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Effect of bias and hydrogenation on the elemental concentration and the thermal stability of amorphous thin carbon films, deposited on Si substrate

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ABSTRACT

Amorphous carbon films have been deposited with various levels of negative substrate bias and hydrogen flow rates using argon and argon + nitrogen as sputtering gas. The effect of hydrogenation and substrate bias on the final concentration of trapped elements is studied using ion beam analysis (IBA) techniques. The elemental concentrations were measured in the films deposited on silicon substrates with a 2.5 MeV H^+ beam and 16 MeV O^{5+} beam. Argon was found trapped in the non-hydrogenated films to a level of up to ~4.6 %. The concentration of argon increased for the films deposited under higher negative bias. With the introduction of hydrogen, argon trapping was first minimized and later completely eliminated, even at higher bias conditions. This suggests the softness of the films brought on by hydrogenation. Moreover, the effect of bias on the thermal stability of trapped hydrogen in the films was also studied. As the films were heated in-situ in vacuum using a non-gassy button heater, hydrogen was found to be decreasing around 400 °C.

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1. Introduction

Amorphous, Diamond-like Carbon (DLC) films have attracted a great deal of attention because of their properties closely related to that of diamond. The material is characterized by its high hardness, low friction, chemical inertness, low electron affinity and can also be made optically transparent. Diamond-like carbon films are currently used as protective coatings on contacting surfaces of machine elements, magnetic storage devices and various tools and dies [1]. DLC microstructure contains tetragonally coordinated sp^3 carbon atoms, similar to those found in pure diamond as well as the trigonal sp^2 coordinated atoms as in graphite and possibly, some sp^1 coordinated atoms. Its properties vary considerably with deposition conditions.

Total hydrogen content critically determines DLC structure at the atomic level and therefore the physical properties of the films. Hydrogen content is also key to obtaining a wide optical gap and high electrical resistivity [2–4]. Raman studies on these films show that heating DLC in ambient air at temperatures above 300 °C, significant conversion of DLC to nano-crystalline graphite takes place [5]. The loss of hydrogen through annealing at high temperatures generally causes a collapse of the structure to a graphite-like phase dominated by sp^2 bonds [6]. DLC films are typically transparent in the infrared, with the exception of the CH_x absorbing bonds, that are weakly absorbing in the visible region and are increasingly absorbing with decreasing wave length in the UV region. Hydrogen content is critical in controlling the optical properties, and removal of hydrogen from DLC films causes the loss of IR transparency [4,7].

A wide range of optical gap values (E_{opt}), spanning the range from 0.38 to 2.7 eV [8] were reported for DLC films prepared under presumably similar conditions, indicating the dependence of the DLC properties on the deposition conditions. For otherwise similar deposition conditions, E_{opt} was found to decrease strongly for DLC films deposited above 250 °C [9]. Films deposited at lower temperatures (in the range of 25–250 °C) contain significant concentrations of hydrogen; most of the sp^3 coordinated carbon atoms, as well as a substantial fraction of the sp^2 coordinated carbons are bound to at least one hydrogen atom. This behavior reflects the role of hydrogen in stabilizing the structure of DLC layers. The index of refraction is also affected by the hydrogen concentration in the DLC films. It generally increases with decreasing hydrogen content [10]. A higher index of refraction usually indicates DLC with higher hardness, and better wear resistance. In order to utilize DLC films for optical applications, it is very important to control the refractive index [11]. The most substantial structural and characteristic changes occur at temperatures higher than 400 °C [12].

Some works on the annealing of amorphous carbon films have been reported by Nadler et al. [13]. They discovered that heating DLC films in vacuum incurred hydrogen loss in the system from 500 ° C to 700 ° C. Temperatures greater than 700 ° C detected no further decrease in hydrogen from the system. Experiments by Wu et al. [14] found no detectable loss of hydrogen when DLC films were rapidly annealed until 500 ° C. Furthermore, Causey [15] also reported that for

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vacuum annealing, temperatures higher than 800 ° C were required to release all the hydrogen.

Akkerman [16] proposed that the removal of hydrogen from hydrogen bonded C(sp^3)–H$_n$ (n = 1,2, and 3) structure is followed by the formation of new hydrogen bonded C(sp^2)–H structure and new double bond C(sp^2)=C(sp^2) structure. Wild and Koidl [17] suggested that the released hydrogen molecules are formed in each individual layer followed by molecular transport to the surface of the top layer. They suggested that the thermal stability of carbon films strongly depends on the film deposition conditions and annealing environment. Additionally, the release of hydrogen from the C–H bonds determines the microstructure of the carbon films [18]. The loss of hydrogen through annealing at high temperatures generally causes a collapse of the structure to a graphite-like phase dominated by sp^2 bonds [6]. It is therefore important to find the temperature at which the evolution of hydrogen takes place.

In this work, we have studied the effect of bias on the trapping of Ar, N, O and H in the DLC films. Moreover, the thermal stability of DLC thin films with respect to hydrogen content is also studied. Both studies were carried out using ion beam analysis techniques. Ion beam analysis (IBA) techniques are generally used to determine the total elemental concentration of a thin film. Ion beam based techniques are the collection of techniques, including Rutherford backscattering spectrometry (RBS), Non-Rutherford backscattering spectrometry (NRBS), nuclear reaction analysis, (NRA) and Elastic recoil detection analysis (ERDA). These techniques are based on collisions between atomic nuclei involving measurement of the number and energy of ions in a beam. Such ions are back or forward scattered after colliding with atoms in the near-surface region of a sample. Knowing ion number and energy in this way, makes it possible to determine atomic mass and elemental concentrations versus depth below the surface. RBS has good mass resolution for light elements but poor mass resolution for heavy elements. An important related issue that forms the basis of ERDA is that He^{++} or heavier projectile will not scatter backwards from H or He atoms in a sample. Elements as light as or lighter than the projectile element will instead recoil at forward trajectories with significant energy. As such these elements cannot be detected using classical RBS. However, by placing a detector so that these forward recoil events can be recorded, these elements can be quantitatively measured using the same principles as RBS. Thus, an accessible and generally used method to determine the total hydrogen content in a thin film is Elastic Recoil Detection Analysis (ERDA) [19]. Ion beam analysis is one of the few techniques that are used for quantitative measurement of hydrogen concentration in the material.

