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Fabrication and mechanism study of CuO layers on double surfaces of polyimide substrate using surface modification

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ABSTRACT

Formation process and mechanism of continuous CuO layers on double surfaces of polyimide films were studied. The composite films were prepared using the facile surface modification and ion exchange technique. By alkaline-induced chemical modification and ion-exchange reaction, Cu^{2+} ions were incorporated into the surface of polyimide substrate. Thermal treatment in ambient atmosphere resulted in the formation of CuO particles that further agglomerated on the film surface and produced well-defined CuO thin layers on the double surfaces of polyimide films. The changes in the chemical structure, surface morphology, crystalline state and the surface roughness with the increase of ambient temperature were investigated. It was interesting to find that the conversion of metallic copper and low valence sub-oxide Cu_2O to high valence oxide CuO was observed in the thermal treatment process. The agglomeration mechanism for the CuO particles was proposed and proved by three steps, which illustrated that copper-catalyzed and oxygen-assisted decomposition of the polyimide overlayer resulted in the agglomeration of CuO particles. The final composite films retained the thermal stability of the pure polyimide.

1. Introduction

Over recent years, aromatic polyimide has been considered to be one of the most important substrates of composite materials, because of its excellent mechanical properties, thermal stability and chemical resistance [1–4]. The fabrication of metal or metal oxide nanoparticles onto polyimide surfaces has attracted much attention due to the combination of both the outstanding properties of polyimide and the unique functions of nanoparticles. Inorganic nanoparticles, such as Ag [5–7], Cu [8–10], Pd [11], Ni [12], Au [13], NiO [14], Fe_2O_3 [15], SnO_2 [16,17], ZnO [17,18] and Co_3O_4 [19], have been incorporated onto polyimide surface respectively to endow polyimide with conductive, reflective, catalytic, semiconductive or magnetic properties. For example, the copper metallization of polyimide substrate is important in the fabrication of microelectronic devices including large-scale integrated circuits (LSI) and printed circuit boards (PCB) [9]. Silver metallized polyimide films with excellent reflective and conductive properties are widely attractive in the microelectronics and aerospace industries [6]. The incorporation of semiconductive metal oxide, such as SnO_2, Co_3O_4, on polyimide surface provides potential applications in catalysis, gas sensing, conducting electrodes, as well as in lithium batteries [16,19].

Conventional approaches for the fabrication of polyimide composite films mainly focused on external deposition process which directly deposited metal phase onto polyimide substrate or further oxidized the deposited metal to metal oxide [20–22]. A well-established inorganic layer could be formed on the film surface. However, this process always leaded to poor adhesive property between inorganic layer and polymeric layer. In the 1990s, Southward and coworkers [23] developed an in situ method, which involved dissolving proper metal salts or complex into polyimide precursor solution. Thermal treatment converted metal salt or complex to corresponding metal or metal oxide nanoparticles which further aggregated on the film surface. This method provided an outstanding adhesion at polymer-inorganic interface. Surface-silvered polyimide films fabricated with this technique can obtain a maximum reflectivity more than 97% and the surface resistivity less than 0.1 Ω/square. However, the metal complex is usually unstable and quite expensive. Furthermore, polyimide substrate suffered from a serious degradation during thermal treatment [24,25].

Recently, surface modification and ion-exchange technique provided the probability of combining the advantages of both external deposition process and in situ synthesis process. An alkaline induced surface hydrolysis was performed on polyimide film surfaces to obtain ion exchangeable carboxylate groups. The thickness of the modified layer can be controlled by the alkali treatment conditions such as concentration, time and temperature. Metal ions were incorporated into the modified layer via ion exchange reaction.

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The corresponding metal or metal oxide particles were formed by reduction, decomposition or oxidization. With this method, polyimide films coated with NiO [14], Co_3O_4 [19], Ag [6,7] or Cu [9,10] layers have been prepared. Much attention was paid on the formation process of inorganic layers on polyimide film surface, but the aggregation mechanism of inorganic nanoparticles has rarely been studied.

As a member of transition metal oxide family, CuO in nanometer-scale dimension exhibits advanced functions in catalyst, semiconductor, gas sensor, and metallurgy [26–29]. Here, we report the fabrication of CuO layer on double surfaces of polyimide film via surface modification and ion-exchange technique. To our knowledge, CuO layers contained polyimide films prepared in this technique have not been reported. Furthermore, a mechanism for the aggregation of CuO particles has been proposed according to the experimental results. The mechanism is scientifically proved by a three-step experiment, confirming to be a copper-catalyzed decomposition of polymer overlayer assisted by oxygen. The thermal stability and adhesion property for the composite film have been extensively investigated.

