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Structural and electrical properties of Ag films sputter-deposited on HCl-doped and undoped polyaniline substrates

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HIGHLIGHTS

- Ag films sputter-deposited on HCl-PANI and PANI.
- The Ag film converts to the AgCl film on the HCl-PANI.
- A variation of conductance of the film on HCl-PANI with time.
- The reaction controlled process dominates the formation of AgCl film.

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ABSTRACT

Ag films were sputter-deposited on HCl-doped polyaniline (HCl-PANI) and undoped polyaniline (PANI) substrates at 300 K. The 50 nm- and 200 nm-thick Ag films grown on HCl-PANI substrates convert respectively to the AgCl film and the AgCl–Ag composite film because Cl ions in the HCl-PANI substrate diffuse into the Ag films and the chemical reaction of Ag atoms with Cl ions occurs. The AgCl and AgCl–Ag composite films are porous. The Ag film grown on PANI substrate has a dense structure and its grain size increases with increasing film thickness. The conductance of the film grown on the PANI substrate does not change markedly with aging time. For the Ag film grown on the HCl-PANI substrate, however, the conductance decreases significantly with increasing aging time. After the aging time reached a threshold value, the conductance does not change with the aging time. The threshold time increases with increasing film thickness. The reaction controlled process dominates the formation of AgCl film on the HCl-PANI substrate.

1. Introduction

Polyaniline (PANI) is an important conducting polymer because of its good environmental stability, low cost, ease of preparation and high conductivity. Silver is a noble metal widely used due to its high visible-light reflectivity and high conductivity. Nanocomposites composed of PANI and Ag nanoparticles have attracted considerable attention for their potential applications in electrocatalysis and electronic devices, e.g. Refs. [1–6]. As reported previously [1–6], the PANI-Ag nanocomposites were synthesized by the chemical methods. On the other hand, a silver thin film can be prepared on PANI by physical vapor deposition, forming a sort of Ag/PANI composite material. An amount of Ag in this composite material can be easily controlled by adjusting deposition time. However, few studies on the Ag thin films grown on PANI have been reported. Krishna et al. [7] used a vacuum evaporation method to deposit Ag films on PANI. They found that the Ag deposition did not disturb markedly the PANI structure although there was a slight diffusion of Ag into the PANI.

Recently, we have prepared nanocomposites composed of HCl-doped PANI and Ag nanoparticles by a chemical and physical combinative method [8]. Since the reaction of Ag with Cl ions in the HCl-PANI occurred, the HCl-PANI-AgCl nanocomposites were obtained although we initially tried to prepare HCl-PANI-Ag nanocomposites. It has been proposed that PANI-AgCl nanocomposites have potential applications in sensors [9]. We consider whether the AgCl film can be prepared on the HCl-PANI substrate by physically depositing the Ag film on HCl-PANI

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followed by the diffusion-reaction of Ag with Cl ions in the HCl-PANI. As it is well known, the AgCl film is a significant electrode for applications in electrochemistry, chemical and biological sensors [10–13]. Furthermore, it is considered that AgCl/HCl-PANI composite materials have potential applications in electrochemistry, chemical and biological sensors. In the present work, Ag films were sputter-deposited on HCl-PANI and PANI substrates at 300 K. Structure and composition of the films were studied by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDX). Electrical properties of the films were measured at room temperature by a four-point probe technique.

2. Experimental procedure

All the chemical reagents were purchased from Beijing Chemical Works and were analytical grade. Only aniline was doubly distilled under reduced pressure and stored in refrigerator (at about 4 °C) prior to using. The other chemical reagents were used without further purification. HCl-PANI was chemically synthesized using the well-established polymerization procedure [14]. The polymerization procedure is summarized as follows: (1) Aniline (0.1 mol) was dissolved in 100 mL aqueous hydrochloric acid (HCl, 1 mol L^{-1}) taken in a three-neck flask. The mixture solution was cooled and stirred at −3 °C by a magnetic stirrer. (2) 51.5 mL ammonium persulfate solution (2.4 mol L^{-1}) in a constant pressure funnel was slowly added into the mixture solution for 1 h in order to avoid heating the reaction mixture. The reaction proceeded at −3 °C for 8 h. (3) The final solution was filtered. (4) The protonated precipitate was washed with deionized water, acetone and ethanol until the washing water, acetone and ethanol became colorless and the pH was equal to 7. (5) The powder was dried at 50 °C in oven for two days. The HCl-PANI powder was obtained.

The preparation method of the undoped PANI powder is similar to that of the HCl-PANI powder, as mentioned above. Only a new step was added between step 2 and step 3. Namely, after finishing step 2, 100 mL ammonium hydroxide (NH_4OH) solution (1 mol L^{-1}) in a constant pressure funnel was slowly added into the reaction mixture solution and the reaction proceeded at −3 °C for 1 h [15,16]. Finally, the PANI powder was obtained.

