



Structure and giant magnetoresistance of carbon-based amorphous films prepared by magnetron sputtering



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ARTICLE INFO

Article history:

Received 15 June 2013

Received in revised form 16 January 2014

Accepted 17 January 2014

Available online 24 January 2014

Keywords:

Granular films

Magnetoresistance

Magnetron sputtering

ABSTRACT

Pure amorphous carbon (a-C) and Co-doped $\text{Co}_x\text{C}_{1-x}$ films were prepared on n-Si(100) substrates by dc magnetron sputtering. In Co–C films, the nano-sized amorphous Co particles were homogeneously dispersed in the amorphous cross-linked carbon matrix. The structures of a-C and $\text{Co}_x\text{C}_{1-x}$ films were investigated by X-ray photoelectron spectroscopy and Raman spectroscopy. The results showed that the a-C films were diamond-like carbon (DLC) films. After doping cobalt into DLC film, the sp^3 -hybridized carbon content in DLC composite films almost had no change. The as-deposited $\text{Co}_x\text{C}_{1-x}$ granular films had larger value of magnetoresistance (MR) than the amorphous carbon film. A very high positive MR, up to 15.5% at magnetic field $B = 0.8$ T and $x = 2.5$ at.% was observed in a $\text{Co}_x\text{C}_{1-x}$ granular film with thickness of 80 nm at room temperature when the external magnetic field was perpendicular to the electric current and the film surface. With increase of the film thickness and Co-doped content, the MR decreased gradually. It remains a challenge to well explain the observed MR effect in the $\text{Co}_x\text{C}_{1-x}$ granular films.

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1. Introduction

Amorphous carbon (a-C) thin films have attracted much attention recently due to their potential applications in hard coating, field emission and microelectronic devices [1–3]. More than one decade, metal containing diamond-like carbon (Me-DLC) films have been extensively studied because they cannot only maintain high hardness, low friction coefficient and high thermal stability, but also have adjustable electrical conductivity. This is obviously advantageous for its applications in the fields of electronics, optics, magnetics and catalysis [4–6]. Various deposition techniques have been used to fabricate Me-DLC composite films, such as ion beam assisted deposition [5], co-sputtering deposition [7], pulsed laser deposition (PLD) [8–10], electrolysis deposition [11], and electron cyclotron resonance chemical vapor deposition [6]. Currently, the researches on these carbon films mainly focused on their fabrication, microstructure, magnetoelectronic properties, and potential applications. For example, it was reported that the a-C films prepared by pulsed laser deposition had shown an apparent voltage-induced switch effect and a magnetoresistance (MR) of about 1% in 1 T magnetic field [10]. As we know, Co and C are immiscible and the metastable Co carbides (Co_2C and Co_3C) decompose easily into Co and C [12]. Co–C composite films therefore form a good metal/insulator system to be investigated. Using PLD method, Zhu et al. [9] have prepared Co–C

films and observed a large positive MR of 22% in the $\text{Co}_{0.02}\text{--}\text{Co}_{0.98}$ granular film on Si(100) at room temperature with $B = 1$ T.

In this article, we report the structure and MR properties of the pure a-C films and Co-doped amorphous $\text{Co}_x\text{C}_{1-x}$ granular films deposited on Si(100) substrates by magnetron sputtering at room temperature.

2. Experimental details

The $\text{Co}_x\text{C}_{1-x}$ thin films with $x = 0\text{--}25$ at.% were deposited on n-Si(100) substrates by magnetron sputtering at room temperature. The purity of the Co and C was better than 99.95% and the targets were pieced together with Co sectors putting on the well-proportioned graphite target. The Si(100) substrates were lightly doped with P resulting in a n-type material. Before deposition, the Si substrates were ultrasonically cleaned firstly in acetone and then in ethanol, etched by diluted HF solution and rinsed in de-ionized water. The working gas was Ar (99.99% purity). The deposition took place inside a chamber where the pressure was kept at 0.7 Pa, and the substrate was kept at room temperature. For comparison, pure carbon films were also deposited by magnetron sputtering. The structure and magnetic properties of the Co–C films were investigated by conventional X-ray diffraction (XRD, Philips X'Pert MPO Pro, $U = 40$ kV/ $I = 40$ mA, X'celerator, $\text{Cu-K}\alpha_1$: $\lambda = 1.54056$ Å, $0.0167^\circ/\text{step}$), scanning electron microscopy (SEM, FEI Nova NanoSEM 430) and physical properties measurement system (PPMS-9, Quantum Design Co.). The atomic concentration and binding energy for each element in the films were determined by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD, $\text{AlK}\alpha$, energy of photoelectron:

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1486.8 eV, $U = 15 \text{ kV/I} = 10 \text{ mA}$), and the intrinsic bonding structure of carbon-based film is also provided by Raman scattering (Ar⁺ laser of 532 nm) spectroscopy.

3. Results and discussion

Co–C films deposited by magnetron sputtering were characterized by XRD, as shown in Fig. 1 for an example. The results show that the film is in amorphous state in the as-deposited films. Scanning electron microscopy observation shows that the film thickness is in the range of 80–240 nm. Deposition rate, determined from the film thickness and deposition time, increases linearly with power about 0.35 \AA/s at 120 W and a total pressure of 0.7 Pa. SEM characterization shows that the microstructure of the carbon-based films are homogeneous distributed with mean particle size of about 30–40 nm, and Co particles are well dispersed in amorphous carbon (Fig. 2). The result is in consistent with some previous reports [9].

Fig. 3a is a typical XPS result for the as-deposited Co–C films. The whole spectrum consists of three main peaks at about 284.5, 531.0, and 778.4 eV, corresponding to the binding energy of C-1s, O-1s, and Co-2p, respectively. The relative atomic Co/C ratio calculated from XPS is about 2.5%. The fine spectrogram of Co-2p is shown in Fig. 3b, which can be assigned to Co atoms bonded to oxygen owing to the surface oxidation when exposed to air. It was reported that cobalt component existed in atomic state, and dispersed randomly in the amorphous carbon matrix indicated by TEM [9]. In our work, the binding energies of the Co-2p peak (Fig. 3b) in pure cobalt and cobalt carbides almost coincide with each other. Moreover, the structural change of the as-deposited samples can be determined by the curve-fitted C-1s spectra according to the Gaussian fitting: C=C (284.5–284.7 eV), C–C (285.5–285.8 eV) and C–O (288.1–288.4 eV) [13]. As shown in Fig. 3c, the C-1s peak was fitted by three Gaussian peaks centered at 284.52, 285.38, and 288.29 eV with area percentages of 78.7%, 16.8%, and 4.5%, respectively. The peaks at 284.52 eV and 285.38 eV correspond to the binding energy of carbon–carbon bonds, and the other peak corresponds to those of C–O bond. No peak corresponding to the binding energy of C-1s in cobalt carbide was observed. It indicated that the C-1s peak in Co doping films did not vary evidently from amorphous carbon film to graphite film, and the doping of Co did not enhance the graphitization of carbon film. This is different from the Fe doping which can increase sp³-hybridized carbon in the films [11]. Fig. 3d shows the fitting result of the O-1s peak in the film. Two major peaks centered at 529.84 and 531.68 eV with area percentages of 12.6% and 82.9%, respectively, correspond to the binding energy of O-1s in cobalt oxide (CoO) and oxygen. It is believed that the formation of CoO is due to surface oxidation of the Co clusters in the film. The contribution of this small amount of CoO to the magnetic properties of the film could be ignored.

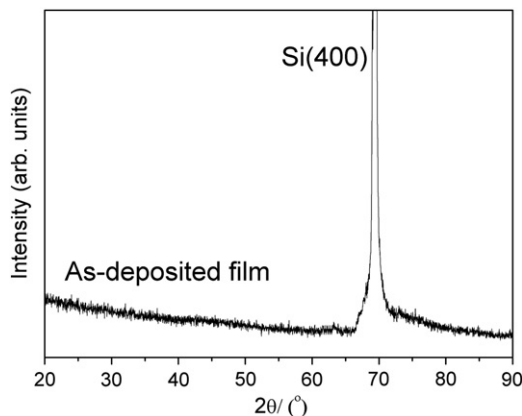


Fig. 1. XRD pattern of as-deposited $\text{Co}_x\text{C}_{1-x}$ ($x = 2.5 \text{ at.}\%$) composite film deposited at room temperature.

