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Characterization of as grown and nitrogen incorporated tetrahedral amorphous carbon films deposited by pulsed unfiltered cathodic vacuum arc process

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Abstract

Reported is a study of the as grown and nitrogen incorporated tetrahedral amorphous carbon (ta-C) films deposited by a pulsed unfiltered cathodic vacuum arc process using Raman scattering, photoluminescence (PL) and Fourier transform infrared (FTIR) spectroscopy. The influence of the substrate bias in as grown ta-C films and the effect of the nitrogen content in nitrogen incorporated ta-C films under a fixed bias condition were studied. The Raman spectroscopic study showed that, in the present study, the as grown ta-C films deposited at 40 V substrate bias possibly have the highest sp^3 bonded carbon concentration, as observed by the large shift in the G peak to ~1596 cm^{-1}. In the case of the nitrogen incorporated ta-C films, the G peak exhibited a shift towards lower wave number with increasing nitrogen content, suggesting an increase in disorder. The PL spectra indicated a strong peak ~2.21 eV arising due to extended defects like dislocations followed by a small one ~1.92 eV which could be identified as a zero phonon line (ZPL) doublet. Another peak at ~2.63 eV could be attributed to TR12 center. PL peak at ~2.21 eV showed an inflexion in ta-C films deposited at 40 V substrate bias. An increase in intensity of the PL peak at ~2.17 eV and its full width at half maximum (FWHM) value was also observed due to the increase in nitrogen content in the films. The FTIR spectra showed the characteristic peaks at 2958, 2366, 2350, 1610, 1512, 1047 and 710 cm^{-1} in as grown and nitrogen incorporated ta-C films.
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Keywords: Raman; PL; FTIR; ta-C; Unfiltered cathodic vacuum arc; Deposition process

1. Introduction

Amorphous carbon films having a high sp^3 bonded carbon content, referred as tetrahedral amorphous carbon (ta-C), continue to draw considerable interest, due to their unique mechanical, electronic, structural and morphological properties [1–5]. The tribological application of the ta-C films as protective coatings over magnetic hard disks and machine tools is well established. Other potential areas of applications include, MEMS, biocompatible coatings, electron emitting cold cathodes and possible electronic and optoelectronic devices [3–7]. These ta-C films were grown by using a wide variety of processes including filtered cathodic vacuum arc (FCVA)—direct and pulsed source, pulsed laser ablation, mass selected ion beam deposition and electron cyclotron wave resonance (ECWR). The above processes being highly energetic, the controlled variation of the of ion energy led to materials with widely varying properties.

Among the successful methods for the preparation of ta-C films, the FCVA technique was particularly useful for industrial applications because it provided a highly ionized plasma of energetic carbon ions, from which dense films could be grown at reasonable deposition rates [8]. However, one of the main limitations of the cathodic vacuum arc process was the presence of macroparticles. The macroparticles were generated due to the extreme conditions in the cathode arc spot, leading to macroscopic fragments of the

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cathode material. The incorporation of these macroparticles in the film not only causes morphological imperfections but also influences the electronic and optical properties. Electromagnetic deflection of the plasma through the 90° bend using a curved solenoid was first used to remove the macroparticle from the carbon plasma by Aksenov et al. [9]. The macroparticle filter, on the other hand, has limited transport efficiency and tends to collimate the plasma leading to a restricted area of deposition. Since a nearly fully ionized vapor stream could be obtained in the vacuum arc, ion energies could also be easily controlled by varying the substrate bias voltage. However, there seems to be subtle variation in the material properties of ta-C films deposited by different processes and under varying conditions of the substrate bias and nitrogen partial pressure. There are not many reports on the ta-C films, deposited using the pulsed unfiltered cathodic vacuum arc process [10–15]. The pulsed arc process offers the advantage of depositing ta-C films with relatively less stress, higher controllable and repeatable deposition rates and very lower macroparticles [10,11]. However, there are even fewer reports on ta-C films using unfiltered pulsed cathodic arc [13–15]. Unfiltered pulsed arc still leads to lower macroparticles than a continuous arc and also to higher deposition rates and ion throughputs [10,13], besides the advantages of the pulsed arc mentioned earlier. With further optimization of the system design, it should be, in principle possible to grow controlled repeatable films with far lower macroparticles. This makes the ta-C material deposited using the pulsed unfiltered cathodic vacuum arc very attractive for the applications mentioned earlier. Reported here is a study of the as grown and the nitrogen incorporated ta-C films deposited by pulsed unfiltered cathodic vacuum arc process using Raman spectroscopy, photoluminescence (PL) and Fourier transform infrared spectroscopy (FTIR). The effect of substrate bias and nitrogen content on the properties of as grown and nitrogen incorporated ta-C films, respectively, are discussed.

