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Hydrogen in diamond-like carbon films

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Abstract

Properties of physical vapor deposited diamond-like carbon films and the migration of hydrogen in co-deposited samples were studied. Measurements utilizing Rutherford backscattering spectrometry and Doppler-shift-attenuation techniques were used to obtain the average mass density of the films. Distributions of co-deposited hydrogen and deuterium were measured by the nuclear resonance reaction $^{1}H\,(^{15}N,\alpha\gamma)^{12}C$, and the elastic recoil detection technique, respectively. Secondary ion mass spectrometry was also used in combination with these two methods. It was observed that in H and CH_4 co-deposited DLC films the temperature of H release varied between 950 and 1070°C depending on the H concentration. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

There has been a recent growing interest in the synthesis and in the study of diamond-like carbon (DLC) films (see refs. [1–3] and references therein). In the next-step fusion device ITER, carbon fiber composites (CFC) have been chosen as divertor armour material. In the presence of plasma, redeposition of sputtered carbon particles, diamond-like carbon films and carbon-based composite films will take place. The uptake and release of deuterium and tritium from these films will significantly affect the recycling of D and T fuel, as well as tritium retention in the fusion device. Therefore, an understanding of the processes which involve trapping and retention of hydrogen isotopes in those films is important.

This work continues our studies on the migration of hydrogen isotopes in DLC films [4,5]. The aim is to characterize the samples and to understand trapping, detrapping and migration of hydrogen isotopes in DLC films, and the influence of the conditions during the deposition process on the properties of the films. The mass density of the films was also measured by two different techniques.

2. Experimental arrangements

The DLC films studied were prepared by the company DIARC-Technology using the arc discharge method. Characterization of the films and the deposition method have been described in detail elsewhere [4]. Several sets of samples were grown. Films with a thickness of about 800 nm were produced on a silicon substrate; films of about 2 μm thick were deposited on stainless steel with a tungsten interlayer. The samples were grown in vacuum, in hydrogen, in deuterium, in methane atmosphere; and by using a methane ion beam. In the case of hydrogen atmosphere, the deposition pressure was varied between 0.06 and 0.6 mPa. The deuterium and methane backing pressures were 0.6 and 0.2 mPa, respectively. In the deposition by methane ion beam, the coatings were made directly from methane gas by establishing a gas flow through a broad-beam ion source developed by DIARC-Technology. The average energy of a CH_4-molecule was approximately 250 eV and the deposition rate was about 0.8 μm/h.

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The ^{1}H and ^{4}He ion beams used as projectiles in Doppler-shift-attenuation (DSA) [6] and Rutherford backscattering spectrometry (RBS) measurements, respectively, were generated by a 2.5 MV Van de Graaff accelerator. The mass density of the DLC films was investigated by RBS with 2.7 MeV ^{4}He. Backscattered particles were detected with a 50 mm^{2} silicon surface-barrier detector placed at a scattering angle of 170°. The counting rate was kept below 1000 cps with a 24 nA beam current. The acceptance solid angle of the detector and the angular divergence of the incident ion beam were confined by slits and apertures to 6.0 msr and 0.02°, respectively. The spectra were analyzed by the Gisa3.99 program [7]. Non-Rutherford scattering cross-sections, needed in an accurate analysis of the 2.7-MeV measurements, are included in the data package of the program. In the DSA measurements, the $E_{\mathrm{p}} = 1.15$ MeV resonance of the $^{13}C(p,\gamma)^{14}N$ reaction was used. The DLC films were implanted (at room temperature) with 10 mC/cm^{2} of 50-keV $^{13}C^{+}$ ions by the 100-keV isotope separator of the laboratory. The optimum energy for the DSA measurement was chosen by maximising the yield of the 2.13-MeV γ rays (corresponding to the 2.13 to 0-MeV transition in ^{14}N). A 20% efficient Ge(Li) detector shielded against background radiation by 5 cm of lead was used. The counting rate was kept below 1000 cps with the 1.3 μA beam current. The Doppler-broadening of the 2.31-MeV γ-ray line shape was detected with the Ge(Li) spectrometer at angles of 0 and 90°.

The isochronal annealings (40 min) were made in a quartz-tube furnace (pressure below 0.05 mPa) at temperatures between 700 and 1100°C.

