. Phase separation, however, occurred during solution blending precursors because of strong interaction between them. It was reported that titanium alkoxide can react with organic acid such as acetic acid, and produce a relatively stable acetyl compound.¹³ In our study, a complex (BTL) was successfully prepared from BaCO_3 , titanium *n*-butoxide, and lactic acid as modifier.

BTL, a light yellow powder and very stable in storage, was found to be easy to dissolve in DMAc, DMF, DMSO, NMP, and water. It is very interesting that BTL has better solubility than barium lactate and titanium lactate. Hence, it is good candidate of dopant. Ba and Ti contents of BTL were determined by ICP, and the mol ratio of Ba to Ti is 1.03. BTL underwent hydrolysis by adding excess water and formed transparent gel by aging and heating. FTIR spectra of the gel with heat treatment under various temperatures are shown in Figure 1. The absorbance around 2930 cm^{-1} representing aliphatic group in lactic acid disappeared gradually with the increase of temperature, while the absorbance around 600 cm^{-1} as-

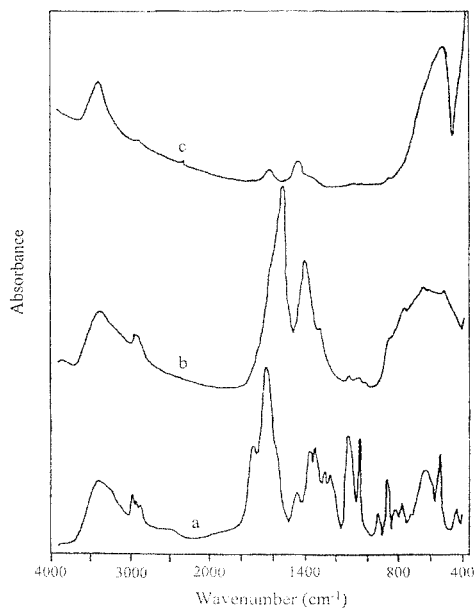


Figure 1 FTIR spectra of BTL. (a) Bottom: heated at 100°C for 1 h; (b) middle: heated at 400°C for 2 h; (c) top: heated at 650°C for 2 h.

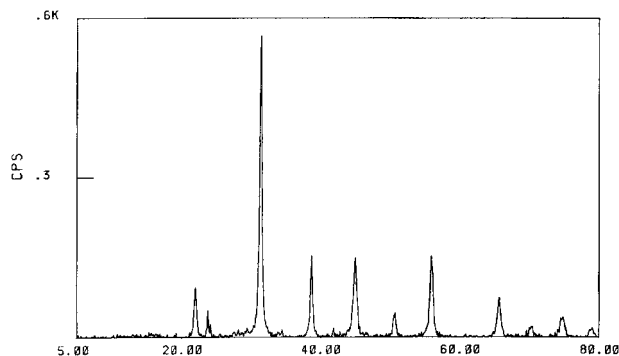


Figure 2 WAXD of as-prepared BaTiO_3 powders.

sociated to the formation of inorganic phase increased with increase in temperature. Thermal conversion of BTL at about 650°C in air into crystalline BaTiO_3 was confirmed by FTIR and XPS analysis as shown in Figures 1 and 2. The structure of the crystalline BaTiO_3 was in very good agreement with the results reported in literature.^{14–16}

Polyimide/Barium and Titanium Oxides (BTO) Nanocomposite Films

The polyimide precursors based on PMDA and ODA was used as polymer matrix in our investigation. The intrinsic viscosities of poly(amic acid) and poly(amic ester) were 1.54 and 0.67 dL/g. Similar to the sol-gel process, doping involves the solution blending followed by a thermal treatment to assist inorganic phase transformation and imidization. In most cases, doping was carried out in poly(amic acid)s solution. For comparison, doping was also conducted in poly(amic ester) solution in our study. In general, codoping employed a dopant containing two kinds of metal elements is less adopted than common doping. We have successfully developed a codoping process by taking the advantages of BTL. Barium titanium lactate can be directly added as a solid or as a solution to the poly(amic acid) or poly(amic ester) solution. The water may come from inner produced by imidization and outer added by additional water.