2. Experimental details

The deposition of amorphous carbon films was carried out by a pulsed unfiltered cathodic vacuum arc process on cleaned highly doped $\langle 100 \rangle$ n^{++} silicon wafer of resistivity 0.001–0.005 Ω cm. The system could be evacuated to a vacuum level better than 10^{-7} Torr. A graphite rod of purity ~99.999% was used as the cathode. Typically the deposition was carried out at a frequency of ~5 Hz, duty cycle of 50%, ignition voltage of about 4 kV and an arc current of ~300 A. A negative substrate bias of 5 to 180 V was applied to the substrate, for varying the energy of incoming ions. For a carbon cathode, the emitted material is primarily C^{+} ions with kinetic energy, broadly peaked at ~20–25 eV [16]. The incident ion energy could be given by the sum of the bias voltage and the initial ion energy of carbon ions. The nitrogen gas of high purity was introduced into the vacuum system with the help of a needle valve and the mass flow controller near the cathode for depositing nitrogen incorporated ta-C films. The partial pressure of nitrogen was varied from 3.3×10^{-6} to 1.0×10^{-3} Torr to deposit nitrogen incorporated ta-C films with different amounts of nitrogen content. Nitrogen content in the ta-C:N films were calculated by the area under the peak studied by the X-ray photoelectron spectroscopy (XPS) and sensitivity values of N (0.38) and C (0.205) using the standard procedure [17]. The detailed analysis of XPS measurements have been described elsewhere [18]. The values of nitrogen content have been found to be 3.6, 7.4, 10.3 and 15.6 at.% at nitrogen partial pressures of 3.3×10^{-6}, 2.6×10^{-5}, 2.3×10^{-4} and 1.0×10^{-3} Torr, respectively. The nitrogen content evaluated is found to increase linearly with the increase of nitrogen partial pressure used in depositing nitrogen incorporated ta-C films, which is consistent with the observations reported in literature [19]. During deposition of the nitrogen incorporated ta-C films, the substrate bias was kept constant at 5 V. The thicknesses of the films were in the range 450–550 Å as measured by Talystep (Rank Taylor and Hobson) thickness profiler.

Unpolarized Raman spectra were recorded at room temperature in backscattering geometry using a Jobin-Yvon T6400 spectrometer coupled with a notch filter. Appropriate care was taken to avoid damaging the sample by the laser excitation. The filtered radiation of 514.5 nm from an argon-ion laser was used as the excitation source. The power on the specimen was 50 mW while the incidence angle was set at 80° from the specimen normal in order to maximize the signal from the films. The spectra were scanned in the region 650–1900 cm^{-1} with steps of 2 cm^{-1}. PL measurements of the films were carried out in the temperature range of 80–300 K by using a xenon arc lamp as the emission source. A Hamamatsu photomultiplier was used as the detector, along with a 1/4 m monochromator. The PL spectra of films deposited at different substrate bias (ion energy) in as grown ta-C films and varying nitrogen content in nitrogen incorporated ta-C films deposited at 5 V substrate bias were recorded at 80, 140, 220 and 300 K. FTIR spectroscopy was carried out on a Perkin Elmer, spectrum 2000 FTIR spectrophotometer in the wave number range from 500 to 4000 cm^{-1}. FTIR absorbance spectra were taken with 4 cm^{-1} resolutions in an N_2 atmosphere to minimize the influence of H_2O vapors.

3. Results and discussion

3.1. Raman spectra of as grown and nitrogen incorporated ta-C films

Fig. 1 shows the Raman spectra of as grown ta-C films deposited by pulsed unfiltered Cathodic vacuum arc process at different substrate bias of 5, 40, 80 and 180 V. The use of visible excitation source of 514.5 nm for the Raman

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