The relationship between structure and mechanical properties of hydrogenated amorphous carbon films

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ABSTRACT

There is increasing interest in the relations between Raman fit parameters and the mechanical properties of diamond-like carbon films. The present work describes these relations in hydrogenated diamond-like carbon films (a-C:H) deposited by an ion beam source operated at varied discharge voltages, *i.e.* kinetic carbon species energies. A number of highly distinct relations between Raman fit parameters and mechanical properties are identified for the a-C:H films investigated. For example the nanohardness (H) and reduced elastic modulus (E) increase almost linearly with an increase in full width at half maximum of the G-band (FWHM (G)). The film elasticity, expressed as H^3/E^2 increases with increasing FWHM (G). In addition, H and E increase linearly with decreasing intensity ratio of the D-band and the G-band (I_D/I_G). H and E also increase with the G-band dispersion (Disp. (G)), *i.e.* the rate of change of the G-band position vs. excitation energy. Hydrogen contents in all films are approximately equal and range from 21.2 to 23.5 at.% over the entire set of investigated samples.

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1. Introduction

Diamond-like carbon (DLC) is a metastable amorphous form of carbon with a significant amount of sp^3 hybridisation [1]. Due to the broad range of possible physical and chemical properties, structure/property relationships are really important in DLC research. In this regard, Raman spectroscopy is the most direct way to determine the carbon structure in all forms of carbon materials ranging from crystalline to amorphous carbon [1].

DLC films show two prominent features in their Raman spectra, the so-called D-band around $1360\ cm^{-1}$ and the G-band which lies around $1560\ cm^{-1}$ [1]. The D-band is due to the 'breathing modes' of all sp^2 atoms in distorted rings and the G-band is due the bond stretching of all pairs of sp^2 atoms in rings and chains [2 and references therein]. The main Raman fit parameters used to describe the structure of DLC are: the intensity ratio of the D-band and the G-band (intensity ratio I_D/I_G), the full width at half maximum of the G-band (FWHM (G)) and the dispersion of the G-band with excitation wavelength (Disp. (G)) [2].

The intensity ratio I_D/I_G is almost zero for tetrahedral amorphous carbon films (ta-C) and for polymer-like amorphous carbon films (polymeric a-C:H) [2]. Since the intensity ratio I_D/I_G is a parameter which probes the amount of ring-like sp^2 clusters and their disorder in a-C:H films, this suggests that in ta-C and polymeric a-C:H films only some sp^2 rings are present. The FWHM (G) gives information on the structural disorder in DLC films, so this fit parameter is proportional to the mechanical properties of the film [2]. Structural disorder arises from the bond angle and bond length distortions in DLC. The FWHM (G) is small when sp^2 clusters have less defects and are ordered whereas a higher FWHM (G) is indicative of an increase in disorder. This effect originates from the higher bond length and higher bond angle in more disordered materials. The FWHM (G) is in direct relation with the Csp^3–Csp^3 bonding content [2].

Disp. (G) is a measure of the topological disorder [2]. Topological disorder arises from the size and shape distribution of sp^2 clusters. Samples with an sp^2 phase entirely constituted of fully π delocalised rings do not show any Disp. (G) and therefore Disp. (G) is zero. Disp. (G) arises from the resonant selection of sp^2 chains of different sizes at different excitation energies [2]. Highest values for Disp. (G) are around $0.35\ cm^{-1}\ nm^{-1}$ for ta-C and polymeric a-C:H. Therefore, Disp. (G) is proportional to the overall sp^3 content (Csp^3–Csp^3 + Csp^3–H1s) in a-C:H films [2]. The presence of hydrogen causes the overall sp^3 content of a-C:H and hydrogenated tetrahedral amorphous carbon films (ta-C:H) to lie

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between 60 and 70 at.%. The hardness values of these two types of films are very different. The ta-C:H films may reach a hardness up to 50 GPa, whereas polymeric a-C:H films with the same overall sp^3 bonding content have a hardness of less than 10 GPa [1]. While the FWHM (G) is correlated with the Csp^3–Csp^3 bonding content *i.e.* structural disorder and mechanical properties, Disp. (G) and I_D/I_G are related with the sp^2 site configuration *i.e.* topological disorder: a low Disp. (G) or high I_D/I_G indicate that the sp^2 sites are arranged in rings; a high Disp. (G) or low I_D/I_G indicate that the sp^2 sites are arranged in chains (as in ta-C, ta-C:H or polymeric a-C:H). Depending on the hydrogen content, two different structural regimes can be observed for a-C:H films [2]:

(1) At hydrogen contents <25–30 at.% the structural (FWHM (G)) and topological disorder (Disp. (G)) vary parallel to the amorphisation trajectory *i.e.* the structural evolution from graphite to ta-C, and relate to the Csp^3–Csp^3 bonding content as seen for ta-C and ta-C:H films.

(2) If the hydrogen content is >25–30 at.%, structural and topological disorder have opposite trends, *i.e.* at higher hydrogen concentrations the overall sp^3 content can in contrary to the Csp^3–Csp^3 content still increase.

In this work we investigate the correlation between structure and mechanical properties of a-C:H films. The properties of the deposited films were investigated by: dual wavelength Raman spectroscopy to study the film structure; Elastic Recoil Detection Analysis (ERDA) to determine the hydrogen content; and nanoindentation to study the mechanical properties.