Both HCl-PANI and PANI powders were compacted to pellets with 0.4 mm in thickness and 15 mm in diameter. The HCl-PANI and PANI pellets were used as the substrates. Ag films were deposited on the HCl-PANI and PANI substrates at 300 K by using a RF sputtering system (SYKY Technology Development). The Ag target (99.99% in purity) with 50 mm in diameter faced the substrate. The distance between the target and the substrate was 100 mm. Prior to deposition, the working chamber was evacuated to a pressure lower than 2×10^{-4} Pa using a turbo molecular pump. The Ar gas (99.9995% in purity) pressure was 1.0 Pa and the sputtering power applied to the target was fixed at 100 W. The deposition rate was 23 nm $\min^{-1}$. The film thickness ranges from 50 nm to 200 nm.

XRD of D/Max-RB (Rigaku) was used to analyze the structure of the films. The XRD measurements were performed in a standard θ–2θ scan using a Cu Kα radiation filtered by a crystal monochromator (wavelength $\lambda = 0.15406$ nm). FE-SEM of SUPRA55 (Zeiss) was used to observe the morphology and the structure of the films. EDX equipped for the FE-SEM was used to analyze the composition of some areas in the films. Resistances R of the HCl-PANI substrate, the PANI substrate and the film were measured at room temperature using a four-point probe technique. The spacing between the two adjacent probe tips was 3 mm. The conductivity σ of the substrate and the film is given by [17,18]

$$\sigma = \frac{1}{3.31 \times R \times d} \quad (1)$$

where $3.31 \times R$ is the sheet resistance. d is the substrate thickness or the film thickness. The conductance of the Ag films is studied as a function of the aging time.

3. Results and discussion

3.1. Structure

Fig. 1 shows XRD patterns of the Ag films grown on the HCl-PANI substrates. As can be seen from Fig. 1, for the 50 nm-thick film, no diffraction peaks of Ag are observed. The XRD patterns only show the diffraction peaks of AgCl. It means that the Ag film converts to the AgCl film and the AgCl film is formed on the HCl-PANI substrate. For the 200 nm-thick film, both AgCl and Ag diffraction peaks are observed. It indicates that the AgCl–Ag composite film is formed on the HCl-PANI substrate for the thick film. It is considered that Cl ions in the HCl-PANI substrate diffuse into the Ag film. The formation of AgCl is attributed to a chemical reaction of the Ag atoms with the Cl ions [1]. The lattice constant of the AgCl is calculated by the diffraction peaks of AgCl(111), AgCl(200) and AgCl(220). The lattice constant of the 50 nm-thick AgCl film is 0.5538 ± 0.0005 nm and that of AgCl in the 200 nm-thick AgCl–Ag composite film is 0.5544 ± 0.0003 nm. The lattice constant of Ag in the 200 nm-thick composite film is 0.4084 ± 0.0002 nm, which is equal within errors to the lattice constant of the Ag bulk (0.4086 nm). The XRD patterns in Fig. 1 show that the HCl-PANI substrates have a crystalline structure of emeraldine salt (ES-I) of PANI [15]. The diffusion of Cl ions from the HCl-PANI substrate into the film could not change the ES-I structure of PANI.

Fig. 2 shows XRD patterns of the Ag films grown on the PANI substrates. As shown in Fig. 2, the diffraction peaks of Ag are observed. The lattice constant of the Ag films is calculated by the diffraction peaks of Ag(111), Ag(200) and Ag(220). The lattice constant of the 50 nm-thick Ag film is 0.4082 ± 0.0001 nm and that of the 200 nm-thick Ag film is 0.4086 ± 0.0002 nm. The lattice constant of the thick Ag film is equal to that of the Ag bulk (0.4086 nm). Comparing Fig. 1 with Fig. 2, it further confirms that the AgCl film or the AgCl–Ag composite film grows on the HCl-PANI substrate. The XRD patterns in Fig. 2 show that the PANI substrates have a crystalline structure of emeraldine base (EB-I) of PANI [15],

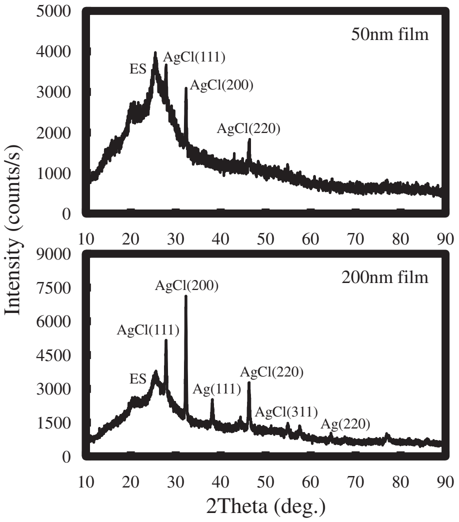

Fig. 1. XRD patterns of the Ag films grown on the HCl-PANI substrates.