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Hard-hydrogenated tetrahedral amorphous carbon films by distributed electron cyclotron resonance plasma

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Abstract

Hard-hydrogenated tetrahedral amorphous carbon films (ta-C:H) are deposited from acetylene-fed distributed electron cyclotron resonance (DECR) plasma over large area (300 mm diameter disk) at near room temperature (below 140 °C). The effects of the ion flux and energy on the structure and physical properties are investigated. For a constant substrate bias V_0 of -150 V, the mass–density, Young's modulus and hardness reach a maximum value of ~2.5 g/cm^3, ~280 GPa, and ~45 GPa, respectively, and the hydrogen content reaches a minimum of 26 at.% at the maximum ion flux ϕ_+ of $\sim 6.3 \times 10^{15}$ ions cm^{-2} s^{-1}. For a constant ion flux and pressure, the mass–density and Young's modulus reach a maximum at a substrate bias of -300 V, and the hydrogen content is minimised. Electron diffraction, and Raman spectra show that the films grown at the maximum ion flux and a negative substrate bias ranging between 150 and 500 V are ta-C:H. The films contain sp^2-carbon clusters and chains. sp^2-carbon clustering increases with the increase of the substrate bias and decreases with the increase of the ion flux. The disorder increases with the ion flux and decreases with the bias. The optical band-gap decreases with disorder and with sp^2-carbon clustering. It depends primarily on disorder rather than on clustering.

Keywords: Tetrahedral amorphous carbon; Diamond-like carbon; DECR; Hardness; Raman spectroscopy; Band-gap

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1. Introduction

There is great interest in amorphous carbon films, hydrogenated (a-C:H) or not (a-C) containing a high fraction of sp^3-bonds between carbon atoms [1]. The sp^3-bonding between carbon atoms of a-C (and of a-C:H) confers on it many of the beneficial properties of diamond, such as its high hardness and large Young's modulus, low coefficient of friction, high wear resistance, smoothness, optical transparency in a wide range of wavelengths, chemical and biological inertness, low electron affinity, high electrical resistance, lack of magnetic response [1]. The films can be grown at near room temperature, and are much cheaper to produce than diamond. Therefore they have widespread applications, mainly as protective coatings in areas such as magnetic storage disks [2], optical windows, micro-electromechanical devices [1], optical storage discs [3,4], tools [5] and engines [6,7].

There are many forms of a-C (and a-C:H) films. The key parameters in such materials are: (1) the sp^3-content; (2) the clustering of the sp^2-phase; (3) the orientation of the sp^2-phase; (4) the cross-sectional nano-structure; (5) eventually, the hydrogen content, and C–H bonding. The sp^3-content alone mainly controls the elastic constants, but films with the same sp^3- and hydrogen contents but different sp^2-clustering, sp^2-orientation or cross-sectional nano-structure can have different optical and electronic properties [1].

The bonding and properties of a-C:H fall into four regimes defined primarily by the energy of the ion

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during the growth process [1]. At low energy, the films have large hydrogen and sp^3-contents (40–50 at.% and up to 60 at.%, respectively). These films are called polymer-like carbon (PLC) as most of the sp^3-bonds are C–H bonds. They are soft and have low mass–density (typically 1.2 to 1.6 g/cm^3). At intermediate energy, the hydrogen content falls (~30 at.%), the sp^3-content is less, but the films are harder and have higher mass–density since the number of C–C sp^3-bonds is higher. These films are called diamond-like carbon (DLC). When the sp^3 C–C content is maximum (~70–85 at.%), but the hydrogen content is ~20–30 at.%, the films are called hydrogenated tetrahedral amorphous carbon (ta-C:H). They are hard and their mass–density reaches 2.4 g/cm^3. At high energy, the hydrogen content falls further and the bonding becomes mainly sp^2-like. These films are called graphitic-like carbon (GLC).

