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Effect of substrate bias in hydrogenated amorphous carbon films having embedded nanocrystallites deposited by cathodic jet carbon arc technique

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ABSTRACT

The effect of substrate bias on the structural, morphological, electrical and mechanical properties of hydrogenated amorphous carbon films having embedded nanocrystallites deposited by cathodic jet carbon arc technique has been investigated. X-ray diffraction exhibits predominantly an amorphous nature of the film with nanocrystallites of diamond embedded in the amorphous carbon matrix. High resolution transmission electron microscope investigations reveal largely a uniform amorphous structure. However, an ultra fine microstructure with the average grain size between 8 and 25 nm was constituting the entire film with the diffused grain boundaries between the grains. Majority of the individual grains are single crystallite with the preferred inter planar spacing of about 0.213 nm and 0.208 nm corresponding to the diamond planes of 102 and 103, respectively. All the evaluated parameters were seen to depend strongly on the negative substrate bias and exhibit maxima or minima in the properties of the films deposited at −60 V substrate bias.

1. Introduction

In recent years, the synthesis of hard protective coatings becomes the extensive field of technological interest for tribological applications [1–8]. The amorphous carbon thin films, either pure (a-C) or hydrogenated (a-C: H) or nitrogenated (a-C: N) have attracted the significant research attention due to their wide range of applications as a protective coating in the various molds, dies, engine parts, sealing parts, cutting tools, drills, wear-resistant tools, machine parts, computer hard disk, etc. because of their exceptional mechanical properties and chemical inertness. Carbon, one of the fascinating elements on the planet is found in various allotropic forms such as sp^3-hybridized diamond, sp^2-hybridized graphite and sp^1-hybridized polymer like structures. The sp^2 hybridization is governed by weak π–π bonding and decides the electrical and optical properties of the films while sp^3 hybridization comes in to play due to strong σ–σ bonding of carbon atoms which offers the mechanical properties to the films. [9]. Apart from these forms of carbon, carbon is also found in various other allotropic forms such as buckyball, nanotubes, nanofibers, fullerene, nanobuds, nanodiamond etc. After the discovery of carbon nanotubes by Iijima [10], carbon based nanomaterials become the extensive field of research [11–19] due to their exceptional physical and chemical properties over bulk carbon materials. Various methods have been developed for the growth of these hard nanostructured carbon materials in thin forms as sputtering [20], plasma enhanced chemical vapor deposition (PECVD) [1], pulsed laser deposition (PLD) [21], electron cyclotron resonance [22] and filtered cathodic vacuum arc (FCVA) process [1,23]. Among the above mentioned techniques, FCVA is one of the most promising techniques, which offers the great opportunity to the researchers to decide the ion energy and environmental conditions for the growth of different forms of carbon ranging from diamond-like to graphite-like and various intermediate materials such as tetrahedral amorphous carbon (ta-C), hydrogen and nitrogen incorporated ta-C (ta-C: H, ta-C: N), nanoclusters, nanocomposite and nanotubes.

The deposition of hard and highly elastic carbon films, which mostly consists of graphitic sp^2 bonding using a graphite cathode with a localized high pressure of helium or nitrogen at the arc spot, has been reported by Amaratunga and his coworkers [16]. Nanotubes formed in the arcing process are carried by the high pressure gas flow to the low pressure vacuum region where they together with the carbon plasma plume [16–19], are condensed onto the substrate. The reports of the formation of hard sp^2 bonded materials by anisotropically pressing C_{60} [24,25] and by embedding distorted fullerene-like nanoparticles in an amorphous carbon matrix [16] were early indications that such a carbon material could be synthesized. The mechanism for nanotube formation by an arc has been reported [26] but there appears to be dearth of data on this new form of amorphous carbon thin films having nanoparticles which have a number of technological applications due to its compatibility with thin film deposition methods since carbon nanotubes prepared by conventional arc method exist in the form of a powder or aligned carbon nanotubes (individual or in bundles). Based on high pressure arc plasma methods developed to produce fullerene molecules and nanotubes [16], we have used a high local hydrogen gas pressure carbon arc technique for thin film deposition. Except for the gas jet,

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the apparatus is similar to vacuum arc systems used for the deposition of ta-C: H films [23,27].

Hard coatings hold the key to improved performance of many types of product. However, the achievement of these improvements requires the selection of appropriate deposition parameters. The huge range of materials properties is mainly due to the ability of carbon to form different types of inter atomic bonds, to take different sites and to adopt different structures. Neuville and Matthews [28] while studying a perspective on the optimization of hard carbon and related coatings for engineering applications discussed issues relating to intrinsic material properties and practical aspects to provide a frame work for the development, selection and use of coatings in practical situations.

The properties of a-C: H films are found to be dependent strongly on the deposition conditions such as base vacuum, substrate bias, gas pressure, chamber geometry, arc current, arc voltage and the strength of the magnetic filter [29,30]. The main objective of the present study is to investigate the effect of negative substrate bias on the structural, morphological, electrical and mechanical properties of a-C: H films having embedded nanocrystallites deposited using cathodic jet carbon arc (CJCA) technique. For comparison purpose, we also refer to the properties of ta-C: H films deposited using an S bend FCVA process [23]. To our knowledge, this is the first study to report detailed investigations of the effect of substrate bias on the film formation and characteristics of amorphous carbon (a-C: H) films having embedded nanocrystallites.

