Hydrogenated amorphous carbon films having embedded nanoparticles deposited by cathodic jet carbon arc technique

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ABSTRACT
This paper reports the formation and properties of hydrogenated amorphous carbon (a-C: H) films having embedded nanoparticles deposited by cathodic jet carbon arc (CJCA) technique in absence of magnetic field. The films have been characterized by XRD, HRTEM, XPS, dark conductivity, activation energy, optical band gap, residual stress, hardness, elastic modulus and plastic index parameter. The properties evaluated of a-C: H films having embedded particles have been compared with that of undoped and nitrogen doped a-C films having embedded nanoparticles deposited by CJCA technique. All the properties of a-C films studied are found to depend on the gaseous environment used during the deposition of the films. These a-C films having embedded nanoparticles act as hard coating materials.

Hydrogenated amorphous carbon films, Nanoparticles, CJCA

1. INTRODUCTION
Carbon in its different thin film forms such as tetrahedral amorphous carbon (ta-C), fullerenes, nanotubes and graphene have been investigated extensively [1-4]. Among the successful methods for the preparation of ta-C films, the filtered cathodic vacuum arc (FCVA) technique is useful for many industrial applications because it provides fully ionized plasma of energetic ions [1,3-5]. The enhanced interest in ta-C films is due to the possibility of tailoring the material with properties varying from highly diamond-like to highly graphite-like materials. The deposition of hard and highly elastic carbon films, which mostly consists of graphitic sp² 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 [6]. Based on high pressure arc plasma methods developed to produce fullerene molecules and nanotubes [6], we have used a high local hydrogen gas pressure carbon arc technique for thin film deposition. The mechanism for nanotube formation by an arc has been reported [7] but there appears to be a 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). Except for the gas jet, the apparatus is similar to vacuum arc systems used for the deposition of ta-C: H films [5, 8]. This paper reports the formation and properties of hydrogenated amorphous carbon (a-C: H) films having embedded nanoparticles deposited by cathodic jet carbon arc (CJCA) technique in absence of magnetic field. The properties of a-C: H films having embedded nanoparticles have been compared with that of undoped and nitrogen doped a-C films having embedded nanoparticles deposited [9, 10] by CJCA technique.

2. EXPERIMENTAL DETAILS
The schematic representation of CJCA process for the deposition of a-C: H film is shown in Fig. 1. It is based on striking the arc 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 chamber was initially pumped to a base pressure of ~10⁻⁶ mbar by the use of turbo molecular and rotary pump combination and then the high purity (99.999 %) hydrogen gas was injected locally through the cathode of 1 mm cavity. The films (200±10 nm thickness) were deposited on cleaned 7059 glass substrate and highly doped < 100 > p⁺ silicon substrates placed on a substrate holder at a distance of ~35 cm away from the cathode, at a gas pressure of ~ 8.6x10⁻³ mbar using arc current of ~ 48 A. The a-C: H films could be deposited only in absence of magnetic field and at less value of arc current. The negative terminal of the D.C. arc supply was connected to the cathode and the positive terminal to the anode striker rod. The films
studied were deposited sequentially for 5 sec and then cooled for 50 sec. The phase analysis of the films was carried out by Philips X’Pert PRO PANalytical diffractometer using CuKα at room temperature. The high resolution transmission electron microscope (HRTEM), (Model FEI, Tecnai G2 F30- 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 HNO₃: 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 XPS measurements were carried out by Perkin-Elmer (model no. 1257) X-ray spectrometer operating at a base pressure of better than 6x10⁻¹⁰ mbar. The dark conductivity (σ₀) was measured in the temperature range from -60 to 190°C on coplanar sample made by evaporating aluminum in a vacuum of 10⁻¹⁰ mbar at an electric field of 10² V/cm. The residual stress (S) in a film was evaluated using curvature method by FSM Frontier Semiconductor (USA) instruments. The value of optical band gap (E₉) was evaluated by extrapolating (αhν)² versus hv curve to zero abscissa. The values of hardness (H), elastic modulus (E) and plastic index parameter (H/E) were evaluated using IBIS nanoindentation (Fisher– Cripps laboratories Pvt. Ltd., Australia) having triangular pyramid diamond Berkovich indenter with normal angle of 65.3° between the tip axis and the faces of triangular pyramid and the curvature of 150-200 nm at the tip at maximum of 5 mN load.