2. Experimental parts

2.1. Materials

Commercial 80 μm thick pyromellitic dianhydride–oxydianiline (PMDA–ODA)-type polyimide films were purchased from Liyang Huajing Ltd., Jiangsu province, China. Films were cleaned using ethanol solution under ultrasonication for 15 min prior to use. Potassium hydroxide (KOH) (analytically pure) and copper(II) nitrate ($Cu(NO_3)_2{\cdot}3H_2O$) (analytically pure) were purchased from Sinopharm Chemical Reagent Co., Ltd., and used without further purification.

2.2. Preparation of composite films

The procedure to prepare the CuO layer on the polyimide surface was similar to those of the surface silvered polyimide films previously reported [6]. Briefly, commercial polyimide films were initially immersed into a 2 M KOH aqueous solution at 15 °C for 13 h to perform alkaline-induced hydrolysis of film surface, and then washed with deionized water. The surface modified films were next immersed into a 0.4 M $Cu(NO_3)_2$ aqueous solution at 15 °C for 1 h to load copper ions into the modified region via ion exchange. After being rinsed thoroughly with copious amount of deionized water, the copper(II)-contained films were thermally treated in an forced-air oven at ambient atmosphere to the target temperature. The cure cycles involved heating over 1 h to a temperature of 135 °C and then holding for 1 h, followed by heating to 350 °C over 2 h, and then keeping the temperature constant at 350 °C.

2.3. Characterization

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra of the PI films were recorded using a Nicolet Nexus670 IR spectrometer with an ATR attachment.

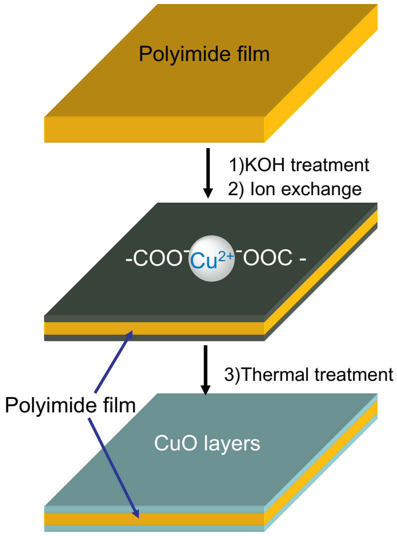
X-ray diffraction (XRD) patterns were performed on an X-ray diffractometer (D/Max2500VB2+/PC, Rigaku, Japan) at a scanning rate of 0.18° per second, in the 30–90° region. The X-ray beam was generated by a Cu Kα radiation source ($\lambda = 0.154056$ nm), using a tube voltage of 40 kV and a current of 200 mA.

Surface morphology was recorded on a Hitachi S-4700 field-emission scanning electron microscope (FE-SEM) operating at an accelerating voltage of 20 kV. All the samples were coated with a ca. 5 nm of platinum layer prior to measurement.

Cross-sectional morphology was observed using a Hitachi H-800 transmission electron microscope (TEM) at an accelerating voltage at 200 kV. The samples were sectioned into slices using an ultramicrotome with a diamond knife. These thin sections were mounted onto the carbon-coated TEM copper grids for observation.

X-ray photoelectron spectroscopy (XPS) measurement was carried out on an ESCALAB 250 spectrometer (Thermo Electron Corporation) with a monochromatic Al Kα X-ray source and a magnetic lens system that yields high spatial resolution and high sensitivity. The pressure in the analysis chamber was maintained at 2×10^{-10} Torr or lower during each measurement.

Atomic force microscopy (AFM) observations were carried out using a Nanoscope IIIa AFM system (Digital Instruments Inc., USA) operating in tapping mode. A scanning area of 2 μm × 2 μm was examined in air at room temperature. The arithmetic mean



Scheme 1. Schematic illustration for the preparation of polyimide/CuO composite films.

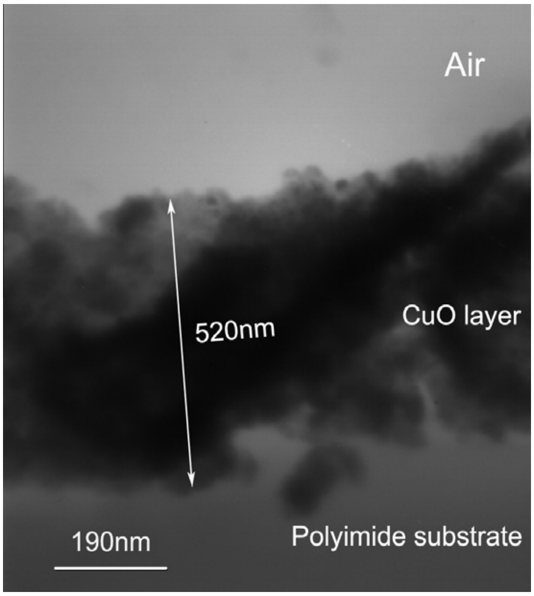


Fig. 1. TEM image for the copper ions contained film thermally treated at 350 °C for 7 h.