

Ion beam analysis of CH/Si layers deposited by ECR-CVD

J.A. Mejía Hernández^{c,d}, G. Murillo^{a,*}, R. Policroniades^a, E. Andrade^b, E. Camps^d, S. Muhl^c, and E.P. Zavala^b

^aAcelerador Tandem, ININ, Depto. del Acelerador,
Apartado Postal 18-1027, 11801 México D.F.

^bInstituto de Física, Universidad Nacional Autónoma de México,
Apartado Postal 20-364, 01000 México D.F.

^cInstituto de Investigaciones de Materiales, Universidad Nacional Autónoma de México,
Apartado Postal 70-360, 04510 México, D.F.

^dDepartamento de Física, ININ,
Apartado Postal 20-364, 01000 México D.F.

Recibido el 2 de marzo de 2006; aceptado el 18 de agosto de 2006

We present in this study the characteristics of CH layers deposited on Si substrates using an electron cyclotron resonance (ECR) microwave plasma source with different H₂/CH₄ mixtures. Quantification of the hydrogen and carbon content and the thickness of the films was determined by Forward Elastic Scattering with a 8.45 MeV ¹²C³⁺ beam. The oxygen concentration in the films was measured by Nuclear Reaction Analysis (NRA) using a 1.040 MeV deuterium.

Keywords: Plasma enhanced chemical vapor deposition; thin films; IBA methods.

En este trabajo se estudia las características de las capas de CH depositadas en sustratos de Si por una fuente de plasma de micro ondas del tipo Resonancia Ciclotrónica Electrónica (ECR), usándose diferentes mezclas de H₂/CH₄. El contenido de hidrógeno y carbono, así como el espesor de las películas se determinó por la dispersión hacia delante de un haz de ¹²C³⁺ con una energía de 8.45 MeV, y el bajo contenido de oxígeno en las mismas se determinó usando un haz de deuterio de 1.040 MeV llevando a cabo un análisis de reacciones nucleares (NRA).

Descriptores: Películas delgadas; métodos de análisis con haz de acelerador.

PACS: 52.Hr; 82.80.Yc; 73.61.r

1. Introduction

The preparation of thin films of amorphous carbon with a high concentration of sp³ type bonds is an example of materials that one can only obtain using a plasma. The properties of such amorphous carbon films depend on the relative quantities of the sp² and sp³ bonds existent between the carbon atoms and the distribution of the clusters of these, both aspects can be controlled by the characteristics of the plasma used. If material mainly has sp² bonded carbon it is very soft and polymer-like. If the carbon is mainly bonded in the sp³ form this type of amorphous carbon is normally referred to as diamond-like carbon (DLC) and was first produced in 1971 by Aisenberg and Chabot [1]. This group obtained films of carbon with an amorphous structure, but with properties similar to diamond (high optic transparency, high resistivity, index of refraction greater than 2, high hardness, a large dielectric constant and a high resistance to attack by hydrofluoric acid). If hydrogen is incorporated with the carbon an equivalent group of material can be obtained, but the properties depend on both the type of bonding and the hydrogen content. The deposited a-C:H phases can vary from polymer-like carbon (PLC), a soft material with a high hydrogen content and predominantly sp² bonded carbon, to diamond-like carbon (DLC), a mechanically hard material with a lower hydrogen content (about 20%) and predominantly sp³ bonded carbon, and finally to tetrahedral amorphous carbon (ta-C:H), which has a very low hydrogen content and sp³ bonded carbon (up to 80%) [2].

In ECR-CVD, the microwave power is used for the plasma generation and a DC substrate bias voltage to control the ion energy, thus allowing independent control of these two important parameters.

Six samples of CH were deposited on Si substrates by ECR Plasma Enhanced Chemical Vapor Deposition (PECVD) using several H₂/CH₄ mixtures.