The Ba and Ti contents in hybrid films were determined by ICP, and the results were listed in Table II. The ratios of Ba to Ti were almost kept at a ratio of equal mol. The structure of doped polyimides was first investigated by FTIR. As showed in Figure 3, there is no significant shift in the vibrational frequency of polyimide IR bands,

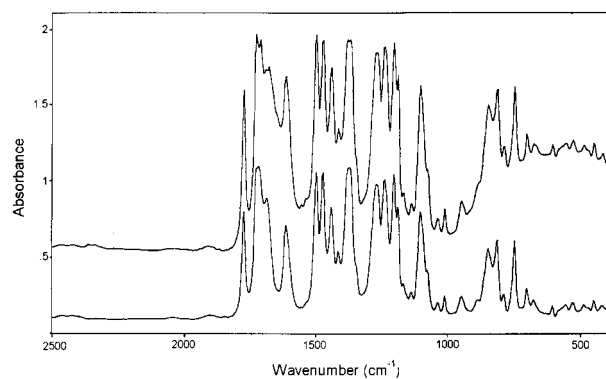


Figure 3 FTIR spectra of (a) bottom: polyimide film and (b) top: polyimide hybrid films.

in particular the polyimide carbonyl frequency. The peaks at 1780 and 1730 cm^{-1} are associated with the imide carbonyl band, and are quite insensitive to the presence of the component of inorganic oxides. However, a marked increase in IR absorption and a distinct broadening of the bands were observed in the 800–500 cm^{-1} region of the spectrum of doped films. This resulted from the formation of inorganic oxides.¹⁷

The chemical states of the barium and titanium compound existed in polyimide matrix were further characterized by XPS analysis, and the binding energies were listed in Table I. XPS data of the hybrid films were obtained at a take-off angle of 90° for maximum sampling depth, showing a well-defined photopeak. Binding energies of Ba and Ti for both sides (etched or nonetched) of these hybrid films were found to be essentially the same (within 0.5 eV). We have also measured binding energies of Ba and Ti in BaO, TiO₂, and BaTiO₃ and summarized them in Table I. It was found that binding energies of Ba and Ti in hybrid films appeared closer in value to those of BaO and TiO₂ than to that of BaTiO₃. This was further

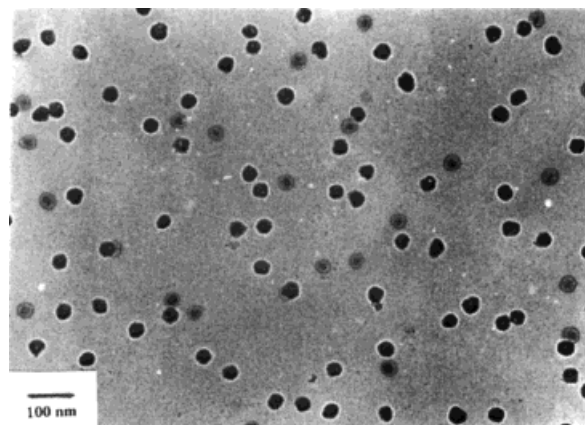


Figure 4 TME microphotograph of hybrid film (PI-20).

supported by XPS data (Table I) for polyimide hybrid film with a new binding energy at 531.3 eV (O1s) that is consistent with those in BaO and TiO₂ rather than that in BaTiO₃. The formation of oxides may be rationalized by the hydrolysis and dehydration of Ba and Ti complex during curing. The source of oxygen for the metal oxides can be the water added in codoping or formed during imidization. In addition, the limitation of temperature of imidization may response for the barrier of transformation from BTL to BaTiO₃.