For depth profiling of H atoms, the nuclear resonance broadening (NRB) technique with the 6.39-MeV resonance of the $^{1}H(^{15}N,\alpha\gamma)^{12}C$ reaction was used [8]. The $^{15}N^{2+}$ beam of 150 nA was obtained from the tandem accelerator EGP-10-II of the University of Helsinki. The yield of the 4.43-MeV γ-rays from the nuclear reaction was detected as a function of the incident ^{15}N energy with a large volume (2600 cm^{3}) annular bismuth germanate oxide detector protected against background radiation with a 10 cm thick lead shield [9].

The concentration profiles of co-deposited D was measured by the elastic recoil detection analysis technique (ERDA) [10]. The beam of 2.4 MeV He ions used to bombard the samples was generated by the 2.5 MV Van de Graaff accelerator of the laboratory. The scattering chamber (diameter 0.7 m) was equipped with standard backscattering apparatus. The angle between the primary beam direction and the target surface was 15°. Recoils were detected by an ion implanted silicon detector centered at an angle of 30° with respect to the incident beam direction. The solid acceptance angle was 3.10 msr. The beam collimation and detector position confined the angular resolution to ±2.0°. The energy resolution of the detection system was typically 13 keV. The spectra were analyzed by the RUMP program [11].

The depth profiling of H and D atoms was also carried out by secondary-ion-mass spectrometry (SIMS) at the Technical Research Centre of Finland. The measurements were done with a double focusing magnetic sector SIMS (VG Ionex IX70S). The current of the 5-keV O_2^{+} primary ions was typically 400 nA during depth profiling and the ion beam was raster-scanned over an area of 240 × 430 μm^{2}. Crater wall effects were avoided by using a 10% electronic gate and 1 mm optical gate. The pressure inside the analysis chamber was 5×10^{-8} Pa during the analysis. The depth of the craters was measured by a profilometer (Dektak 3030ST). The uncertainty of the crater depth was estimated to be 5%. The detection limit for hydrogen is 0.01–0.1 at.% in the present SIMS set-up.

3. Results and discussion

A typical RBS spectrum for a DLC film deposited on silicon substrate is shown in Fig. 1. The computer simulation result obtained by Gisa3.99 program is also depicted. Typical impurities in the samples, which originate from the graphite used as a cathode in the film preparation, are V, Fe, and Ni. The total amount of these impurities was determined to be about 0.12 at.%. The coatings contain tungsten at the interface between the DLC films and Si substrates (this part of the spectrum is not presented in Fig. 1). Tungsten was deposited during the etching process of the substrate surface and the amount was determined to be 0.7 at.%. For more details, the reader is referred to our previous work [4]. The mass density can be calculated using the areal density and thickness obtained by RBS and SIMS techniques, respectively. An average value of 2.6 ± 0.1 g/cm^{3} for mass density was obtained. The given uncer-

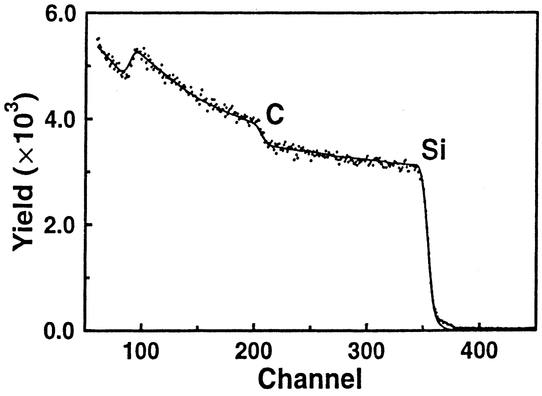

Fig. 1. RBS spectrum of the DLC sample deposited on Si substrate in vacuum. The solid line is the best-fit computer simulation of the experimental data (dots).

tainty is mainly due to differences in mass density among the samples.

In the DSA analysis of the experimental γ-ray line shapes, the Monte Carlo (MC) method was utilized [6]. The corrections for solid angle attenuation due to the finite size of the detector and for the finite initial velocity distribution of the recoiling ^{14}N ions were determined from the fully-shifted γ rays of primary transitions. The mass density of the film was obtained from a χ^2 fit to the experimental line shape of the 2.13-MeV γ-ray. In the MC simulation, the density of the film was varied while keeping fixed the other parameters affecting the γ-ray line shape. These parameters include the mean lifetime of the 2.13-MeV level ($\tau_m = 98 \pm 4$ fs [12]) and the electronic and nuclear stopping powers of carbon for nitrogen ions. The electronic stopping power was taken from Ref. [13], and the nuclear stopping power was calculated by the MC method using the universal Ziegler–Biersack–Littmark interatomic potential [13]. A best-fit γ-ray line shape simulated by the MC calculations is shown in Fig. 2. The density of the films of 2.7×0.1 g/cm^3 obtained from DSA measurements agrees with results of RBS experiments.

