Hydrocarbon isotope detection by elastic peak electron spectroscopy

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Abstract

Experimental results on the hydrocarbon isotope analysis by elastic peak electron spectroscopy are presented. Amorphous hydrocarbon samples (a-C:H, a-C:D) are prepared by PCVD and analyzed by nuclear reaction analysis (NRA), elastic recoil detection analysis (ERD), X-ray photoelectron spectroscopy (XPS) and elastic peak electron spectroscopy (EPES). Electron energy spectra show a clear signal from the hydrogen isotopes deuterium and protium. Different incident energies and scattering geometries help to resolve plasmon and elastic energy losses.

Keywords: Isotope detection, NRA, ERD, EPES, XPS, Fusion

INTRODUCTION

Quantitative analysis of the hydrogen content in the near-surface layer of a sample is one of the key tasks in many studies. Implantation and deposition of hydrogen isotopes from a thermonuclear plasma, formatting PCVD coatings or developing H-storage materials - all these techniques need information on atomic or isotope depth profiles[1, 2]. Most common techniques are elastic recoil detection analysis (ERD), secondary ion mass spectrometry (SIMS) or nuclear reaction analysis (NRA) [3]. They are known to be isotope sensitive and have a depth resolution of up to 0.5 nm. However, all of them have one well known disadvantage: these are not *in-situ* methods. Kimura et al. [4] performed ERD analysis of hydrocarbon CVD films and has shown, that most of the hydrogen is localized mainly in the first several monolayers. In this case *in-situ* analysis techniques are required, for example elastic peak electron spectroscopy (EPES).

Boersch *et al.* presented the idea and experimental realization of EPES for the first time in 1961 [5]. The main concept behind EPES is a well known solution for the elastic scattering of electron with the mass m_e on the scattering atom with the mass M_A . For this case the elastic energy loss ΔE is proportional to the primary energy E_0 of the electron and the scattering angle θ .

$$\Delta E = E_0 \frac{2m_e}{M_A} (1 - \cos \theta) \quad (1)$$

Equation (1) shows that the elastic energy loss is of the order of 10 eV for $E_0 = 30$ keV and decreases with decreasing primary energy. Therefore the most important prerequisite for this technique is high energy resolution. As a result the development of EPES started only in the recent 20 years, when high resolution energy analyzers became commercially available. A series of works by Vos *et al.* shows how elastic energy losses can be resolved and used to determine the mass of the scattering atom and the surface composition for thicknesses of the order of 10 nm [6–8]. The depth of EPES analysis can be approximated from the inelastic mean free path (IMFP) and the incident and reflection angles towards the surface normal - ξ, η .

$$d_{analysis} = \frac{IMFP(E_0)}{\frac{1}{\cos \xi} + \frac{1}{\cos \eta}} \quad (2)$$

Equation 2 shows that the EPES technique can be applied for IMFP determination, which is difficult by other methods [9–13]. Additionally, EPES could be applied for the analysis

of hydrogen isotopes concentrations in polymers [14], frozen water (D_2O , H_2O)[15] and also in CD_4 and CH_4 gases [16].

In contrast to SIMS the depth profiling by EPES does not need sputtering layer by layer. Analysis depth can be changed by changing the primary energy of electrons or by choosing another scattering geometry. Using electrons is convenient in compare to the NRA technique where the maximum incident energy and therefore the analysis depth is specified by the nuclear reaction. Taken together, the main aim of this work is to demonstrate the application of EPES for element analysis of CVD films with different isotopes like protium and deuterium, which are of main importance, for example, for plasma-wall interaction research in thermonuclear fusion devices.