2. Experimental details

Fig. 1 shows a schematic representation of the experimental configuration of the cathodic jet carbon arc (CJCA) deposition technique. Briefly, the CJCA process is based on striking the arc (arc voltage ~20–24 V with an arc current of ~48 A between two graphite electrodes (50 mm dia. graphite cathode of purity 99.999% and a retractable graphite anode rod of 7 mm dia. and purity 99.999%). The a-C: H films were deposited on cleaned 7059 glass, and highly doped $<100>p^{++}$ silicon substrate (size: 2 cm × 2 cm) placed on sample holder of size 8 cm × 8 cm at a distance of ~35 cm away from the cathode at a hydrogen pressure of $\sim 7.9\times10^{-4}$ mbar. Additional negative substrate biases (direct current) ranging from 0 to −300 V were applied to the substrate to enhance the energy of incoming ions. The chamber was initially pumped to a base pressure of $\sim10^{-6}$ mbar by the use of turbo molecular and rotary pump combination in the system and then the high purity hydrogen gas was injected locally through the cathode of 1 mm cavity. The negative terminal of the D.C. arc supply was connected to the cathode and the positive terminal to the anode striker rod. The body of the whole system was grounded and the duct was not biased. The films studied were deposited sequentially for 5 s and then cooled for 50 s. The process was repeated until the required thickness is obtained. The thickness of the film was in the range 200 ± 10 nm as measured by Talystep (Rank Taylor and Hobson) thickness profiler. The deposition rate achieved was ~5 nm/s.

The phase analysis of the films was carried out by Philips X'Pert PRO PANanalytical diffractometer using CuKα radiation at room temperature which was fully automated and configured in 0–2θ geometry. The high resolution transmission electron microscope (HRTEM), (Model FEI, Tecnai G2F30-STWIN with field emission electron gun source) was operated at the electron accelerating voltage of ~300 kV to explore the nano and sub nano scale structural information present in these films. HRTEM samples were prepared by dissolving the silicon substrates into HNO_3: HF solution and then diluting it heavily in distilled water. Subsequently, these self supported films were lifted on a 200-mesh copper grid of 3.05 mm in diameter. The surface morphology of a-C: H films were investigated by scanning electron microscopy (SEM) (Leo Electron Microscope — model no. LEO 440) in the secondary emission mode. The atomic force microscope (AFM) micrographs of the a-C: H films were evaluated by AFM (Nanoscope Veeco — V). The surface morphology was investigated in terms of surface profiles and surface roughness. The XPS measurements were carried out by Perkin-Elmer (model no. 1257) X-ray spectrophotometer operating at a base pressure of better than 6×10^{-10} mbar. From the dual anode X-ray source, Mg Kα (1253.6 eV) line was used for the present analysis. The spectra of the samples were recorded before and after sputter ion cleaning the top surface for 5 min by a differentially pumped argon ion gun. The binding energy (B.E.) was calculated with respect to contaminant free Ag3d line using MgKα line as the incident photon and calibrated with high purity graphite. The XPS wide scan was acquired using a 100 eV pass energy at a step of 1.0 eV and XPS C1s core level spectra were acquired at 0.05 eV step with a pass energy of 60 eV. To neutralize the charge generated on the sample, we used a metallic clamp which was grounded with the system. Unpolarized Raman spectra were recorded at room temperature using a Renishaw InVia Reflex micro Raman spectrometer with a notch filter. Appropriate care was taken to avoid damaging the sample by laser excitation. The filtered

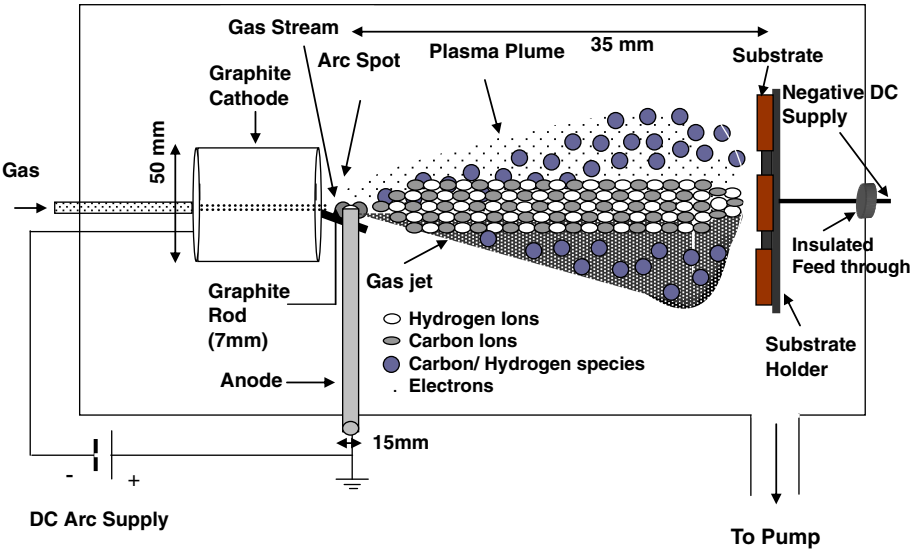

Fig. 1. Schematic representation of cathodic jet carbon arc technique for the deposition of a-C: H films having embedded nanocrystallites.