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Synthesis of amorphous hydrogenated carbon thin films by magnetized radio-frequency discharge in argon–acetylene mixture at very low gas pressure

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ABSTRACT

This paper presents a characterization study of carbon thin films grown on crystalline silicon substrates using a magnetized high-frequency discharge in argon–acetylene mixture at very low pressure. Thin films with different morphological structure are obtained. Depending on the gas pressure, acetylene percentage and process time, it is possible to categorize the surface film morphology into three categories: smooth, cracked or microstructured. Moreover, when applying external magnetic field, it has been observed that depending on the substrate direction (perpendicular or parallel) to the reactor axis, it is possible to obtain different film morphologies. For specific conditions, energetic argon ions are formed which lead to film surface damaging and to their inclusion when they impinge the film surface. Chemical pathways and most likely isomers that contribute to the growth are also identified and discussed. Synthesizing materials in such low pressure conditions is of particular interest for better understanding the complex phenomena taking place in the plasma such as instabilities induced by particles and infra-red spectra of carbonaceous interstellar dust.

1. Introduction

Hydrocarbon based-plasmas are of great interest for industrial applications as well as for fundamental physics. They are used in combustion [1,2], in thin film deposition (diamond, diamond-like carbon, amorphous carbon…) [3–6], in carbon nanomaterial (nanotubes, nanowalls, nanoparticles...) synthesis, etc. [7,8]. Hydrocarbon plasmas are also of importance for understanding the behavior of fusion devices based on graphitic divertors [9,10]. These plasmas can also provide insight into the fundamental mechanisms leading to the formation of protoplanets in the interstellar space [11] and to determine the composition of the hydrocarbon rich atmosphere of Titan (moon of Saturn) [12].

In laboratories, the techniques mainly used to transform hydrocarbons into carbon-based materials are chemical vapor deposition (CVD) and plasma-enhanced CVD (PECVD). Even though these techniques have found their way for several industrial applications, the fundamental physical and chemical mechanisms governing the precursor decomposition and material growth are still not well understood. This is because carbon is able to form simple, double and triple bonds, hence leading to a very large variety of species; radicals, molecules and ions. Many precursors can be used as carbon suppliers, including alkane (C_nH_{2n+2}), alkene (C_nH_{2n}) and alkyne (C_nH_{2n-2}). These molecules are formed of carbon and hydrogen atoms in various ratios and their carbon–carbon bond is simple, double and triple in alkane, alkene and alkyne, respectively. Other carbon precursors that contain chemical groups (*e.g.* oxygen, nitrogen, chlorine, etc.) can be also used for specific applications resulting in highly complex plasma chemistry [13,14].

A large number of carbon allotropic forms and phases can be obtained by the combination of sp^3, sp^2, and sp hybridized atoms. For example, diamond is the unique solid form of purely sp^3 hybridized carbon atoms while graphite and fullerene are well-known solid forms of pure sp^2 hybridized carbon atoms. In addition, there are many transitional forms in which sp^2 and sp^3 hybridization bonds coexist in the same solid such as in amorphous carbon, carbon black, soot, cokes, glassy carbon, etc. [15,16]. Using CVD and PECVD techniques, it is unlikely to obtain hydrogen-free carbon materials especially in the case of sp^2 and sp^3 hybridized bond mixtures. Therefore, the material is referred to as hydrogenated carbon [17,18]. The synthesis of solid sp hybridized carbon is more complicated than other hybridization forms [19]. However, in interstellar clouds, linear carbon chains have been found in which carbon atoms are linked by alternating single and triple bonds (polyyne) or single and double bonds (polycumulene) with stabilizing molecular complexes at the end of the chains. In laboratories, researchers have successfully produced this kind of chains by different chemical routes [20,21]. However, the formation mechanisms are not yet fully identified and their identification necessitates a better understanding of these complex media [22].

As a hydrocarbon precursor, acetylene (C_2H_2) exhibits several properties that make it of greater interest compared to other precursors. Its

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molecular chain is linear and the two carbon atoms are linked together by a strong triple bond (~10 eV) while each carbon atom is linked to a hydrogen atom. In addition, acetylene plasmas lead to the formation of soot or dust particles [23]. At very low pressure (~Pa), their use is not suitable for applications (*e.g.* synthesis of materials) because the growth rate is too low to make the process cost-effective compared to recently developed CVD techniques at atmospheric pressure (AP-PECVD) [24,25]. However, synthetizing materials under such low pressure conditions is of interest for better understanding the complex phenomena taking place in the plasma such as instabilities induced by particles [26,27] and infra-red spectra of carbonaceous interstellar dust [28].

In this article, we present a material characterization study of thin films obtained in very low pressure (0.27 to 2.67 Pa) plasma generated in different gas ratio of argon and acetylene using high frequency electromagnetic waves. We examine the influence of the magnetic field intensity (from 0 to 150 Gauss) and its orientation on films grown on silicon substrates. The films are characterized ex-situ by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Ellipsometry and Raman spectroscopy.

The paper is organized as follows. After a brief description of the experimental setup in Section 2, the results concerning the material characterization including the effect of the magnetic field, gas pressure and acetylene percentage are discussed is Section 3. We then conclude in Section 4.

