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Incorporation of hydrogen and oxygen into (t)a-C:H thin films deposited using DECR plasma (*)

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ABSTRACT

A distributed electron cyclotron resonance (DECR) plasma reactor powered by a microwave generator operating at 2.45 GHz (800 W) was used to deposit (t)a-C:H thin films at RT on <100> Si substrates RF biased within the range $25 \leq |V_0| \leq 600$ V. C₂H₂ was used as precursor. The plasma pressure was varied within the range $0.1 \leq P \leq 1.5$ mtorr. The films were analysed using spectroscopic ellipsometry (SE) and Fourier transform infrared (FTIR) spectroscopy. The hydrogen content N_H and the density of the films were determined from nuclear reaction analysis (NRA) using the resonance at 6.385 MeV of the reaction: $^{15}\text{N} + ^1\text{H} \rightarrow ^{12}\text{C} + ^4\text{He} + \gamma$. Positron annihilation spectroscopy was used to detect the porosity. The evolutions of N_H as a function of the substrate ion current density n₊ and as a function of V₀ show that the hydrogen incorporation results from the competition between chemisorption and deposited energy density related effects. The increase of the hydrogen incorporation leads to a decrease in the film density and a lower deposition rate. The porosity of the films deposited at low pressure (~0.1 mTorr) with V₀ = -80 V has been detected. The comparison between results of SRIM-2000 simulations and the evolution of N_H as a function of V₀ shows that the porosity and the hydrogen content are not correlated. The absorption of oxygen and nitrogen for the low density films has been detected from the observation of the 3250-4000 cm⁻¹ infra-red (IR) band.

INTRODUCTION

Hydrogen is known to be a fundamental constituent of the plasma deposited amorphous hydrogenated carbon (t)a-C:H films. The hydrogen content N_H is usually close to 35 % and can reach ~62 % [1]. Studies have shown that N_H decreases when V₀ increases [2]. Although the hydrogen incorporation mechanisms have been extensively studied, there are not fully understood. The goal of the present work is to shed more light on those mechanisms. The film structure and some of the physical properties such as the film hardness and the density are known to depend closely on the hydrogen content [3] and on the nature of the C-H bonds [4]. Little is known about the film porosity. In this study, the correlation between the film density, the deposition rate, the hydrogen content and the porosity is studied.

EXPERIMENTAL DETAILS

The (t)a-C:H films were grown at RT on $\langle 100 \rangle$ Si substrates using a DECR plasma reactor. The microwave power operating at a frequency of 2.45 GHz was applied to 12 antennas located in the vicinity of the cylindrical reactor walls equipped with magnetic racetracks providing the 87.5 mT isomagnetic surface necessary for the resonance. The racetracks were designed to confine fast electrons. The experiments were performed using a microwave power of 800 W. The desired plasma pressure was obtained using a variable gas flow and measured using a MKS Baratron. C_2H_2 was used as the precursor gas and the plasma pressure was varied from 0.1 to 1.5 mTorr. The substrate holder was water cooled enabling deposition in the vicinity of RT. The negative bias V_0 applied to the substrate holder was regulated within the range between 25 and 600 V using a power supply operating at 13.56 MHz. The accelerating voltage was kept constant during deposition by an automatic modulation of the RF power. The hydrogen content was determined from nuclear reaction analysis (NRA) using the resonance at 6.385 MeV of the reaction: $^{15}N + ^1H \rightarrow ^{12}C + ^4He + \gamma$. The effect of the hydrogen outdiffusion occurring during the bombardment with nitrogen ions has been taken into account. The films thickness was determined from spectroscopic ellipsometry (SE) combined with NRA data. The SE data were recorded using a phase modulated variable angle spectroscopic ellipsometer manufactured by Instruments S.A./Jobin-Yvon-Spex. They were recorded in the 1.5–4.5 eV spectral range in steps of 0.05 eV at an incidence angle of 70° . Reference optical properties for Si and SiO_2 were used. The (t)a-C:H layer was modelled using the Tauc-Lorentz dispersion model [5]. FTIR spectroscopy was performed using a Bio-Rad FTS-40 APC spectrometer in the transmission mode using a resolution of 4 cm^{-1} . The evolution of the $3250\text{--}4000\text{ cm}^{-1}$ band intensity and the evolution of the shape of the CH stretching band ($2800\text{--}3100\text{ cm}^{-1}$) as a function of V_0 for films deposited at 0.1 and 0.3 mTorr were investigated to obtain qualitative informations concerning the films structure. In order to access the films porosity positron annihilation experiments were performed with a slow positron beam.

RESULTS and DISCUSSION

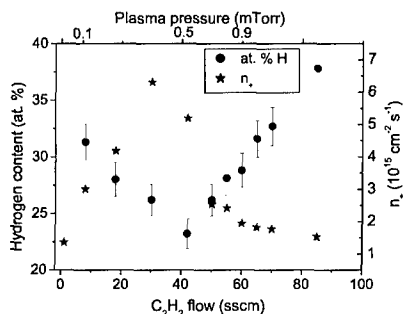


Figure 1. Hydrogen content and substrate current density n_s as a function of the gas flow and pressure ($V_0 = -150$ V).

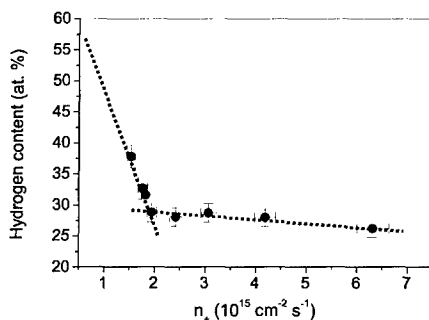


Figure 2. Hydrogen content as a function of the substrate current density ($V_0 = -150$ V).

