

Deuterated amorphous carbon films: film growth and properties

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Abstract

Deuterated amorphous carbon films (DLC) have been studied in the last few years in order to investigate possible isotopic effects in the film properties. When compared with films deposited in methane atmosphere, an important reduction of the deuterium content of the films was observed and the reasons for that are not well understood. In this work, we deposited amorphous carbon films by PECVD using methane and deuterated methane gas mixtures as precursor atmospheres. The hydrogen and deuterium content was measured by elastic recoil detection analysis and we observed the preferential incorporation of hydrogen over deuterium. The precursor atmosphere was monitored by mass spectrometry and only small differences can be observed in the obtained mass spectra. The possible reasons for the total hydrogen content are discussed.

Introduction

Diamond-like carbon (DLC) films have attracted much attention due to their outstanding physical and chemical properties [1]. DLC can be defined as an amorphous carbon material, that can be hydrogenated (a-C:H) or not (a-C), with a significant fraction of sp^3 carbon-bonds and with high mechanical hardness and wear resistance, chemical inertness and low friction. The properties of films, which are closely related to their microstructure, can be tuned by the deposition technique employed and by the growth conditions, with the energy of the impinging species playing the main role in the control of the film properties [1-3]. Deuterated amorphous carbon films (a-C:D) deposited by plasma assisted chemical vapor deposition (PECVD) using deuterated hydrocarbons as precursor gases were also investigated for some specific applications, like storing ultra cold neutron devices [4] or as neutron mirror [5]. In order to tailor the film properties in a controlled way, a fundamental understanding of the microscopic deposition process is necessary. Among the several aspects that need to be clarified, the preferential incorporation of hydrogen over deuterium in amorphous carbon films deserves investigation.

Experimental procedures

Amorphous hydrogenated carbon films (a-C:H) were deposited by plasma enhanced chemical vapor deposition (PECVD) with CH_4 - CD_4 mixtures as precursor gas employing an asymmetrical capacitively coupled deposition system. Silicon substrates were mounted on a water-cooled copper cathode fed by a rf power supply. The films were deposited with a total pressure of 8 Pa and total incoming gas flux of 10 sccm up to a thickness of about 400 nm. Details of the deposition procedure can be found elsewhere [6]. The self-bias voltage (V_b) was fixed at -350 V and the CH_4 partial pressure varied from 100% (a-C:H films) to 0% (deuterated carbon films, a-C:D). A quadrupole mass analyzer was installed in the deposition chamber connected through a 1 mm diameter collimator. The region between the collimator and the quadrupole mass analyzer was pumped by a turbomolecular pump with pumping speed of 55 l/s for H_2 .

The chemical composition was determined by Rutherford backscattering spectrometry (RBS) and ERDA employing a 4 MV Van de Graaff accelerator to produce a 2 MeV $^4He^+$ beam. For RBS the particle detector was positioned at 165° with respect to the incident beam, while for ERDA measurements the detector was positioned at 30° . The sample was tilted by 75° with respect to the incident beam. The atomic density was inferred by combining the areal atomic density (at/cm^2) provided by RBS and ERDA and the thickness obtained by stylus profilometry.

Results and discussions

Elastic recoil detection spectra obtained from different films are presented in fig. 1. The spectra show that both H and D concentrations are constant throughout the film.

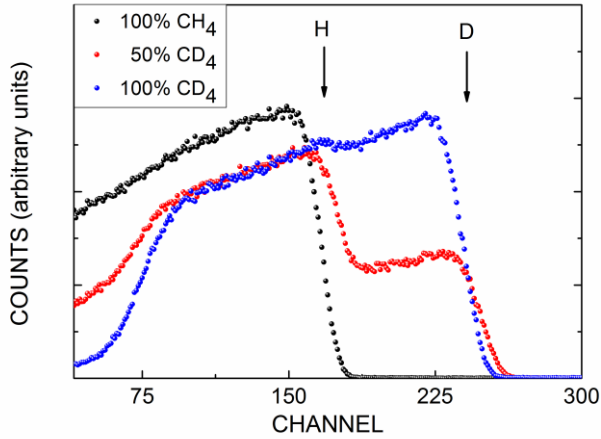


Figure 1: Elastic recoil detection spectra obtained from a a-C:H film; a-C:D film and an a-C:H:D film deposited by PECVD with CD₄-CH₄ gas mixture as precursor atmosphere. The positions of H and D when they are at the sample surface are indicated by arrows.

The atomic density, the deposition rate, the hydrogen and deuterium concentrations are presented in Table I. Absolute hydrogen and deuterium concentrations were obtained using the accurate measurements of the absolute cross sections for elastic recoil of H and D using low-energy ⁴He⁺ beams [7]. The results for the absolute H or D concentrations quoted in the literature show a large deviation that is usually higher than the errors stated by the experimentalists [8]. In this work, more relevant than the absolute value are the relative errors for the ratio between the hydrogen and deuterium cross sections that are $\pm 2\%$ [7].