Ion Beam Analysis (IBA) was used to measure the elemental composition of CH films, with the idea of determining the total elemental composition profile, including the hydrogen content. The sensitivity of the Backscattering Spectrometry (BS) methods is low for light elements in heavier substrates and it cannot be applied to detect hydrogen. In this work, Elastic Forward Analysis (EFA) [3] using a ¹²C³⁺ beam was used to obtain the elemental composition and thickness of each of the a-C_xH_y films. Oxygen is a frequently contaminant found in these films, and therefore Nuclear Reaction Analysis (NRA) using a ²H⁺ beam was applied to measure the concentrations of O in the films.

2. Experimental details

2.1. a-C:H films deposition

The a-C:H films were produced using a ECR microwave plasma source through the decomposition of mixtures of methane-hydrogen; 80% H₂ – 20% CH₄ for the films labeled as T6, T9, T12 and T15, 70% H₂ – 30% CH₄ for T19 and T20. The details of the deposition system can be found in

reference [4]. A microwave incident power of 400 W at 2.45 GHz was guided through circular and rectangular waveguides and introduced into the resonant cavity through a quartz window. In all cases the samples were deposited on silicon. The system base pressure was 3×10^{-6} Torr and during deposition was kept between 4.9×10^{-4} Torr and 5.8×10^{-4} Torr.

2.2. Films characterization

The atomic profiles of the carbon-hydrogen films were measured using two particle accelerators. A Van de Graaff tandem accelerator (HVECO EN model) located in the Instituto Nacional de Investigaciones Nucleares, equipped with a SNICS II ion source to generate a $^{12}\text{C}^{3+}$ beam at an energy 8.45 MeV that was used for the EFA [3] technique to find the $\text{C}_x\text{H}_y/\text{Si}$ ratio. The incident beam bombarded the samples at an angle of 60° relative to the target surface normal and the surface barrier detector scattering angle was set at 45° . The $^{12}\text{C}^{3+}$ ions elastically scattered by the Si and C nuclei in the forward direction and the emitted hydrogen recoil nuclei were measured in the same spectra with a good mass resolution.

A single ended 5.5 Van de Graaff (HVECO CN model) located at the Universidad Nacional Autónoma de México with a 1.040 MeV $^2\text{H}^+$ beam was used to measure the O concentration in the films by NRA. In this case, the targets were positioned normal to the incoming beam and the surface barrier detector was set at an angle of 150° . Since it is possible detect the signals from the $^{12}\text{C}(\text{d},\text{p}_0)^{13}\text{C}$ and $^{16}\text{O}(\text{d},\alpha_0)^{17}\text{O}$ reactions, it was possible to determine the oxygen concentrations in the samples, provided that the carbon concentrations are known, by using the following expression:

$$n_{\text{O}(\text{O})} = \frac{A_{\text{O}} \sigma_{\text{O}}}{A_{\text{C}} \sigma_{\text{C}}} n_{\text{C}} t_{\text{C}} \quad (1)$$

where $n_i t_i A_i$ and σ_i are the corresponding (O or C) concentrations, the spectra areas and the cross section of oxygen or carbon, respectively; the carbon concentration corresponds to that obtained by EFA for each sample.

3. Results and discussion

Figures 1 and 2, show typical EFA experimental spectrum (dots) for the 8.45 MeV $^{12}\text{C}^{3+}$ beam from an a-CH film. The solid line represents the SIMNRA [5] simulated fit to the spectrum. From the set of six samples analyzed, the thinnest films were simulated considering 2 sublayers:

- the surface sublayer, which provides the film C_yH_z stoichiometry and thickness and
- the silicon substrate. The other two thicker samples were simulated with 6 sublayers: one for the surface sublayer for the stoichiometry and thickness, four for the interfacial sublayer, which provides the $\text{C}_x\text{H}_y\text{Si}_z$ composition and thickness and
- the silicon substrate.

