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Nuclear Instruments and Methods in Physics Research B 242 (2006) 324–327
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

Studies of the composition, mechanical and electrical properties of N-doped carbon films prepared by DC-MFCAD

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Available online 16 September 2005

Abstract

N-doped carbon films were prepared on Si(100) and Ti–6Al–4V substrates using direct current magnetically filtered cathodic arc deposition (DC-MFCAD) at room temperature for various different N_2 pressures. The structure and composition of the films were characterized by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Ball-on-disk and microhardness tests were used to characterize the mechanical properties of the films, and Hall effect tests were employed to study the electrical properties.

PACS: 61.14.Qp; 81.70.Bt; 33.20.Fb

Keywords: N-doped carbon film; Raman spectra; Mechanical property; Hall effect

1. Introduction

Carbon nitride material has evolved to be a topic of considerable interest following the initial work by the theorist Cohen [1,2], who proposed in 1985 that a covalently bonded carbon–nitrogen compound might be as hard as diamond and could have many diamond-like properties, such as high hardness, wear resistance, low friction coefficient, chemical inertness and high optical transparency. In the recent years, various deposition techniques have been used for the preparation of amorphous carbon nitride thin films, such as magnetron sputtering [3], laser ablation [4] and RF plasma enhanced chemical vapor deposition (PECVD) [5], etc.

In the work described in this paper, N-doped carbon films were prepared by direct current, magnetically filtered, cathodic arc deposition (DC-MFCAD). Our research was focused on the composition, structure and electrical properties. Up to now, few papers have reported on the electrical properties of N-doped carbon films using the Hall effect, by which means the semiconductor type, resistivity, carrier concentration and mobility rate of the N-doped carbon films can be obtained.

2. Film synthesis and characterization

N-doped carbon films were prepared on Si(100) wafers and Ti–6Al–4V substrates by DC-MFCAD at room temperature. A high purity (99.99%) graphite cathode was used to serve as the carbon plasma source. The samples were cleaned in turn by acetone, alcohol and deionized water. Vacuum system pressure was about 6.0×10^{-4} Pa. The samples were sputtering cleaned for 10 min using Arions formed by 800 W ECR power, and a 1.6 kV negative substrate bias voltage. A range of N_2 gas pressure was used to prepare six kinds of N-doped carbon films:

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0168-583X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2005.08.070

(1) 7×10^{-3} Pa, (2) 3.0×10^{-2} Pa, (3) 7.0×10^{-2} Pa, (4) 1.6×10^{-1} Pa, (5) 2.5×10^{-1} Pa and (6) 4×10^{-1} Pa.

The composition and structure of the films were measured by Raman spectroscopy (T6400 type, Jobin Yvon Co., France) and XPS (Type XSAM800, KRATOS Co., England). The Si(100) wafers were only partially coated so that we could measure the film thickness using a step device (Alpha-Step®-500) surface profiler; the measured film thickness was about 510 nm. Wear testing by ball-on-disk, and microhardness testing by a Knoop indenter were carried out to determine mechanical properties. The Hall effect measurement was used to estimate the resistivity, carrier concentration and carrier mobility rate of the as-deposited films.

3. Results and discussion

Fig. 1 shows the Raman spectra of as-deposited N-doped carbon films on Si(100). Compared with disordered graphite, all of the spectra show a broad peak at around 1560 cm^{-1} and a lower shoulder at approximately 1350 cm^{-1}, commonly referred to as the G-band and D-band, respectively [6]. From inspection of the spectra, it is interesting to note that the shoulder peaks become more and more obvious with increasing N_2 pressure, which express that sp^2 cluster in the films increase.

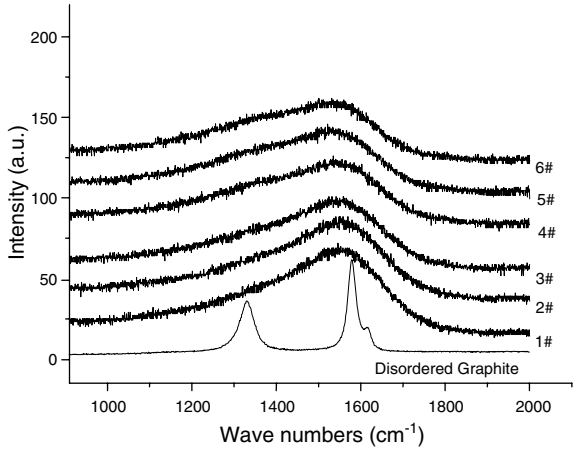

Fig. 1. Raman spectra for different N_2 pressures: (1#) 7×10^{-3} Pa; (2#) 3.0×10^{-2} Pa; (3#) 7.0×10^{-2} Pa; (4#) 1.6×10^{-1} Pa; (5#) 2.5×10^{-1} Pa; (6#) 4×10^{-1} Pa.