sp^3-bonding is promoted by the deposition from a source of medium-energy ions [1]. At present, hydrogen-free ta-C with high sp^3-content is deposited by mass selected ion beam, filtered cathodic vacuum arc or by pulsed laser deposition [8–14]. From an industrial point of view, it is desirable to achieve good mechanical properties in a-C:H films grown by plasma enhanced chemical vapour deposition (PECVD) from a hydrocarbon precursor. ta-C:H has been deposited by high plasma density techniques, such as the plasma beam source (PBS) [15] and electron cyclotron wave resonance source (ECWR) [16,17]. The maximum reported sp^3-content and Young's modulus are 75% [15,18] and 300 GPa [19] respectively, and a maximum mass–density of ~2.4 g/cm^3 [18,19]. Early claims of a mass–density of up to 2.9 g/cm^3 for ta-C:H [15,16] were overestimated, due to an incorrect choice of the electron effective mass for mass–density evaluation via electron energy loss spectroscopy (EELS). Once the correct effective mass is taken into account the mass–density decreases to 2.4 g/cm^3 [18]. Standard RF-PECVD a-C:H does not achieve such properties [1,20–23], due to the low degree of ionisation of the deposition flux, and dispersion of the ion energy.

This paper reports on large area deposition and characterization of hard ta-C:H films from an alternative technique using distributed electron cyclotron resonance (DECR). The effects of the ion flux and energy on the structure and physical properties are studied.

2. Experimental

The films were grown on Si⟨100⟩ and polycarbonate (PC) substrates using a DECR plasma reactor described previously in details [24]. A micro-wave power P_{MW} of 800 W at a frequency of 2.45 GHz was used together with C_2H_2 as precursor. The plasma pressure P (pressure during plasma operation) was varied from 0.1 to 1.1 mTorr (from 13.3 to 146.6 mPa). Torr will be used as pressure unit (1 Torr = 133.32 Pa). The negative bias V_0 applied to the 300 mm diameter stainless steel substrate holder was varied in the range 25–600 V using a power supply operating at 13.56 MHz. The bias was kept constant during deposition by an automatic modulation of the RF power. The substrate holder was water-cooled enabling near room temperature deposition. In the experimental conditions considered, the temperature at the surface of the substrate holder during deposition remains lower than 140 °C, the PC glass temperature. No damage of the PC substrates was observed after deposition. Prior to deposition the silicon substrates were exposed to an Ar plasma cleaning for 5 min ($P_{MW} = 800$ W, $P = 0.5$ mTorr, $V_0 = -50$ V). The expected low dispersion of the ion energy [25], especially when C_2H_2 is used as precursor [15] in the range of pressure considered, and the possibility of controlling the ion flux by varying the pressure, confer to the DECR technique interesting advantages over other techniques to control the film structure [26].

The hydrogen content N_H and thickness were determined from nuclear reaction analysis (NRA) [27] and spectroscopic ellipsometry (SE) [24,27], respectively. The density ρ was deduced from the SE and NRA data [24,27]. The mean bond length r_1 and angle α were deduced from electron diffraction [28,29]. SE was used to estimate the optical band-gap [24,27].

Unpolarized Raman spectra were acquired at 244 and 514.5 nm using two different spectrometers. The UV spectra at 244 nm were excited using an intracavity, frequency-doubled Ar ion laser. They were collected using a Renishaw micro-Raman 1000 spectrometer on a 40 × objective with 244 nm filter, and an UV-enhanced charge-coupled device camera. The spectral resolution was of ~4–6 cm^{-1}. UV Raman measurements are prone to damage hydrogenated samples. To avoid damage the power on the sample was kept below 1 mW. The spectra were collected for 90 s while the samples were rotating at a high speed (>3000 rpm). This ensured no visible damage and no change of the spectral shape during the measurements. A Renishaw Raman microscope system 2000 was used to get the spectra at 514.5 nm (argon ion laser). The power was kept below 1 mW [28,29].

Fourier transform infrared spectroscopy (FTIR) measurements were performed using a Bio-Rad FTS-40 APC spectrometer in the transmission mode to assess the C–H bonding [27–29].

The Young's modulus E was estimated by laser induced surface acoustic waves (LISAW) [30]. The thickness of the films analyzed is between 70 and 190 nm.

Optical emission spectroscopy (OES) was performed using a Jobin Yvon HR 320 monochromator to record the evolution of the H_α (656.3 nm), CH (432.4 nm) and C_2 (512.9 and 516.5 nm) spectral lines with the plasma pressure.