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Structural and electrical properties of nitrogen-doped Cr–C:H films synthesized by a cathodic-arc activated deposition process

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Abstract

Nitrogen-doped Cr–C:H/N films were synthesized by using a cathodic-arc activated deposition process. Chromium plasma with intensive ion energies catalyzes the decomposition of hydrocarbon gas (C_2H_2), and results in the deposition of amorphous carbon films. Nitrogen was introduced to form nitrogen-containing Cr–C:H/N films, which contained a mixture of sp^2 and sp^3 carbon bonds. The deposited carbon films consist of nanocomposite Cr–C:H/N films on top of a graded chromium nitride interlayer. It has been found that the structural and electrical properties of the films were correlated as a function of nitrogen doping. The nature of the heterojunction is confirmed by the spreading resistance characteristics of the Cr–C:H/N film/Si junction showing a behavior dependant on the nitrogen doping induced structure changes. With increasing nitrogen concentration, the increasing π states of sp^2 hybridization results in a more pronounced enhancement of conductivity.

Keywords: Nitrogen; Amorphous carbon; Electrical properties

1. Introduction

The amorphous carbon (a-C) and hydrogenated amorphous carbon (a-C:H) films have a meta-stable, amorphous phase of carbon with sp^3 and sp^2 bonds. This a-C:H film has received considerable interest over the past two decades because of their high hardness, wear resistance, as well as attractive optical and electrical properties [1,2]. Amorphous carbon and a-C:H films showed more than 10 orders of magnitude difference in room temperature electrical conductivity, depending on how they were prepared [3,4]. Such a large variation in electrical behavior can be expected due to the diverse bonding possibilities of carbon atoms. Electronic structures of a-C:H are shown varying with clustering properties of sp^2 sites, which can be affected by doping and thermal treatment after the deposition process [5]. Traditional approaches to obtain carbon nitride (CN_x) films involve reactive sputtering, filtered arc deposition and plasma enhanced chemical vapor deposition [6–10]. Some efforts [11–19] have been directed toward improving the adhesion of amorphous carbon films by depositing an interlayer or graded interlayers between the film and its substrate. The interlayer of Ti, Zr, W, Nb, Si, Cr or WC demonstrated its potential in improving film adhesion and wear properties. Among various PVD processes, cathodic-arc plasma possesses the highest ionization ratio, which ensures the deposition of an amorphous carbon film with a high deposition rate and compact film microstructure. In the cathodic-arc activated deposition (CAAD) process [20], high-energy metal plasma assists the cracking and decomposing of hydrocarbon feed gases, such as CH_4 and C_2H_2. As a result, a diamond-like carbon (DLC) film doped with the cathode metal is deposited on the substrate showing good tribological performances [20–23].

In the present work, metal plasma with high ion energies induces the decomposition of nitrogen and hydrocarbon gas (C_2H_2), and facilitates the formation of a metal-doped and

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nitrogen-containing a-C:H (a-C:H/N) films. Because nitrogen is a weak dopant in carbon [18], techniques which include Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared (FTIR) spectroscopy are utilized to obtain information on bonding and electronic structure in this study. The influence of sp^2 bonded carbon atoms in undoped Cr–C:H and nitrogen-doped (Cr–C:H/N) amorphous carbon films on their electrical properties are investigated.

2. Experimental details

Nitrogen-containing Cr–C:H films were deposited on silicon substrates using a CAAD system [20,21]. Chromium was selected as the cathode material for depositing nitrogen-containing Cr–C:H films. In conventional cathodic-arc evaporation systems, the cathode spot also emits macro-particles from cathode materials. If the macro-particle adhered to the prepared coating, the film quality, including mechanical and electrical properties, may be degraded. In the present study, the CAAD system, as shown in Fig. 1, is equipped with a filter duct around the cathode to avoid the presence of macro-particles adhered to the prepared coating. Our previous studies showed the deposited Cr–C:H films possess smooth surface morphology [22,23]. Details of the experimental parameters are shown in Table 1. A graded chromium nitride interlayer was deposited to reduce the internal stress of the composite Cr–C:H/N coating. The transition layer from metal nitride to Cr–C:H and Cr–C:H/N was formed by switching the reactive gas gradually from N_2 to mixed N_2/C_2H_2. The deposition rate of the deposited films was controlled at about 0.05 μm/min.