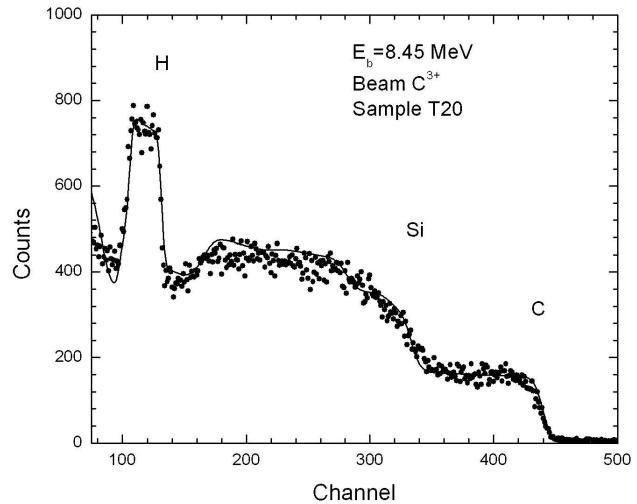


FIGURE 1. A typical elastic forward scattering (EFA) experimental spectrum (dots) for the 8.45 MeV $^{12}\text{C}^{3+}$ beam bombardment of a $\text{C}_x\text{H}_y/\text{Si}$ film prepared by ECR-PECVD using a ratio of $\text{H}_2/\text{CH}_4 = 4.0$. The detector scattering angle was set at an angle $\theta = 45^\circ$ and the sample surface normal formed an angle $\alpha = 60^\circ$ relative to the beam direction. The solid line shows the SIMNRA fit to the spectrum.

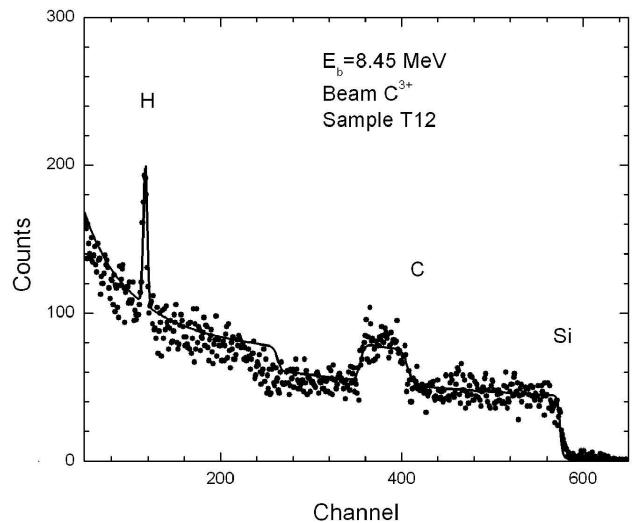


FIGURE 2. Shows a typical elastic forward scattering (EFA) experimental spectrum (dots) for a $\text{C}_x\text{H}_y/\text{Si}$ thin film prepared by ECR-PECVD using a ratio of $\text{H}_2/\text{CH}_4 = 7/3$. The solid line represents the SIMNRA fit to the spectrum.

Table I summarizes the fitting parameters for each CH/Si spectrum. The composition parameters x:y of the C_xH_y film were determined for the homogeneous region of the film, away from the interface and substrate. The total thickness of a particular element is given as atomic percentage. The corresponding standard errors are given in parenthesis as the error in the last digit.

Figure 3, shows the experimental spectrum (dots-line) produced by a 1.01 MeV $^2\text{H}^+$ beam bombardment of the same CH/Si film shown in Fig. 1. The identified NR peaks were: $^{16}\text{O}(\text{d},\text{p}_1)^{17}\text{O}$ and $^{12}\text{C}(\text{d},\text{p}_0)^{13}\text{C}$. The $^{16}\text{O}(\text{d},\text{p}_1)^{17}\text{O}$

TABLE I. A summary of the EFA and NRA fit parameters for the 6 samples. Stoichiometry parameters x:y of the $C_x:H_y$ film were taken for the homogeneous region of the film, away from the interface and surface. Standard errors are given in parenthesis as the mean error in the last digits.

