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Fabrication of silver interdigitated electrodes on polyimide films via surface modification and ion-exchange technique and its flexible humidity sensor application

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ABSTRACT

In this paper, the flexible capacitive humidity sensors using the polyimide foils as the substrate together with the moisture sensitive materials had been investigated. A simple and low cost inkjet-printing method had been developed to form silver interdigitated electrodes on PI foils. Two kinds of capacitive humidity sensors with Ag IDEs were constructed. And the humidity sensor characteristics such as sensitivity and hysteresis were analyzed. The results indicated that the metallization of Ag on PI is potential for various future flexible applications.

1. Introduction

Humidity, which is the amount of water vapor in the air, is a fundamental concern in a wide variety of commercial and industrial applications. Various kinds of humidity sensors are available based on different measurement principles such as resistive, capacitive, hygrometric and thermal techniques. Nowadays, related to the requirement of low energy consumption, low cost and high performance, the classic transduction mechanism of these humidity sensors is capacitive. Modern CMOS compatible technologies are capable of fabricating capacitive humidity sensors. Normally, the sensor configuration is silicon or glass as the substrate and the polymers, like polyimide, as the humidity sensitive element [1–6]. However, they are rigid and not sufficient for the cases such as non-rigid and non-planar detection. In addition, the processes are complex and the long fabrication cycles and the expensive facilities are required.

Methods for fabricating small devices with flexible substrates, such as polyimide [7–9] and parylene [10], have been developed recently. Among these flexible materials, various polyimide products (tapes, films, etc.) are common utilized due to its outstanding characteristics such as excellent electrical and thermal insulation, good mechanical strength, high chemical resistance and high temperature stability. Polyimide tapes can be chosen to as both the substrate and the sensing element for humidity. There is a lot of interest at present in fabricating humidity sensors on polyimide. The most frequently used structure is depositing the sensing layer, always polymers, over the interdigitated electrodes (IDE) capacitor. The polyimide here is only used as substrate, and the electrodes are fabricated by metal sputtering [11–13]. The other interesting type is to use the polyimide as humidity sensing material, and the electrodes are fabricated by screen printing or inkjet-printing [14]. Overall, for flexible sensor application, it is necessary to establish a kind of PI/metal formation technique which can make use of the humidity properties of PI film while maintaining the excellent properties of PI and metals. The surface modification and ion-exchange technique is a desirable route to this kind of purpose, which has been mainly used to prepare surface metallized polyimide films [15–18]. This technique comprises the surface hydrolysis of PI film in alkali solution resulting in the cleavage of the imide rings and the formation of carboxylic acid groups, the loading of metal ions through the ion exchange of the carboxyl group with the metal cations in the inorganic metal salt aqueous solution, and the final heat treatment to generate the surface metallized PI films. The advantage of this surface modification and ion-exchange technique includes that the microstructures and the thickness of the metal layers could be systematically controlled by initial alkali treatment and subsequent ion-exchange conditions (concentration, time and temperature), as

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well as the final thermal treatment procedure [15,16,18]. In addition, in the ion-exchange process, no anionic groups, such as Cl^-, SO_4^{2-} and NO_3^-, are incorporated into the films, which can maintain the excellent thermal and mechanical properties of PI films. This technique also has other advantages such as simple processing, low cost and batch fabrication.

The aim of this study is to prepare PI/Ag nanocomposite films on its film surface layers via the surface modification and ion-exchange technique. In this study, the commercial available polyimide tape was used not only as humidity sensing material but also the flexible substrate, and the simple surface modification and patterning self-metallizing procedure had been utilized to fabricate the silver IDE on polyimide. The humidity sensing behaviors of the sensors employed simplified process were investigated.

2. Experimental

2.1. Material

Commercial available 50 μm thick pyromellitic dianhydride–oxydianiline (PMDA–ODA) polyimide films were purchased from Qian Feng Insulating Material Company (Shanghai, China). $AgNO_3$ (99.8%) were purchased from Aladdin Industrial Corporation (Shanghai, China). KOH, $NH_3{\cdot}H_2O$ and H_2O_2 (30%) were of analytical quality and used without further purification.

2.2. Ag metallization and Ag IDEs preparation

The preparation procedure for PI/Ag nanocomposite films comprises hydrolyzing, ion exchange, and thermal treatment steps, just as shown in Fig. 1. A rapid silver reduction method has also been developed here to make a contrast. After cleaning, polyimide films were first immersed in 4 M KOH aqueous solutions at 25 °C for 3.5 h and then washed with large amount of DI water. Through this step, it was believed that K^+ ions were embedded in the polyimide surface and polyimide surface was chemically modified into poly (amic acid), which is known as PAA [18]. After that, the films were immersed in 0.02 M $AgNO_3$ and $NH_3{\cdot}H_2O$ solution for 20 min subsequently. K^+ ions were then displaced by Ag^+ ions. After being rinsed with copious amount of DI water, the PI films were dried at room temperature.