EXPERIMENT

Amorphous hydrocarbon layers containing either protium (CH) or deuterium (CD) were deposited on silicon substrates in CH_4 or CD_4 plasmas, respectively, at gas pressures of 2 Pa at a bias voltage of -300 V. The layer thicknesses as determined by ellipsometry were about 70 nm and 160 nm, respectively. The amount of deuterium was determined by nuclear reaction analysis (NRA) using the $\text{D}(^3\text{He},\text{p})\alpha$ reaction at 2.5 MeV incident energy and a reaction angle of 135° . The amount of carbon was determined by NRA using the reactions $^{12}\text{C}(^3\text{He},\text{p}_0)^{14}\text{N}$ and $^{12}\text{C}(^3\text{He},\text{p}_1)^{14}\text{N}$ at 2.5 MeV incident energy and the reaction angle of 135° . The accuracy of measurements was about 5 %. The amount of H was determined with 3 MeV incident ^4He applying elastic recoil detection analysis (ERD). The SIMNRA program [17] with SigmaCalc cross-section for the hydrogen recoils [18] was used for the data evaluation. The absolute accuracy of ERDA is about 15 %. The sample properties are summarized in Table 1.

Concentration, atoms/ cm^{-2}		
	a-C:H	a-C:D
Carbon	$6.27 \cdot 10^{17}$	$1.20 \cdot 10^{18}$
Protium	$3.35 \cdot 10^{17}$	-
Deuterium	-	$7.53 \cdot 10^{17}$

TABLE I. Properties of the a-C:H and a-C:D layers

Electron spectroscopy experiments were performed in ultra-high vacuum conditions ($p=2.5 \cdot 10^{-10}$ mbar). The standard experimental setup consists of a μ -metal UHV chamber and is equipped with a Specs Phoibos 225 analyzer with 2D-CCD detector. The energy range of the analyzer is 0-15 keV with the best resolution of 0.03 eV at the maximum kinetic energy. The angular range of the analyzer is $\pm 13^\circ$ and could be adjusted by an iris diaphragm. The system is equipped with a non-monochromatic X-ray source SPECS XR50 with Ag/Mn anodes. Two Kimball Physics EG-4212 electron guns can accelerate electrons up to 30 keV. They realize two scattering angles - 45° for glancing geometry and 120° for reflected geometry. The guns are equipped with BaO cathodes for minimizing of the energy spread.

The deposited samples were exposed to ambient atmosphere before being measured by electron spectroscopy. In order to save hydrogen in the surface, especially in the first several monolayers, the samples were not annealed or degassed. First information on the surface composition was received by XPS with non monochromatic Mn $K\alpha$ source.

Under the X-ray beam the pressure in the chamber raised to about 10^{-9} mbar. To avoid a surface degradation the low emission mode of the Kimball Gun was used. This keeps the pressure at $4 \cdot 10^{-10}$ mbar during the EPES measurements. The emission was set to be constant and was 50 nA for all EPES experiments. EPES spectra have been measured with primary energies of 3, 5 and 8 keV. The energy range was 50 eV in order to include the contribution from plasmons. Such an energy range corresponds sometimes to reflected electron energy loss technique EELS. The pass energy of 40 eV defines the energy resolution of the analyzer which was about 0.05 eV. The step size was minimized to the value of the energy resolution with a dwell time of 0.3 s at each step. The angular range was minimized for $\pm 2^\circ$.

RESULTS AND DISCUSSIONS

Fig. 1-a shows the XPS spectrum of the CD sample, which contains a carbon and an oxygen peak. The shape of the spectrum for the CH sample (Fig. 1-b) is similar, although it has different peak intensities. Both spectra were fitted in CasaXPS software. The relative concentration of carbon is 93 % for the CD sample (7 % oxygen) and 95 % (5 % oxygen) for the CH sample. A zoomed region with the Auger carbon peak is shown in Fig. 1-c and

FIG. 1. XPS spectra of the hydrocarbon samples

provides information about the carbon binding structure. The shapes of the spectra for both samples are similar to graphite.

