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

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ABSTRACT

Ni films with a thickness of 45–240 nm were sputter-deposited on HCl-doped polyaniline (HCl-PANI) substrates at 300 K, forming the Ni/HCl-PANI composites. All the Ni films grow with columnar grains. The grain size increases with increasing film thickness. A temperature dependence of the resistance within 5–300 K reveals that all the Ni/HCl-PANI composites exhibit a metal–semiconductor transition. The transition temperature lowers with decreasing film thickness. The composite shows a metallic conduction behavior at temperatures below the transition temperature and a semiconducting behavior at temperatures over the transition temperature. A temperature coefficient of resistance increases with film thickness in the temperature range of the metallic conduction. A decrease of the resistance with temperature becomes more significant with decreasing film thickness in the temperature range of the semiconducting behavior.

Ni films as an important magnetic material have been investigated by many research groups, e.g. Refs. [1–5]. Polyaniline (PANI) is an important conducting polymer because of its good environmental stability, low cost, ease of preparation and high conductivity. The conducting PANI composites containing Ni nanoparticles (PANI-Ni composites) were mostly studied because of their potential applications in catalyst, electromagnetic and electronic devices [6–10]. However, few studies on the Ni film grown on PANI have been reported. Damian and Omanovic [11] electrodeposited Ni film on PANI preparing the Ni/PANI catalyst. They found that this catalyst had a higher catalytic activity compared with the tradition Ni catalytic material. Prasad et al. [12] electrodeposited PANI thin films on Ni obtaining the PANI/Ni catalyst. The PANI/Ni catalyst exhibited a higher catalytic activity relative to Pt. Corte et al. [13] electrodeposited PANI particles on Ni film preparing the PANI/Ni composite electrode. The composite electrode with a higher PANI particle content had a higher catalytic activity. It is considered that the Ni film grown on PANI (Ni/PANI) or the PANI film grown on Ni (PANI/Ni) can also be a sort of the composite. The Ni/PANI and PANI/Ni composites also have potential applications like the PANI–Ni composites. A study on the Ni/PANI and the PANI/Ni is significant for fundamental and practical viewpoints.

As mentioned above, the Ni/PANI and PANI/Ni composites were prepared by electrodepositing and their catalytic activities were mainly studied [11–13]. On the other hand, sputter deposition is the usual method to prepare thin films because it can easily control the composition, structure and physical property of the films and can enhance the adhesion of the film to the substrate. Besides, the sputtered atoms have a high energy when they arrive at the substrate surface or the growing film surface. These energetic adatoms could improve the structure of the film sputter-deposited at room temperature. Room temperature deposition can eliminate a thermal stress in the film and shorten the film preparation time due to no heating process as well as is suitable for the polymer substrates having a low decomposition temperature. Moreover, ferromagnetic conducting HCl-PANI–Ni composite was successfully prepared by direct current magnetron sputtering at room temperature [8]. Thus, in the present work, Ni films are sputter-deposited on HCl-doped PANI substrates obtaining the Ni/HCl-PANI composites. Structural and electrical properties of the Ni/HCl-PANI composites are studied as a function of the Ni film thickness.

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)

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was dissolved in 100 mL aqueous hydrochloric acid (HCl, 1 mol/L) 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) 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 HCl-PANI powder was compacted to pellets with 0.35 mm in thickness and 15 mm in diameter. The HCl-PANI pellets were used as the substrates. The DC magnetron sputtering system (KYKY) with the target inclined to the substrate at an angle of 45° was used [5]. The HCl-PANI substrates were placed in the working chamber via a load-lock chamber, which prevents the working chamber from air during changing the sample. 45 nm-, 140 nm- and 240 nm-thick Ni films were sputter-deposited on the HCl-PANI substrates at 300 K, obtaining the Ni/HCl-PANI composites. Prior to deposition, the working chamber was evacuated to a pressure lower than 4×10^{-4} Pa by using a turbo molecular pump. The Ar gas (99.9995% in purity) pressure was 1.0 Pa and the sputtering power applied to the Ni target (99.99% in purity) of 50 mm in diameter was fixed at 100 W. A distance between the target and the substrate was 100 mm. The substrate holder was rotated at a rotary rate of 8 rotation/min during deposition in order to obtain the uniformly thick film. The average deposition rate was 11 nm/min.

FE-SEM of SUPRA55 (Zeiss) was used to observe the morphology and the crystalline structure of the films. 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). A resistance R of the HCl-PANI substrate or the Ni film was obtained at room temperature using a four-point probe technique. The spacing between the two adjacent probe tips was 3 mm. The resistivity ρ of the substrate or the film is given by Ref. [8,15]

$$\rho = 3.31 \times R \times d \tag{1}$$

where $3.31 \times R$ is the sheet resistance. d is the substrate thickness or the film thickness. A resistance of the Ni/HCl-PANI composite was measured in the temperature range of 5–300 K using the Cryogen-Magnet system of CFM-5T-H3-CFVTI-1.6K-24.5 with the four-point probe (Cryogenic Inc.).