Sample	Time (min)	Vbias sample	Ion Beam Analysis			
			Thickness (10^{15} at/cm 2)	H %	C %	O 10^{15} at/cm 2
T6	25	0	1070 (5)	0.425 (2)	0.575 (4)	0
T9	15	-40	1462 (5)	0.483 (2)	0.517 (4)	0
T12	11	-100	921 (5)	0.295 (3)	0.705 (4)	0
T15	10	-100	1885 (20)	0.341 (3)	0.659 (4)	16
T19	5.33	-175	5980 (30)	0.210 (3)	0.790 (4)	61
T20	15	-175	5589 (30)	0.246 (3)	0.754 (4)	28

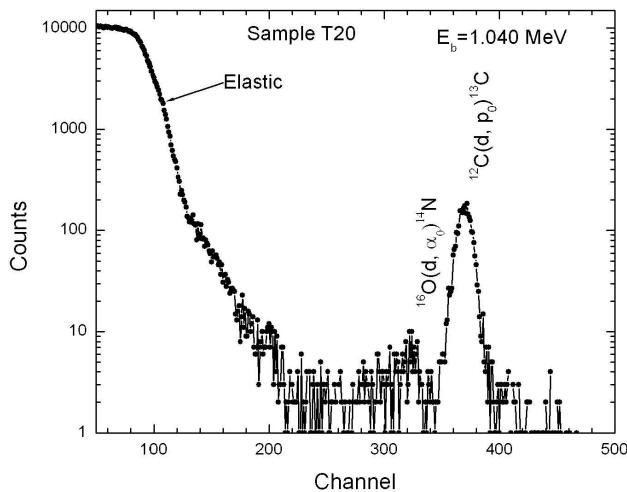


FIGURE 3. The experimental spectrum (dots) produced by a 1.040 MeV $2H^+$ beam bombardment of the same film of Fig. 1. The spectrum plot present NR high energy region that corresponds to the indicated NR peaks produced by the $2H^+$ bombardment from C and O nuclei.

and $^{12}C(d, p_0)^{13}C$ NR cross sections were taken from www-nds.iaea.org/ibandl and were used to obtain the oxygen concentrations of the films; these are also summarized in Table I.

4. Conclusions

With the IBA techniques used it was possible to determine the thickness and composition of the C-H films produced by ECR-PECVD and the possible contaminants. The origin of the low O concentration found in the films could be the outgassing of water and hydrocarbon molecules absorbed on the walls of the reactor chamber; although, the oxygen incorporation can occur by the post-deposition absorption of water vapor in the films.

In our experimental EFA set-up, the cross section for the kinematically reversed recoil process $^1H(^{12}C, p)^{12}C$ corresponds to $^{12}C(p, p)^{12}C$, for a proton energy of 0.608 MeV and an angle of 85.2° . A search in the www-nds.iaea.org/ibandl compilation showed that the cross sections for this energy are well described by Rutherford cross sections. Similarly, with the EFA it was possible to simultaneously measure the contributions from carbon and silicon. Since the contamination of oxygen was not adequately determined from these spectra, a RBS/NRA method was used to determine these contaminants.

Acknowledgements

The authors wish to thank P. Villaseñor for the operation of the Tandem Accelerator. This work was partially supported by DGAPA-UNAM under the project 228603-3.

* Tel. +52 55 5329-7200, ext. 2335, e-mail: gmo@nuclear.inin.mx

1. S. Aisenberg and R. Chabot, *J. Appl. Phys.* **42** (1971) 2953.
2. J. Robertson, *Materials Science and Engineering R* **37** (2002) 129.

3. S. Romero, M. Fernández, G. Murillo, and H.M. Berdejo, *Nucl. Instr. and Meth. B* **194** (2001) 164.
4. E. Camps *et. al.*, *Rev. Sci. Instrum.* **66** (1995) 3219.
5. M. Mayer, *SIMNRA Users Guide*, Report IPP 9/113, Max-Planck-Institut für Plasmaphysik, Garching, 1997.