Non-Rutherford backscattering (NRBS) is useful in the case of light element concentration determination. This phenomena takes place when the incident nuclei and target nuclei come so close to each other that nuclear forces start playing their role in the scattering process. The nucleus of the target in this scattering stays intact and scattering probability is enhanced. At certain energies, even resonant scattering can give rise to peaks that are signatures of the target nuclei. The depth scale (10^{15} atoms/cm^2) is characteristic of the RBS and NRBS measurement, which only determines the number of target atoms per cm^2 visible to the analysis beam. If the sample density is known, this scale is readily converted to a linear depth scale. Composition profiles are determined by comparing SIMNRA computer simulations of the spectra with the original data [20].

2. Experimental details

Ultra high vacuum (UHV) stainless steel chamber is used for thin films deposition of carbon by magnetron sputtering. The sputtering target of 75 mm, which in our case was high purity graphite, goes on the magnetron sputter head. The length of the sputter head inside the chamber is adjustable, which allows us to vary the position of the head with reference to the substrate holder. The substrate holder is 10 × 10 cm^2 copper plate and was fixed at 18 cm from the sputter head for the purposes of deposition. The sample holder is insulated from the rest of the chamber for biasing. A variable biasing power supply with a capability of supplying 0–200 V was connected to the sample holder.

The chamber and the anode of the magnetron head were maintained at electrical ground. The temperature of the magnetron head and the substrate were maintained at 6 °C. The sample holder was biased using metallic water lines. In the case of zero biased deposition the sample holder was grounded to the chamber. Ultra high vacuum was produced inside the chamber by cryogenic pump. The chamber was pumped for at least 24 h before carrying out the deposition. This is done to reduce the partial pressure of water vapors inside the chamber. In order to be consistent, depositions were carried out after a pressure of 2×10^{-8} Torr was achieved. The residual gas pressure (RPG) inside the chamber was monitored by a mass spectrometer as well as an ion gauge.

Hydrogenated DLC films were deposited by the process of Unbalanced Magnetron Sputtering (UBM). Hydrogenation was carried out by adding hydrogen along with argon during the growth process. Substrates were maintained at negative bias of 0, 25, 50, 75, 100, 125, and 150 V. Argon was diluted with hydrogen with a separate flow controller, but the mixture was introduced into the chamber through a common inlet. Argon flow rate was kept fixed at 200 sccm and hydrogen flow rates were varied from 0 to 70 sccm, with the increment of 10. Samples were named in such a way that it included the bias and hydrogen flow rate information for the respective sample. For example, sample 0–50 indicates that it was deposited at zero bias and with the hydrogen flow rate of 50 sccm. All the depositions were carried out at low temperature of 6 °C. Magnetron plasma was stimulated by a DC power supply that was used in constant current mode, maintained at 0.5 Amps. The base pressures for the deposition was in lower 10^{-8} Torr range. All the films were deposited at 6.4 mTorr of working pressure.

For the preparation of argon + nitrogen sputtered films, 200 sccm of argon was used to sputter the graphite target. Nitrogen was added along with the argon through a separate flow controller but was introduced inside the chamber through a common inlet. Nitrogen was varied from 1 to 9 sccm with an increment of 2. A negative bias of 25 or 50 V was used to deposit these films. These samples were named to include the bias, hydrogen and nitrogen flow rates. For example the name 25–0–90 indicates the sample was deposited with zero bias and hydrogen flow rate and with 9 sccm of nitrogen. Same steps were followed for depositing the argon + nitrogen sputtered films as were followed for depositing argon sputtered films. All films were deposited for 1.5 h achieving thickness in the range of ~100 to 150 nm. Silicon was used as the substrate, and each substrate was masked with carbon tape to obtain the thickness of the films. The conducting carbon tape ensures that the bias from the substrate holder comes to the films. This arrangement is especially useful for the insulating substrates. After the deposition process, x-ray diffraction (XRD) was carried out to confirm the amorphous structure of the films. XRD spectra for samples only gave the peak for the Si substrate which indicates the amorphous nature of the deposited films. XRD spectrum for the sample 0–50 is shown in the Fig. 1.

Characterization of the sample was carried out using ion beam analysis (IBA) techniques; Rutherford backscattering spectrometry (RBS), Elastic Recoil detection analysis (ERDA) and non-Rutherford backscattering (NRBS). Ion beam analysis of these samples was performed using 6 MeV Tandem Van de Graaff accelerator at the Western Michigan University Department of Physics in Kalamazoo, Michigan. Rutherford backscattering spectra (RBS) and non-Rutherford backscattering spectra (NRBS) were recorded using 2.5 MeV beam of H$^+$ ions, incident at 67.5° from the normal to the sample surface. Backscattered ions were collected using a silicon surface barrier detector at a scattering angle of 165°, and an exit angle of 68.31° as measured with respect to the sample's surface normal. This configuration was chosen so that the position of the sample remains

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