Table 1
Deposition parameters of CAAD synthesized Cr–C:H/N films

Parameters	Values
Base pressure (Pa)	5×10^{-3}
Reactive gas pressure (Pa)	1.5
Deposition time of CrN layer, transition layer, and Cr–C:H/N layer (min)	10, 15 and 20
Distance of cathode to substrate (mm)	180
Cathode target	Cr (100 mm in diameter)
Cathode current (A)	60
Bias voltage at ion cleaning stage (V)	−1000
Bias voltage at coating stage (V)	−100 (100 kHz pulsed)
Substrate temperature (°C)	120–160
N_2/C_2H_2 ratio during Cr–C:H/N coating stage (%)	0, 3.5, 15, 25, 170

Structural and morphological characterizations were performed using an atomic force microscope (Digital Instrument Nanoscope D3100, tapping mode), a MAC MXP18 X-ray diffractometer (XRD) and a high-resolution transmission electron microscope (HRTEM). A Si probe with 125 μm long cantilever was used in the AFM measurement. The set point of the cantilever vibration amplitude is 1.0 V. The coated samples were scanned in the range of 2000 nm×2000 nm with 256 pixels per line and a scan rate of 1.001 Hz. The surface roughness parameter, the mean roughness (R_a), is defined as the mean value of surface profile relative to the calculated center plane, where the volumes enclosed by the image above and below the plane are the same. Crystal structures of all the coatings were analyzed by XRD using Cu Ká radiation and the X-ray was operated at 40 kV and 30 mA. HRTEM (JOEL LEM-4000EX) equipped with a LaB_6 electron gun and operated at an accelerating voltage of 400 kV possesses a point resolution of 0.17 nm. It is used for

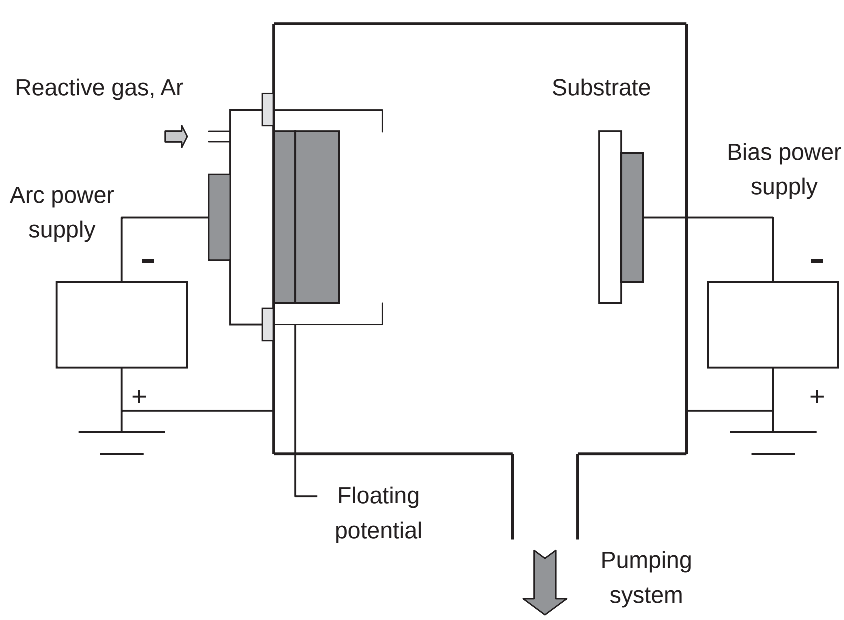

Fig. 1. Schematic diagram of the CAAD deposition system.