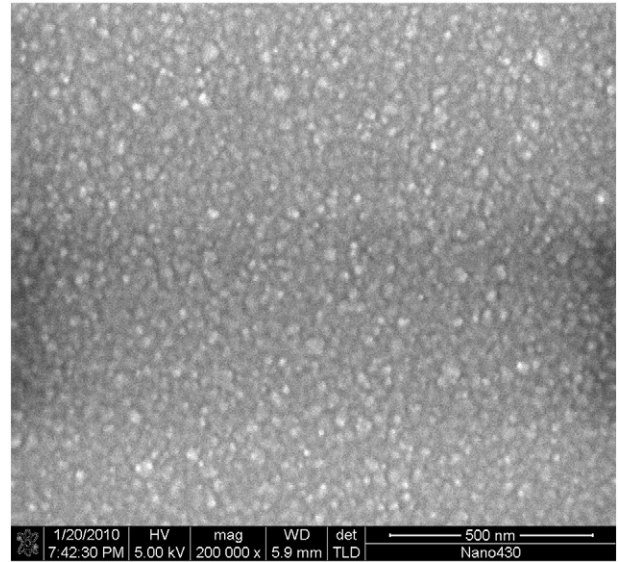


Fig. 2. The SEM pattern of as-deposited Co-DLC films (2.5 at.% Co) deposited at room temperature.

Furthermore, the intrinsic bonding structure of carbon-based film is also provided by Raman scattering (Ar⁺ laser of 532 nm) spectroscopy. And the main characteristics are the D and G bands appeared in the range of $1200\text{--}1700 \text{ cm}^{-1}$ [14]. As shown in Fig. 4, both D and G bands centered at 1388 and 1573 cm^{-1} appear in the as-deposited samples, which are typical DLC Raman spectrum. Therein, the G band is attributed to E_{2g} vibrational mode arising from the bond stretching of all pairs of sp² atoms in both rings and chains, whereas the D band is assigned to the breathing modes of sp² ring structure in disorder graphite [14,15]. To further identify the internal structure of the as-deposited samples, all the Raman spectra are fitted with a Gaussian profile after background correction. From Fig. 4a and b, the positions of D and G bands do not shift obviously, and the I_D/I_G ratio almost has no variation compared with that of pure DLC films. Ferrari and Robertson found that there is a relationship between the visible Raman spectra and the sp³ fraction in amorphous carbon films and the sp³ content increased

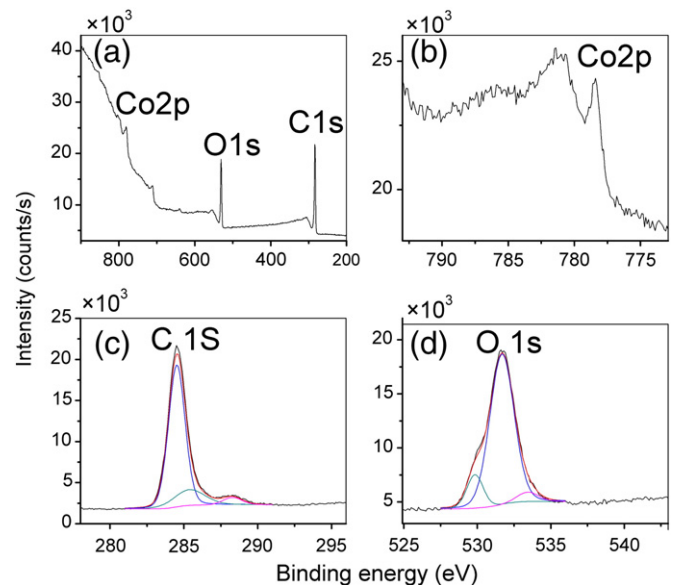


Fig. 3. XPS analysis of as-deposited Co-DLC films (2.5 at.% Co) deposited at room temperature: (a) the full-spectrum of Co-DLC; (b) Co2p; (c) C1s in Co-DLC film; and (d) O1s in Co-DLC film (curve fitted).

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