2. Experimental details

2.1. Film deposition

The a-C:H films were deposited by using an ALS340L linear anode layer source from Veeco Instruments (Woodbury, NY, USA). The source was operated with 20 sccm acetylene (nominal purity >99.96%), which was flushed directly into the discharge channel. A detailed description of the ion beam source in use is given in references [3] and [4]. Discharge voltages ranging from 1 to 3 kV were applied to the anode for deposition. The discharge voltage is proportional to the effective kinetic energy of accelerated species, being typically 25-45% of the discharge voltage. Boron doped silicon wafers (100) with a thickness of 500 μm were used as substrates. The wafers were fixed on a grounded substrate holding carrousel situated at a distance of 15 cm from the anode layer source. For plasma cleaning of the wafers prior to deposition the ion source was operated at a discharge voltage of 2 kV with 20 sccm argon. Plasma cleaning and film deposition was carried out by oscillation of the carrousel in front of the anode layer source, providing homogeneous cleaning and film deposition over the whole substrate holder. The movement of samples was perpendicular to the major ion beam axis of the anode layer source. For all depositions the chamber was evacuated to a base pressure of $\leq 5 \cdot 10^{-5}$ mbar, whereas the process pressure was $1.3 \cdot 10^{-3}$ mbar. The substrate temperature, which was measured with a K-type thermocouple installed at the backside of the substrate holding plate, ranged between 40 and 70 °C. The films were deposited to a thickness of 250 nm.

2.2. Film characterisation

Two Raman micro-spectrometers (Jobin-Yvon, Villeneuve d'Ascq, France) were used to characterise the structure of the a-C:H films. They are equipped with lasers at excitation wavelengths of 325 and 532 nm, respectively. Olympus 40× (for 325 nm) and 100× objectives (for 532 nm) were used to focus the laser-beams on the sample. The laser power was kept well below 0.25 mW on the sample. The entrance slit to the spectrometer was set at 100 μm. A holographic grating with 1800 grooves mm^{-1} was used for the 532 nm excitation

wavelength whereas for the 325 nm excitation wavelength a grating with 2400 grooves mm^{-1} was chosen. The Raman spectra were fitted with symmetric Gaussian lines.

Nanoindentation measurements were performed on a Hysitron Triboscope (Hysitron Inc., Minneapolis, MN, USA) using a cube-corner indenter with a tip radius <50 nm. The Hysitron Triposcope transducer was mounted on the scanner head of an atomic force microscope Dimension 3100 (Veeco Instruments, Woodbury, NY, USA), consisting basically of an indenter tip attached to a capacitive force-displacement transducer indenting vertically into the DLC films. Loads ranging from 200 to 750 μN were applied, with rates of 100 to 350 μN/s and held for 8 s at the maximum to ensure sufficient time until eventual indentation creep has vanished. Quantitative hardness and reduced modulus values were determined from the unloading part of the load–displacement curves by applying the method introduced by Oliver and Pharr [5]. The so-called reduced modulus takes into account the deformation of the indenter tip and the lateral deformation of the sample material via its Poisson's ratio [5]. Influence from the substrate [6] and indentation size effect [7,8] were excluded by careful choice of the indentation depth.

Hydrogen contents were determined by ERDA with a 2 MV tandetron accelerator using a beam of 4.2 MeV ^{7}Li ions [9]. The beam was collimated by a 1×2 mm rectangular shaped slit placed in front of the entrance of the experimental chamber which was equipped with two silicon detectors; the Rutherford backscattering spectroscopy (RBS) detector at the scattering angle of $\theta = 150°$ and the ERDA detector at the recoil angle of $\varphi = 30°$. The incident beam angle and the exit angle, as measured from the normal to the sample surface, were both 75°. An 11 μm thick aluminium absorber foil was inserted in front of the ERDA detector to block the scattered ^{7}Li ions. The measured RBS and ERDA spectra were analyzed using SIMNRA [10] code.

3. Results and discussion

In previous papers [3,4] we have shown that a-C:H films can be deposited using a rather new method, employing a the so-called anode layer source. We have shown that the structure and the mechanical properties of the deposited films can be tailored effectively by the discharge voltage applied to the source, *i.e.* since this affects the kinetic energy of carbon species. Within the applied deposition parameters it is possible to increase the deposition rate in linear way from 4 to 10 nm min^{-1} when increasing the discharge voltage from 1 to 3 kV at a constant C_2H_2 flow of 20 sccm [3,4]. Elevation of the C_2H_2 flow by a factor of three results in a fourfold increase of the deposition rate. The nanohardness could be tuned up to 36 GPa. The films deposited by this source are almost defect free and show a root mean square roughness of 0.1 nm [3,4].

In the present paper we study the relationship between structural and chemical properties of the deposited films and their nanomechanical properties. Fig. 1 shows Raman spectra taken at 325 and 532 nm excitation wavelength of an a-C:H film deposited at a 3 kV discharge voltage. The G-peak position changes with the wavelength, as indicated by a dashed line in Fig. 1 and was found to have the value of 0.16 cm^{-1}/nm. The lowest applied discharge voltage of 1 kV resulted in a significantly increased Disp. (G) of 0.23 cm^{-1}/nm, being in consistency with intermediate discharge voltages showing a systematic variation with Disp. (G) (Fig. 2).

Such a strong increase in Disp. (G) can be attributed to a significant increase of Csp^3–Csp^3 and/or Csp^3–H1s bonds in the films [1]. A similar trend was demonstrated for the intensity ratio $I_D/I_G^{532\ nm}$ as a function of the discharge voltage (Fig. 2). The overall sp^3 content is highest in films deposited with the lowest discharge voltage and decreases almost linear with the discharge voltage which can be extracted from an increasing I_D/I_G ratio (Fig. 2).