Hybrid polyimide films were transparent. The morphology of hybrids was further investigated by TEM and AFM, and microphotographs were showed in Figures 4 and 5, respectively. TEM microphotographs revealed a uniform distribution of spherically shaped particles with no more than 50 nm in size throughout the bulk of the film. AFM image was performed to show the morphology of the hybrid film surface. In a 2D image, bright domains refer to the inorganic particles together with relatively less bright surroundings

Table I Binding Energy of Related Atoms (eV)

Sample	O1s	N1s	C1s	Ba3d _{5/2}	Ti2p _{3/2}
BaO	530.9			779.6	
TiO ₂	531.8				458.4
BaTiO ₃ ^a	529.1			778.8	457.7
PI film	534.0	402.0	287.0		
Hybrid film ^b	534.0, 534.6, 531.3	402.0, 403.0	287.0	779.7	458.4

^a Obtained by stearic acid-gel method.

^b Polyimide hybrid with 20 wt % BTL (PI-10).

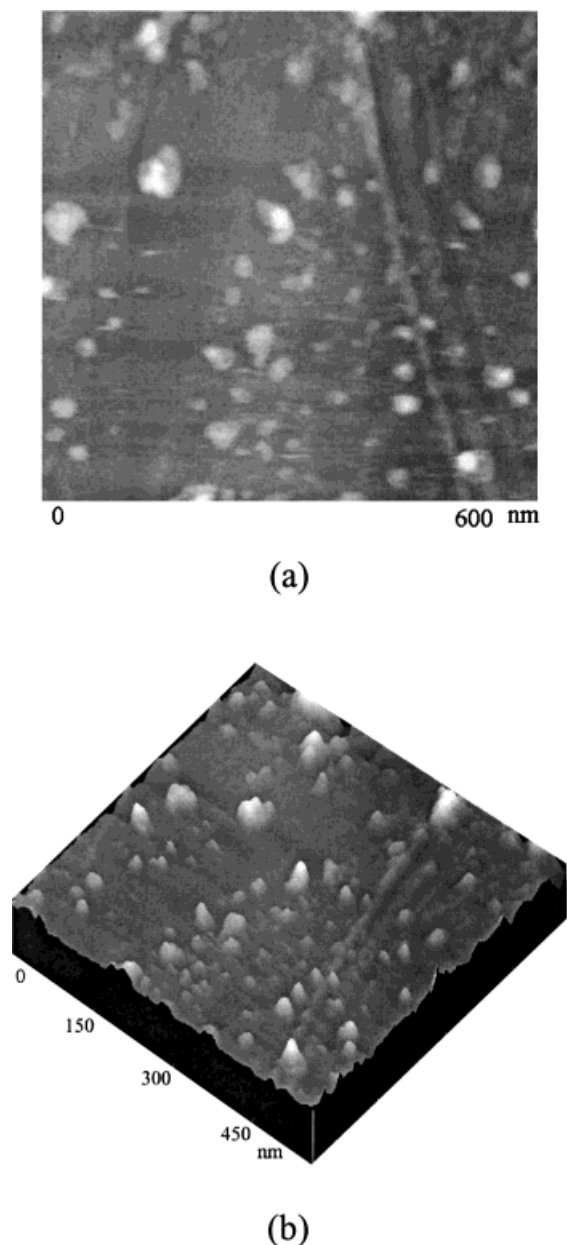


Figure 5 AFM images of hybrid film (PI-20).

were observed. To investigate more precisely the film surface, the 2D image was reconstructed as a 3D image, which shows that inorganic particles seem to be embedded in the film surface. The surface roughness of hybrid film was below 30 nm. This result is quite different from many doped systems reported, which possessed layer structure with agglomeration and migration of inorganic phase.^{5–7} Also, an opaque film was obtained when poly(amic ester) was used a precursor. This result may indicate that BTL have good compatibility with poly(amic acid) and the carboxyl group in poly(amic acid) can have strong interaction with metal centers. Compared with the undoped film, new binding energy at 403.0 eV appeared in hybrid film could be attributed to nitrogen (1s) for the amide nitrogen of poly(amic acid)s caused by the incomplete imidization. The new nitrogen binding energy could be correlated with the appearance of an oxygen (1s) binding energy at 534.6 eV (Table I). Similar phenomenon was observed by Taylor and coworkers.¹⁸

A comparison of thermal stability of doped film with nondoped film was carried out using a TGA technique. The data of TGA, listed in Table III, indicated that the incorporation of barium and titanium mixed oxide decrease the thermal stability of the polyimide, especially in air atmosphere. It was reported that some dopants facilitated thermal degradation of polyimide caused by the catalytic effects of metal oxides.^{6, 10} Even so, the hybrid film has fairly good thermal stability with decomposition temperature of 5% weight loss above 500°C. For the mechanical properties, the modulus was improved but the tensile strength and elongation at break worsened compared with the nondoped control sample. However, the hybrid film codoped with 15% BaO/TiO₂ was still a flexible thin film.