Fig. 2-a,b,c shows EPES spectra of the CH and CD samples for 3 primary electron energies: 3, 5 and 8 keV at the scattering angle 120°. All spectra present a zoomed region containing the tail part of the elastic peak. The subplot in the Fig. 2-a shows the overall shape of the obtained spectra. The width of the elastic peak at half maximum is for both samples 0.8 eV at 3 keV and 1.2 eV at 8 keV. The error bar depicts the relative accuracy of the instrument which is about 3%. Generally, the width of the measured elastic peak is the sum of contributions from energy resolution, the energy spread of the electron gun and Doppler effect. The obtained energy resolution (0.05 eV) is about one order of magnitude lower than the energy width of the electron beam (0.3 eV for BaO cathode), therefore it contributes only minimally to the width of the elastic peak. Instead, the Doppler broadening gives the most significant contribution for light atoms.

Elastic energy losses by electrons on carbon, protium and deuterium were calculated at the given primary energy and scattering angle from Eq. (1) and are presented as lines. It is evident that the small peaks at about 2994 eV and 2997 eV (Fig. 2a), 4991 eV and 4995 eV (Fig. 2b), 7986 eV and 7993 eV (Fig. 2c) correspond exactly to elastic scattering of the electrons on hydrogen isotopes. Nevertheless, Fig. 2 demonstrates that elastic energy losses can be close to the position of plasmons. It is important to point out that we have not found any significant intensity of the carbon π -plasmon despite the graphite-like shape of the Auger carbon peak. Only small intensities can be seen at Fig. 2b,c.

The energy of the π -plasmon in carbon or hydrocarbon depends on the structure and

FIG. 2. EPES spectra at the different primary energies and scattering angles

chemical composition of the sample. According to the graphite-like shape of the Auger carbon peak (Fig. 1c) we took the value for the graphite π -plasmon as a reference. The energy position ($\Delta E = 6.7$ eV) of the graphite π -plasmon is shown. For several energies the intensity of the π -plasmon can affect the accuracy of measuring the intensity of independent elastic peaks. Fig. 2-b,c demonstrates this situation. This problem is especially important regarding the small relative intensity of the protium elastic peak. By changing the primary energy one can clearly distinguish between two energy loss channels, because the energetic position of a plasmon is energy-independent. However, a change of the primary energy is not always possible. Occasionally, changing the scattering geometry is quite useful in this case. Fig. 2-d shows shifting of the protium elastic peak with a change of the scattering angle for the CH sample at a primary energy 8 keV. Additionally, changing the scattering angle can also help to verify the elemental composition. Of course, changing of the scattering geometry is limited by the geometry of the system. Nevertheless, glancing and backscattering geometries together make both quantitative and qualitative EPES analysis

significantly clear.

Increased energy means increase of the length of the trajectory of electrons in the surface. The scanning depth can be found from Eq. 2. For carbon at 3, 5, 8 keV we can estimate the scanning depth as 2.7 nm, 4.0 nm and 6.1 nm respectively. According to Kimura *et al.*[4] we can not consider the surface to be homogeneous at this region as it is done, for example, in NRA.

The quantitative analysis of EPES spectra is known to be relatively simple in first approximation [19]. The intensities of elastic peaks should be proportional to the differential elastic cross-section. In our case this method is not applicable for several reasons. The first reason is the unknown shape of the elastic peak and the plasmon background. The second is a significant contribution of oxygen, which is present in the XPS spectra, into the intensity of the main elastic peak. Fitting of the spectra with a simple Gaussian or Voigt line shape is possible, but is based on a large number of fitting variables, which results in several solutions for the depth profile. The shape of the elastic peak could also be more complex because of multiple elastic scattering [20]. We can conclude, that the quantitative analysis of EPES, measured with a high energy resolution, of hydrocarbon PCVD films is not trivial and is an aim for a detailed discussion. However, proper EPES interpretation can provide valuable information on the depth profile in the first 6 nm of the surface, which is very hard to achieve with NRA or ERD techniques.

Taken together, this work is showing for the first time the detection of deuterium and protium isotopes in the first several nanometers of PCVD films by EPES at different primary energies and scattering angles. In fusion experiments the thickness of hydrocarbon films is about 100 nm. Thus, shown isotope sensitivity of the EPES technique could help to combine it with ion sputtering for the depth profiling. Another possibility is live analysis of the depositing films, instead of the standard Auger electron spectroscopy technique.

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