3. RESULTS & DISCUSSIONS

3.1 XRD, HRTEM and XPS study

Fig. 2 shows a typical XRD pattern of a-C: H film having embedded nanocrystallites which reveals a broad peak at ~26°, a sharp reflection at 31.0° and three dominant peaks at 40.5°, 42.3° and 43.2°. The broad peak at ~26° exhibits the dominant amorphous nature of carbon film. The sharp reflection observed at ~ 31° may be due to silicon substrate and the subsequent peaks
at 40.5°, 42.3° and 43.2° are attributed to diamond planes \((hkl)\): 100, 102 and 103, respectively. This is in agreement with the results reported in literature[11]. HRTEM was employed to characterize the film in both real and reciprocal space and a typical micrograph is shown in Fig. 3. In general, the film microstructure was uniform with ultra-fine grains distributed throughout the film. The grain size was measured between 8 to 25 nm with the separation of diffused boundaries among each other. Lower inset in figure denotes one such ring surrounded with fine nanocrystallites (marked with white arrows) leading to a pentagonal morphology. The core region of the ring is about 6 nm in size whereas the thickness of individual crystallite at the periphery of the ring varies between 6 to 8 nm. The magnified view of atomic scale image shows the individual crystallites are consisted of the interplanar spacings of 0.213 and 0.208 nm, corresponding to the planes of 102 and 103 with the crystalline carbon. There are several such ultra-fine size nanocrystallites embedded in the featureless contrast of amorphous structure in the matrix. Although revelation of every individual nanocrystallite in the recorded atomic scale image is difficult in real space, the corresponding reciprocal space pattern (upper inset in Fig. 3) elucidates the evolved rings due to different interplanar spacings with a diffused background due to coexisting amorphous phase. Two planes (102 and 103) are marked from the two consecutive rings appearing in the calculated reciprocal space pattern (upper inset in Fig. 3) of atomic–scale resolved image as depicted in Fig. 3. The XPS spectra in the a-C: H film showed only oxygen \((O 1s - 532 eV)\) as a surface contaminant in addition to the main peak of carbon \((C1s \sim 284.56 eV)\). The surface was cleaned by sputter etching using a rastered argon ion beam at 4 keV at a base pressure of \(\sim 10^{-8} mbar\) for 5 min. The oxygen peak completely diminished after cleaning by argon ion bombardment, indicating that the oxygen was present on the surface and not throughout the bulk of the film. Fig. 4 shows the typical C1s spectra and deconvoluted spectra of the a-C: H films having embedded nanocrystallites. It is evident from the figure that C1s peak occurred at 284.38 eV and its
full width at half maximum (FWHM) value is 2.07 eV. Diaz et al. [12] were the first to evaluate the sp³ content from the C 1s peak of carbon by deconvolution method which has been used for the direct determination of sp³ and sp² content in a-C: H films in the present investigation. The deconvoluted peaks have been located at ~284.41 (FWHM=1.68 eV) and 285.87 eV (FWHM = 3.50 eV) which were assigned to the C=C sp² hybridized carbon atoms and C-C sp³ hybridized carbon atoms, respectively. The observed peaks positions of the two different deconvoluted components are well corroborated with the reported values in the literature [10, 12]. Thus, the area under these curves directly gives the sp² and sp³ contents, respectively. Kleinsorge et al. [8] have reported that the hydrogen content of the ta-C: H films vary linearly from 0.2 at. % at a system base pressure of 10⁻⁷ mbar to ~15 at. % when hydrogen partial pressure increases from base pressure (10⁻⁷ mbar) to 10⁻³ mbar. Similar values of hydrogen content may be present in a-C: H films having embedded nanocrystallite deposited in the present study. The value of sp³ content evaluated (60.3%) in a-C: H films having embedded nanocrystallites in the present study is found to be larger than the value of sp³ content (50%) evaluated in a-C film having fullerene and nanotubes by Chhowalla et al. [13] and less than the sp³ content evaluated (~80-87%) using x-ray induced Auger electron spectroscopy method in ta-C: H films deposited by S bend FCVA process [5] at -300 V substrate bias at comparable hydrogen partial pressure.

3.2 Electrical, optical and mechanical properties of a-C: H films

Fig. 5 shows the variation of dark conductivity (σ₀) of a-C: H films having embedded nanocrystallites versus inverse of temperature. It is evident from the figure that the variation of σ₀ is a thermally activated process which follows a relation of the form of σ₀ = σ₀ exp (-ΔE / kT). The symbols σ₀ is the conductivity pre exponential factors, k the Boltzmann's constant, T the temperature in Kelvin and ΔE the activation energy. The values of σ₀, ΔE and E_g of a-C: H films having embedded nanocrystallites are found to be 1.0 x 10⁻⁷ ohm⁻¹ cm⁻¹, 0.30 eV and 2.28 eV, respectively. The as grown a-C films are reported to be p-type [14]. The conductivity data suggests that the conduction of carriers (holes) is occurring from the localized states in the region of the Fermi level into the extended states in the valence band. The value of σ₀ observed in a-C: H having embedded nanocrystallites is found to be much lower than those (10⁻⁵ ohm⁻¹ cm⁻¹) reported by Amaratunga and his coworkers [13, 15] in a-C with nanoparticle whereas the value of ΔE and E_g observed in a-C: H having embedded nanocrystallites is found to be much larger than the value of ΔE =0.20 eV and E_g =1.4 eV reported in a-C with nanoparticles [13, 15]. The values of σ₀ and E_g observed in a-C: H films with embedded nanocrystallites are found to be nearly consistent with the values of σ₀ and E_g observed in ta-C: H films deposited by S bend FCVA process by us [16, 17] at -300 V substrate bias at comparable hydrogen partial pressure whereas the value of ΔE observed in a-C: H films having embedded nanocrystallites are found to be less than the value of ΔE) (0.38 -0.45 eV) observed in ta-C: H films deposited by S bend FCVA process by us [16].