Precursor gas mixture	Atomic concentration (at.%)		Atomic density (1023 atoms/cm ³)
	D	H	
100 % CH ₄	-	22	1.3
75% CH ₄ + 25% CD ₄	5	15	1.3
50% CH ₄ + 50% CD ₄	8	11	1.3
25% CH ₄ + 75% CD ₄	11	7	1.3
100 % CD ₄	17	-	1.3

Table I: Atomic density and hydrogen and deuterium concentration measured by nuclear techniques as functions of the precursor gas mixture and the self-bias voltage

Our data confirm previous results and show an important preferential incorporation of H over D [9]. In fact, in our experimental conditions, hydrogen concentration in an a-C:H film is 18% higher than deuterium concentration in a-C:D films. The same is observed in a film deposited using a 50:50 mixture of CD₄ and CH₄. One of the possible explanations for these results was presented by Johnson and collaborators [10]. They attributed the preferential incorporation of H to the different pumping speeds for the different molecules when turbomolecular pumps are used since they are more efficient for heavier molecules. In order to compensate this effect higher flow ratios for CD₄ can be used. However, our chamber is pumped by a diffusion pump and the differences in the pumping speeds are minimal for this range of molecular weight.

Differences in deuterium plasma chemistry can also be responsible for the differences in the incorporation of H and D, but there are few available experimental data [10]. In order to bring new information to this subject, we monitored the precursor atmosphere by mass spectrometry during the film deposition. The mass spectra are presented in fig. 2 for several CD₄-CH₄ mixtures. The spectra show a small peak at mass 2 (4) due to H₂ (D₂), a group due to CH₄ (CD₄) and its fragments around mass 16 (20) and a third group at around 28 (32) attributed to C₂H_n (C₂D_n) at around mass 28 (32). The same relative intensity between the second and the third group is observed for all CD₄-CH₄ mixtures. The mass spectra were also measured without power applied to the cathode. The spectra are similar than those shown in fig. 2 with some differences: the peak due to H₂ (D₂) is below the detection limit of our quadrupole analyzer and the intensity of the peaks attributed to C₂H_n (C₂D_n), when we normalized the spectra by the mass 16 peak, are much smaller than one can observe in fig. 2. The mass spectra did not indicate any isotopic effect during deposition. In fact, the intensities of C_nH_m or C_nD_m radical peaks observed in the mass spectra can be directly correlated with the partial pressure in the precursor atmosphere of methane or deuterated methane,

respectively. The same was observed for the peaks corresponding to mass 2 and 4. These results also support the statement made above that there is no preferential pumping of deuterated species over hydrogenated ones in our deposition system.

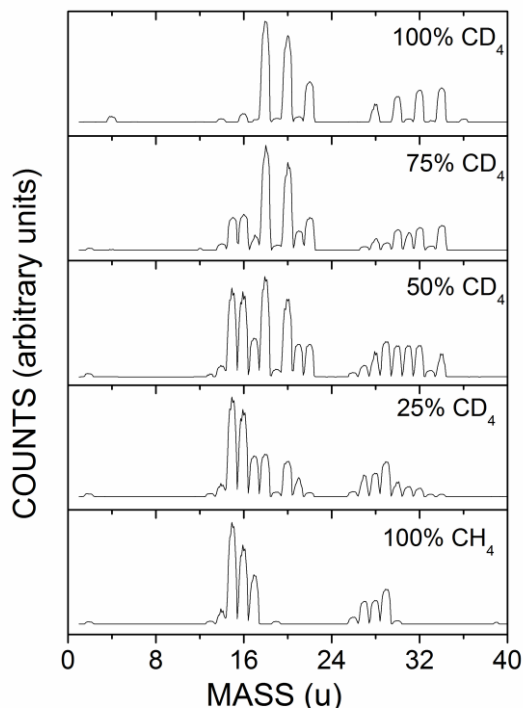


Figure 2: Mass spectrum obtained during film deposition by PECVD (8Pa, -350V) with different precursor atmosphere, as indicated in the figure.

The preferential incorporation of H over D can be attributed to an enhancement of the dehydrogenation process when deuterium is involved, favoring the loss of the heaviest isotope. The energy of the plasma is sufficient to allow subplantation of hydrogen ions, which have enough kinetic energy to modify the subsurface by removing bonded hydrogen. For the same V_B , both D and H ions will have the same kinetic energy, but probably, a shallower modified layer will be found in a-C:D films resulting in a more efficient hydrogen species removal during deposition, explaining at least partially, the less efficient D incorporation.

The film atomic density is, within our experimental errors ($\pm 10\%$), independent on the precursor gas used. The deposition rates for films deposited at different gas mixtures are also measured and a progressive reduction on the deposition rate was observed for films deposited in CD_4 richer plasma atmospheres. The differences in deposition rate suggest that films with different microstructure were formed.

Conclusions

We deposited a-C:D, a-C:D:H and a-C:H films by PECVD using methane and deuterated methane mixtures as precursor atmospheres. We measured the hydrogen and deuterium content in the films and verify the preferential incorporation of hydrogen over deuterium. In our experimental conditions, both the purity of the precursor gas and effects of the pumping system can be discarded as possible reasons for this result. We suggested that it can be attributed to a more efficient dehydrogenation process when deuterium is present in the plasma atmosphere and favoring the desorption of the heaviest isotope.

Acknowledgements

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