2. Experimental setup

The experimental setup is schematically depicted in Fig. 1. The high-frequency power is coupled to the plasma through a quartz tube surrounded by a Ro-box surface wave launcher at a frequency of 200 MHz. As shown in Fig. 1, shortly after the Ro-box, the quartz tube (15 cm in diameter) is connected to a stainless steel cylindrical chamber with an inner diameter of 20 cm and a length of 96 cm. The magnetic field is generated by four coils connected in series and placed around the stainless steel chamber. The relative position of the coils is adjusted to achieve a magnetic mirror configuration. The coil current is adjustable and its maximum value can reach ~200 A, which results in a magnetic field intensity of 150 G at the middle of the reactor between the two set of coils. The mirror ratio is equal to 1.9, which corresponds to the maximum value of the magnetic field of 285 G at the coils position.

Acetylene (C_2H_2) mixed at various percentages with argon (purity of 99.999%) is used as gas precursor. The mixture is introduced in the chamber by means of MKS Mass-Flow Controller with a maximum flow limit of 20 sccm (standard cubic centimeters per minute). The total gas flow during the deposition was 3 sccm and it was kept constant for all deposition conditions. The percentage of C_2H_2 was calculated according to its pressure in the reactor.

Before experiments, the chamber was pumped to a base pressure of ~10^{-8} Pa (measured by an ionization gauge). Between each plasma produced in acetylene mixtures, an oxygen plasma was run for a few tens of minutes in order to clean up the reactor walls. The gas pressure in the chamber was measured by means of a Baratron gauge from MKS instruments ranging from 0 to 13.3 Pa.

We used a sample holder that allows us to position one sample perpendicular to the chamber axis and the other parallel. In a first approximation, these samples are perpendicular and parallel to the magnetic field lines, respectively. We used (100)-oriented silicon samples with area of ~5×5 mm^2 and thickness of 500 μm. Before introducing the substrate holder into the chamber, the samples were cleaned by methanol and exposed to dry air. The sample holder is floating, and the floating potential (deduced from the Langmuir probe measurements) does not vary much with the experimental conditions.

The materials deposited were characterized by Scanning Electron Microscopy (SEM). Using the field emission gun scanning electron microscope JEOL JSM-6300F FEG equipped with a micro-EDX (Energy Dispersive X-ray), we were able to observe the surface and to perform elemental analysis of the samples. The deposited films were characterized by X-ray diffraction (XRD) at grazing angle of 2° using a Philips X'PERT instrument with a Cu-Kα (1.54056 Å) radiation source. Raman spectrometry (Renishaw 3000) was also used to characterize film structure at a laser wavelength of 514 nm and a beam attenuation of 90% to avoid film damage. Ellipsometry spectroscopy (J. A. Woollam Co., Inc. M2000), with an angle of 75° in the wavelength range of 200–1700 nm, was finally used to estimate the thickness and the optical properties of the deposited films.

The reproducibility of the film was investigated for one set of conditions (20% acetylene, pressure of 0.27 Pa, 10 min of process, and power of 350 W), and the films were found to be reproducible within over 90%.

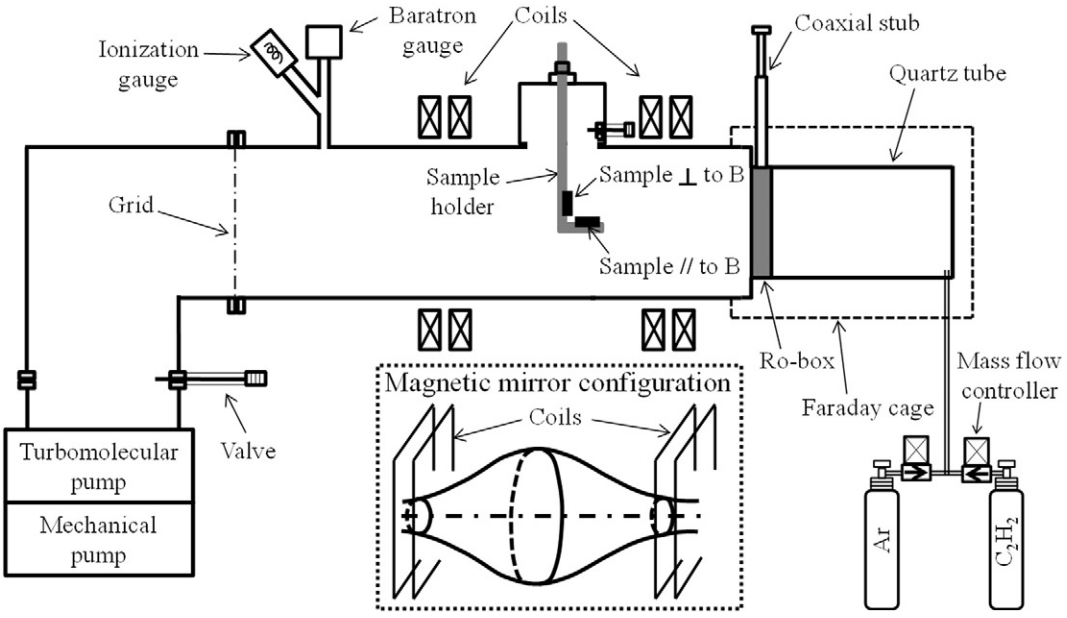

Fig. 1. The experimental setup.