For further studying, XPS was used to analyze composition and structure of films. Fig. 2 shows the XPS spectra of C1s and N1s. It is observed from the XPS spectra that C1s for sample 1# shows similar characteristics of DLC films due to its low N_2 pressure. The core level of C1s shifts to low binding energy from 286.1 to 285.5 eV with increasing N_2 pressure, showing that the C=C sp^2 bonds in the film increase. Similarly, the core level for N1s spectra shifts from 399.0 to 398.5 eV, implying that N–C sp^3 bonding in the films increases. It can be seen from Fig. 2(b) that the intensity of the N1s spectra increases slowly from samples 1# to 4#, and no change can be seen for 4#–5#. As the N_2 pressure is increased up to 4×10^{-1} Pa (sample 6#), the intensity of the N1s spectra decreases. These results imply that N is difficult to incorporate in the films, because the intensity of the N1s spectra does not increase when the N_2 pressure is increased up to $\sim1.6\times10^{-1}$ Pa (sample 4#); there may even be a small decrease. For quantifying the C and N atomic concentration in the films, XPS spectra for C1s and N1s were fitted by Gaussian–Lorentzians and by approximating the contribution of background by the Shirley method [7]. The N content of the films was estimated by deconvolution of XPS spectra using sensitivity factors 0.22 for C, and 0.47 for N [8], which is between 1.8% and 6.1%.

Knoop-indentor micro-hardness measurements were used to obtain the coating hardness with 25 g load. An increase from 583 HK (1#) to 1174 HK (3#) in micro-hardness is first observed followed by a gradual decrease to 557 HK with increasing N_2 pressure. Dry ball-on-disc tribological tests were performed with 0.98 N load, 4 cm/s rotation speed, 4 mm rotation radius, with 6-mm diameter SiC balls as the counterpart material for as-deposited films coated on

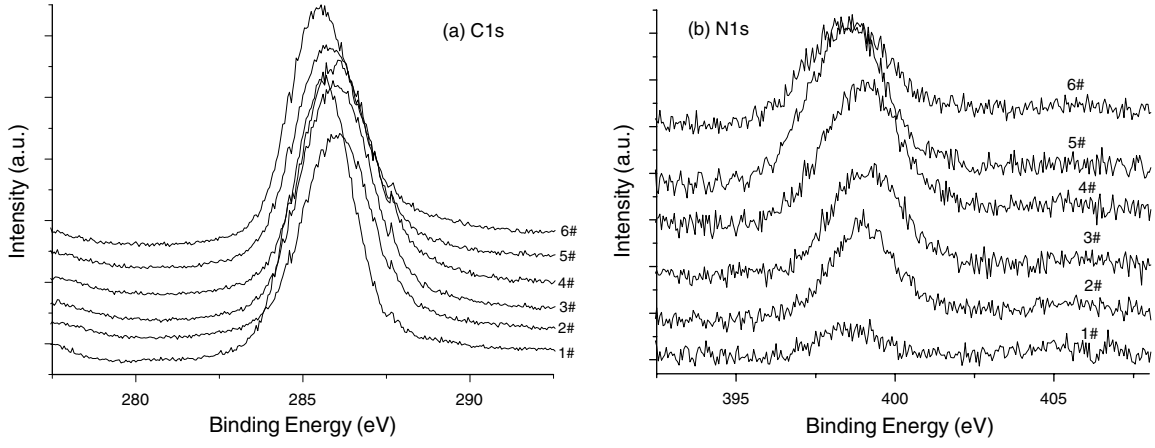

Fig. 2. (a) C1s and (b) N1s XPS spectra for as-deposited N-doped carbon films spectra for different N_2 pressures: (1#) 7×10^{-3} Pa; (2#) 3.0×10^{-2} Pa; (3#) 7.0×10^{-2} Pa; (4#) 1.6×10^{-1} Pa; (5#) 2.5×10^{-1} Pa; (6#) 4×10^{-1} Pa.