Fig. 6 shows the load-displacement curve obtained by nanoindentation of a-C: H films having embedded nanocrystallites. A maximum load of 5 mN was applied in the present study. The penetration depth of a-C: H film was 96.8 nm. The residual stress (S) present in a-C: H films having embedded nanocrystallites are found to be compressive in nature. The values of S, H, E, H/E, at 5 mN load of a-C: H films are found to be 2.22 GPa, 27.11 GPa, 245.84 GPa and 0.106, respectively. The plastic index (S) present in a-C: H films having embedded nanocrystallites are found to be compressive in nature. The values of σ₀, ΔE and E_g observed in a-C: H films having embedded nanocrystallites are found to be much lower than those (10⁻⁵ ohm⁻¹ cm⁻¹) reported by Amaratunga and his coworkers [13, 15] in a-C with nanoparticle whereas the value of ΔE and E_g observed in a-C: H having embedded nanocrystallites is found to be much larger than the value of ΔE =0.20 eV and E_g =1.4 eV reported in a-C with nanoparticles [13, 15]. The values of σ₀ and E_g observed in a-C: H films with embedded nanocrystallites are found to be nearly consistent with the values of σ₀ and E_g observed in ta-C: H films deposited by S bend FCVA process by us [16, 17] at -300 V substrate bias at comparable hydrogen partial pressure whereas the value of ΔE observed in a-C: H films having embedded nanocrystallites are found to be less than the value of ΔE) (0.38 -0.45 eV) observed in ta-C: H films deposited by S bend FCVA process by us [16].
fullerenes and nanotubes deposited using helium gas with S~5 GPa and H~42±4 GPa evaluated at 5 mN load using similar method by Chhowalla et al. [13]. Thus, a-C: H films having embedded nanocrystallites are as hard as ta-C and ta-C: H films deposited by S bend FCVA process [17, 18]. The values of σ₀ at room temperature, ΔE, E₀, sp³ content, S, H, E and H/E evaluated of a-C: H films having embedded nanoparticles have been summarized in Table 1 together with the values of these parameters evaluated for a-C and a-C: N films having embedded nanoparticles using helium and nitrogen gas by CJCA method for comparison purpose [9, 10]. The residual stress evaluated of a-C: H films embedded with nanoparticles under different gas environment are found to be in the range 1.55- 2.67 GPa. It has been observed that the a- C: H film deposited under hydrogen gas environment has the highest value of sp³ content (60.3%), H (~27.11 GPa), E (245.84) and H/E (0.106) ratio accompanied by the lowest σ₀ (1.0x10⁻⁷ ohm⁻¹ cm⁻¹) whereas the a-C film deposited under helium gas environment has the highest σ₀ (2.2 ohm⁻¹ cm⁻¹) accompanied by the lowest value of E₀, sp³ content (37.0 %), H (~17.20 GPa), E (208.02) and H/E (0.082) ratio and a-C: N film deposited under nitrogen gas environment exhibits properties in between that of a-C: H and a-C film. The value of E₀ remains the same 2.28-2.30 eV in a-C: H and a-C: N films. Neuville and Matthews [19] have provided a coherent perspective on the many factors which are important for the optimization and appropriate use of hard carbon coatings while also challenging certain preconditions.

4. CONCLUSIONS

The formation and properties of a- C: H films having embedded nanoparticles deposited by CJCA technique have been studied. X- ray diffraction exhibits an amorphous nature of the film having embedded nanocrystallites. HRTEM investigations
reveal largely an amorphous structure due to the presence of significant fraction of grain boundaries with the nanocrystalline grain size between 8 to 25 nm. The individual grains are single crystalline 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. The values of $\sigma_D$, $\Delta E$, $E_g$, sp$^3$, H, E, H/E ratio obtained in a-C: H films having embedded nanoparticles have been compared with that of undoped and nitrogen doped a-C films having embedded nanoparticles. All the properties of a-C films grown are found to depend on the gaseous environment used during the growth of the film. The formation of amorphous carbon having embedded nanoparticles may have the potential to be a thin film equivalent of carbon nanotubes in terms of mechanical properties and may act as hard carbon coatings.

5. ACKNOWLEDGEMENT

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6. REFERENCES