The KOH-modified PI films were then pasted on A4 paper flatly and the masking patterns were inkjet-printed on the treated PI films. The printed PI films were baked at 86 °C for 30 min. The carbon ink was used as the masking for Ag metallization. Ag IDEs were fabricated by two strategies: one is that the inkjet printed PI films were directly dipped into H_2O_2 (30%) solution to reduce silver ions to silver atoms. The other is that the inkjet printed PI films were stepwise thermally cured in a forced air oven. The curing cycles in detail was as follows:

$$\text{Room temperature} \xrightarrow{20\ \text{min}} 130^\circ\text{C}/20\ \text{min} \xrightarrow{120\ \text{min}} 280^\circ\text{C}/120\ \text{min} \xrightarrow{20\ \text{min}} 300^\circ\text{C}/120\ \text{min}$$

The stepwise thermal curing not only induced the silver ions reduction, but also re-cycloimidized the PAA to the polyimide [18]. The structure change of the PI is also shown in Fig. 1. In the context, two kinds of sensors were denoted as PAA-based and PI-based sensor, respectively.

2.3. Sensor characterization and humidity measurement system

The prepared Ag IDEs were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Hall Effect measurement system. The sensitive materials were characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). X-ray diffractions (XRD) of the composite films were performed using an X-ray diffractionmeter (D/Max2500VB2+/PC, Rigaku, Japan). The X-ray beam was generated by a Cu Kα target (λ = 0.154056 nm), using a tube voltage of 40 kV and a current of 200 mA. All the samples had the scanning angle between 5° and 90°. The surface morphology of the composite films was characterized with a scanning electron microscope (SEM) (SEM-4700, Hitachi, Japan) at an accelerating voltage of 20 kV after samples were coated with ca. 5 nm of palladium–gold alloy. The resistivity value of Ag films was performed by RH2035 Hall effect measurement system with the magnetic field of 0.425 T. ATR-FTIR spectrum of the film was recorded at room temperature, with a spectral resolution of 0.09 cm^{-1} in the range of 12000–350 cm^{-1} on Nicolet 6700 with diamond crystal.

The humidity testing was proceeded in the Humidity Detecting Box (Changwang JKZ1 Radiosonde detection box, Shanghai, China). And five kinds of saturated salt solution: 16%, 33%, 50%, 73%, 90% RH achieved by LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, K_2SO_4 saturated solutions at 25 °C, were used as the humidity standard. The capacitance values were tested by precision LCR meter (Tonghui TH2817A, Changzhou, China), and the output data were recorded by software.

3. Results and discussion

3.1. Sensor characterization

Ag IDEs can be formed quickly and easily by the two developed themes. Fig. 2(a) depicted the optical images of a sensor array

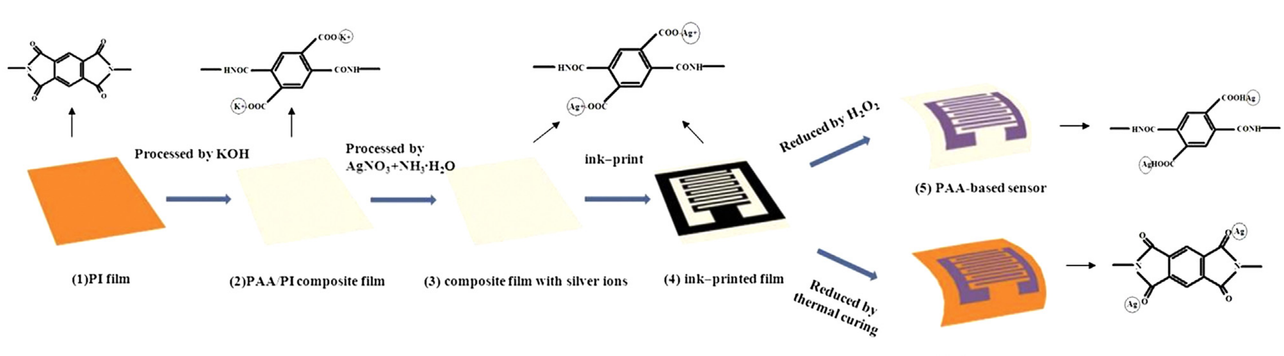

Fig. 1. The process procedure of the PI capacitive humidity sensors with Ag IDEs.