Fig. 3 illustrates the NRB results for samples deposited in hydrogen atmosphere. It can be seen that H concentrations in the samples deposited at different pressures were relatively constant throughout the film. As shown in the inset of Fig. 4, hydrogen content is proportional to the square root of the deposition pressure up to 0.6 mPa.

Annealing experiments showed a decrease of the hydrogen concentration with increasing temperature, via H release and migration to the interface (Fig. 4). It was observed that the release temperature varied between 950 and 1070°C depending on the H concentration.

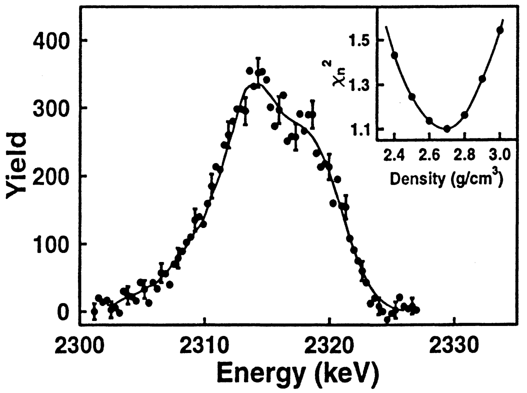

Fig. 2. Portion of a γ-ray spectrum illustrating the Doppler-broadened line shape of the 2313-keV γ-ray peak. The solid line is the best-fit computer simulation of the shape.

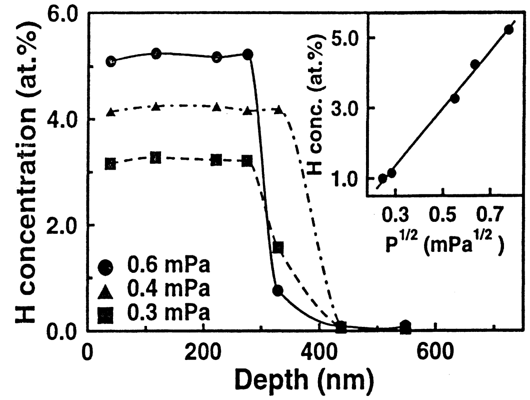

Fig. 3. Hydrogen concentration distributions observed in NRB measurements for DLC samples deposited in hydrogen atmosphere at different deposition pressures. The inset shows H concentration as a function of square root of the deposition pressure. Solid line is a linear fit of the experimental data.

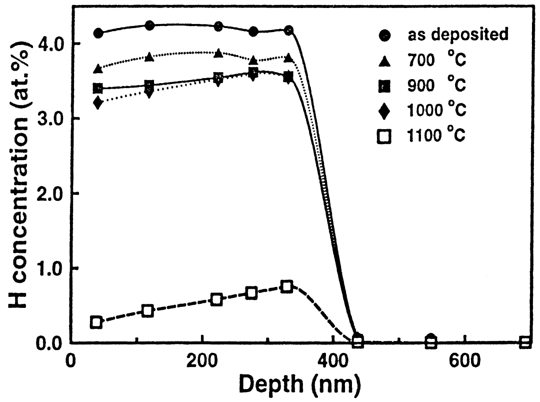

Fig. 4. Hydrogen concentration distribution observed in NRB measurements for DLC samples deposited in hydrogen atmosphere at a deposition pressure of 0.4 mPa. The distributions were measured after the deposition and after 40 min annealings at the indicated temperatures.

Fig. 5 illustrates the hydrogen concentration profiles measured with SIMS for coatings deposited in methane atmosphere. The amount of hydrogen in these samples is approximately the same as in the samples grown in hydrogen atmosphere at the same deposition pressure (0.2 mPa). In methane co-deposited films, migration of hydrogen with increasing temperature also takes place. As can be seen from the Fig. 5, a remarkable H release from the surface region occurs upon annealing. There is also a noticeable change of the profile shape at the interface region where hydrogen concentration has a peak.