Fig. 1 shows FE-SEM microphotographs of the Ni films sputter-deposited on the HCl-PANI substrates. As can be seen from Fig. 1, the films grow with thin columnar grains perpendicular to the substrate surface and many voids are formed at the grain boundaries, i.e., the films have a porous structure. The grain size increases with increasing film thickness.

Fig. 2 shows XRD pattern of the 240 nm-thick Ni film sputter-deposited on the HCl-PANI substrate. As shown in Fig. 2, only diffraction peaks of Ni are observed. A lattice constant of the Ni film is calculated by the diffraction peaks of Ni(111) and Ni(220). The lattice constant of the Ni film is 0.3524 ± 0.0005 nm, which is almost equal to the lattice constant of the Ni bulk (0.35238 nm). The XRD pattern in Fig. 2 also shows that the HCl-PANI substrate has a crystalline structure of emeraldine salt (ES-I) of PANI [16].

According to the four-point probe technique measurements, a resistivity of the HCl-PANI substrate is $(2.51 \pm 0.03) \times 10^{-2}$ Ωm. Thus the resistance of the Ni/HCl-PANI composite is a parallel of the two resistances of the Ni film and the HCl-PANI substrate because both of them are conductive. The resistance R of the Ni/HCl-PANI composite is expressed as

$$R = \frac{R_F \times R_S}{R_F + R_S} \tag{2}$$

where R_F is the resistance of the Ni film and R_S is the resistance of the HCl-PANI substrate. Using Eq. (2), the R_F value can be calculated by the R and R_S values. Using Eq. (1), the resistivities of the Ni films grown on the HCl-PANI substrates are calculated to be 7.97×10^{-6} Ωm for the 45 nm-thick film, 3.82×10^{-6} Ωm for the 140 nm-thick film and 4.33×10^{-6} Ωm for the 240 nm-thick film, respectively. They are larger than a resistivity of the Ni bulk (6.16×10^{-8} Ωm). It is attributed to a large number of structure defects existing in the film compared with the bulk material.

Fig. 3 shows a temperature dependence of the resistance of the Ni/HCl-PANI composites with different film thicknesses. In Fig. 3, the resistance R at each temperature is normalized to the resistance R_5 at 5 K. As can be seen from Fig. 3, all the composites exhibit a metal–semiconductor transition. The transition temperature increases with increasing film thickness. The composite shows a metallic conduction behavior at temperatures below the transition temperature and a semiconducting behavior at temperatures over the transition temperature. A temperature coefficient of resistance increases with increasing film thickness in the temperature range of the metallic conduction. A decrease of the resistance with temperature becomes more significant with decreasing film thickness in the temperature range of the semiconducting behavior.

According to Eq. (1), Eq. (2) can be written as

$$R = \frac{1}{3.31 \times (d_F/\rho_F + d_S/\rho_S)} \tag{3}$$

where d_F and d_S are the Ni film thickness and the HCl-PANI substrate thickness, respectively. ρ_F and ρ_S are the resistivity of the Ni film and the resistivity of the HCl-PANI substrate. Eq. (3) can be further simplified as

$$\begin{cases} R = \frac{\rho_F}{3.31 \times d_F} & d_F/\rho_F \gg d_S/\rho_S \\ R = \frac{\rho_S}{3.31 \times d_S} & d_S/\rho_S \gg d_F/\rho_F \end{cases} \tag{4}$$

The resistivity ρ_F of the Ni film increases linearly with increasing temperature, i.e., the temperature dependence of the resistance is the metallic behavior. The resistivity ρ_S of the HCl-PANI substrate decreases with increasing temperature and it is similar to a semiconductor [17]. According to Eq. (4), when $d_F/\rho_F >> d_S/\rho_S$, the temperature dependence of the resistance of the Ni/HCl-PANI composite is dominated by the Ni film and exhibits the metallic behavior, i.e., the resistance increases linearly with increasing temperature. When $d_S/\rho_S >> d_F/\rho_F$, the temperature dependence of the resistance of the Ni/HCl-PANI composite is dominated by the HCl-PANI substrate and shows the semiconducting behavior, i.e., the resistance decreases with increasing temperature. Actually, the d_S value is 0.35 mm, which is very large compared with the d_F value. The room temperature resistivity of the Ni film is very small compared with that of the HCl-PANI substrate. Therefore, when $\rho_F << \rho_S$, i.e., in the low temperature range, the $d_F/\rho_F >> d_S/\rho_S$ condition can be satisfied. According to Eq. (4), the temperature dependence of the resistance of the Ni/HCl-PANI composite exhibits the metallic behavior in the low temperature range. Furthermore, the difference between ρ_S and ρ_F in the high temperature range is smaller than that in the low temperature range. Thus the $d_S/\rho_S >> d_F/\rho_F$ condition can be satisfied in the high temperature range. According to Eq. (4), the temperature dependence of the resistance of the Ni/HCl-PANI composite shows the