The electric properties of the polyimide were actually changed by introducing inorganic oxides. Table III lists the lowered surface resistivity and

Table II The Surface Atomic Concentration of Related Elements (%)

PI-n ^a	O1s	N1s	C1s	Ba3d _{5/2}	Ti2p _{3/2}
PI-0 ^b	16.09	5.98	77.93		
PI-10 ^b	17.78	5.71	75.50	0.51	0.50
PI-10 ^c				0.55	0.53

^a PI: PMDA/ODA; n: BaO-TiO₂ wt %.

^b Measured by XPS method.

^c Calculated based on the ICP analyses.

Table III Properties of Polyimide Film and Polyimide Hybrid Films

PI-n ^a	PI-0	PI-5	PI-10	PI-15
BTL (wt %)	0	10	20	30
Ba/Ti (wt %) ^b	0	2.54/0.86	5.07/1.75	7.65/2.63
$T^{5\%}$ (°C), ^c in air	597		521	
$T^{5\%}$ (°C), ^c in N ₂	623		543	
Strength (MPa)	193.84		134.06	
Elongation (%)	16.98		3.51	
Modulus (GPa)	2.14		2.87	
Surface resistivity (Ω)	> 10 ¹⁷	5.6 × 10 ¹⁴	3.2 × 10 ¹⁴	1.8 × 10 ¹⁴
Volume resistivity (Ω · cm)	> 10 ¹⁸	8.4 × 10 ¹³	2.7 × 10 ¹³	1.1 × 10 ¹³
ε	3.5		4.2	
tgδ(×10 ⁻³)	2.1		6.2	
d33(×10 ⁻³ c/N)	3.8		5.2	

^a PI: PMDA/ODA; n: BaO-TiO₂ wt %.

^b Determined by ICP.

^c Temperature at 5% weight loss.

volume resistivity for the doped polyimides. The hybrid films made a slow increase of conductivity with the increase of content of inorganic oxides. To date, the minimum volume resistivity we have been able to attain has been 10¹³ Ω·cm. In comparison with the original polyimide film, the decrease of volume resistivity was more remarkable than that of surface resistivity in contrast to other doped polyimide systems.^{6, 8} This can be attributed to the different types of distribution of the inorganic phase in the polyimide matrix. In addition to the results of TEM and AFM mentioned above, XPS study also supported that inorganic oxides in hybrid films had an even distribution rather than layer structure near the surfaces. As shown in Table II, the surface atomic concentrations (XPS data) of Ba and Ti elements were very close to that in the bulk (averaged values based on the ICP data). Oxygen atomic concentration in hybrid film (surface and bulk) would be expected to be higher than that in polyimide film due to the formation of oxides. However, the difference of oxygen concentrations between surface of hybrid film and parent polyimide film was only 1.69%, which was almost equal to the increase (1.61%) of oxygen concentration averaged by surfaces and bulk. This may infer that the inorganic oxides did not agglomerate on the surface. Finally, the dielectric constant and piezoelectric constant of hybrid films were bigger than the polyimide.

CONCLUSION

A new barium and titanium precursor to BaTiO₃ or barium and titanium oxide, depending on the

varied condition, was developed. The homogeneous incorporation of the barium and titanium complex into poly(amic acid) solution results, on heating a solution-cast film, in polyimide hybrid material containing bimetallic oxide. The films produced by this technique are transparent, flexible, and high thermal stable. The low surface and volume resistivities and high dielectric and piezoelectric constant of hybrid film are due to mixed metal oxides homogeneous dispersed in the polyimide matrix.

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