DLC films deposited by methane ion beam were also investigated. This set of films was quite different from the other ones. Due to a high concentration of hydrogen (10 at.%) density of these films is only 1.6 ± 0.1 g/cm^3. The ion source used for deposition employed a tungsten filament which was the reason for W distributed through

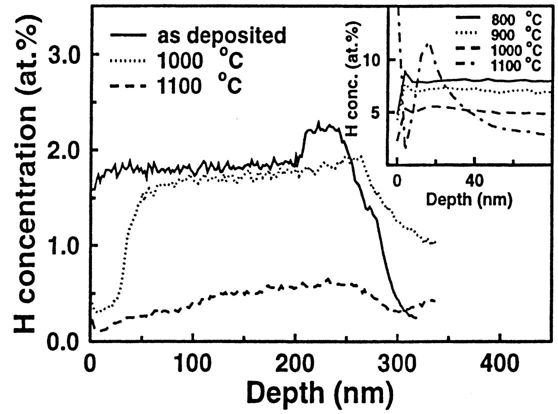

Fig. 5. Hydrogen depth distribution observed in SIMS measurements for DLC samples deposited in methane atmosphere at a deposition pressure of 0.2 mPa. The inset shows hydrogen behaviour at the surface region for the samples deposited by methane ion beam. Distributions observed after the deposition and after annealings at different temperatures.

the films. There was a surface layer with a thickness of 10 nm containing 0.17 at.% of W, a layer 340 nm thick with 0.04 at.% of W and an interface layer with a W content of 0.08 at.%. The hydrogen migration study shows that hydrogen behaves differently in these films with temperature increase compared to samples deposited in methane or hydrogen atmosphere. For all annealing temperatures, the hydrogen content in the bulk decreases evenly without producing any peak at the interface. The inset of Fig. 5 presents the hydrogen concentration profile near the surface region. As can been seen from the figure, the H amount decreases as a function of increasing annealing temperature. At 1100°C there is, however, a peak at the surface region of the profile.

Because the deuterium co-deposited DLC film (deposition pressure of 0.6 mPa) has a thickness of 3.2 μm, a He ion energy of 2.4 MeV in the ERDA experiment was not high enough to project through whole sample, and the D and C signals partly overlapped. Consequently, the fit to the deuterium signal was done only for the non-overlapped part. The position of the carbon signal was determined from the spectrum of a Kapton foil. Subsequent SIMS measurements made it possible to conclude that D is distributed evenly over the film (see Fig. 6) and has concentration of 8.3 ± 0.4 at.%

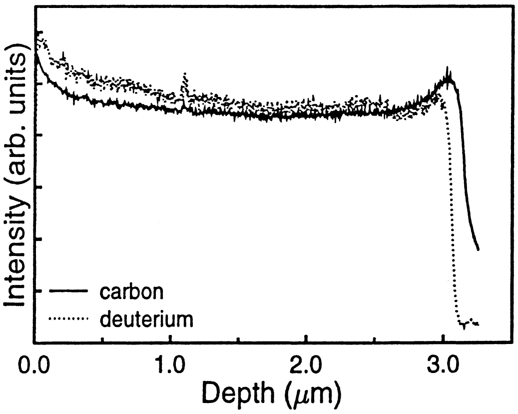

Fig. 6. Deuterium depth distribution observed in SIMS measurements for the DLC sample deposited in deuterium atmosphere at a deposition pressure of 0.6 mPa.

uncertainty limits. Such a low mass density could be explained by graphite particles embedded in the films during the preparation process.

4. Conclusions

Properties of physical vapour deposited DLC films and migration of hydrogen in these films has been studied. Mass densities of the films obtained by two different techniques agree with each other within the uncertainty limits. Such a low mass density could be explained by graphite particles embedded in the films during the preparation process.

The films were annealed in vacuum at temperatures between 700 and 1100°C. In the hydrogen and methane co-deposited samples, hydrogen migrates towards the interface between the film and substrate and also releases from the surface region. The overall amount of hydrogen decreases as a function of annealing temperature. In the case of samples deposited by methane ion beam, the overall amount of hydrogen decreases at first and then, at the highest annealing temperature, produces a peak at the surface region. The differences in the annealing behaviour might be caused by the differences in the initial hydrogen concentrations, but further investigations are obviously needed to clarify this point.

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