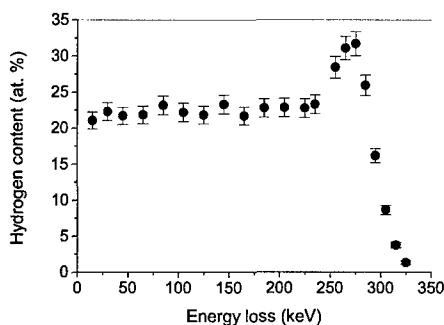


Figure 3. Hydrogen depth profile for a film grown at 0.5 mTorr with $V_0 = -250$ V.

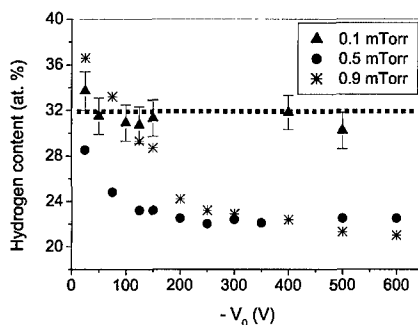


Figure 4. Hydrogen content as a function of the substrate bias for several pressures. The dot line has been added to underline the trend.

Figure 1 shows the evolution of N_H and of the substrate current density n_+ as a function of the pressure, for a substrate bias of $V_0 = -150$ V. N_H is extracted from the NRA depth profiles. The n_+ value is deduced from the RF generator power delivered for a specific bias. The secondary electron emission is assumed to be negligible within the energy range investigated [6]. The n_+ value is representative of the amount of the predominant ions in the C_2H_2 plasma which are known to be $(C_2H_x)^+$ ions [2]. However a variable production of H^+ and $(C_4H_x)^+$ ions as a function of the pressure is also expected to contribute to n_+ . Figure 1 shows that N_H is inversely proportional to n_+ .

The correlation between N_H and n_+ is further demonstrated in figure 2 where N_H is plotted as a function of n_+ . Two hydrogen incorporation regimes can be distinguished depending on the n_+ value. At the current densities higher than the threshold value $T \sim 1.9 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ the hydrogen desorption rate is almost in dynamic equilibrium with the adsorption and subplantation rates. When the ion flux n_+ is reduced below the threshold value the hydrogen adsorption is significantly enhanced and the hydrogen content increases. Interestingly, when linearly extrapolated to $n_+ = 0$ the hydrogen content reaches $\sim 70\%$, a value close to the maximum content of 62 % reported in the literature [1]. The hydrogen incorporation mechanisms are considered to be related to the subplantation, the passivation of dangling bonds and to the exothermic hydrogenation of double bonds [7]. Experimental evidence of the role of dangling bonds is demonstrated in FIG. 3 showing the NRA depth profile of a film grown on Si substrate at 0.5 mTorr using $V_0 = -250$ V. The hydrogen content almost doubles at the interface (t)-a-C:H/Si where both carbon and silicon dangling bonds contribute to hydrogen adsorption during the initial phase of the growth. The hydrogen chemisorption was also observed for films deposited in the same reactor using Ar plasma and a graphite sputtering target. Films deposited at the floating potential have been shown to incorporate between 12 and 39 at.% of hydrogen depending on the amount of hydrogen desorbed from the reactor walls [8].

The hydrogen desorption process is significantly enhanced by the energy deposited in atomic collisions. The ion flux threshold value of $1.9 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ above which the desorption is reduced (FIG.2) is interpreted as corresponding to a complete coverage of the substrate surface by the individual ion impact zones. We note that according to SRIM-2000 simulations [9] the average energy density in an individual binary collision cascade induced by a 80 eV C^+ ion is close to 7 eV/atom. This value is much higher than the hydrogen displacement energy

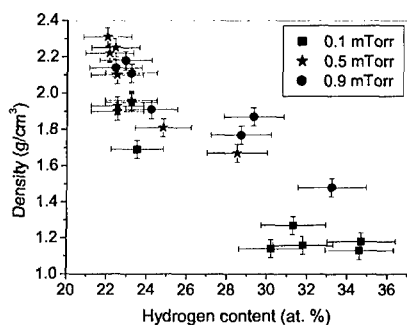


Figure 5. Films density as a function of the hydrogen content.

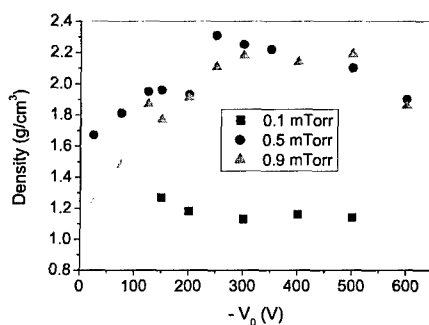


Figure 6. Density as a function of the substrate bias for several pressures.

(~ 2.5 eV) and higher than the hydrogen surface binding energy (< 4.5 eV). It is also underestimated since the cascades created by the two carbon atoms from a $(C_2H_x)^+$ ion overlap. The amount of hydrogen remaining within the material depends on the outcome of the competition between the chemisorption, subplantation and desorption. Consequently it is expected to be strongly dependant on the ion energy. Figure 4 shows the evolution of N_H as a function of V_0 for several P values. At low pressure (0.1 mTorr) $N_H \sim 32\%$ and remains constant within the investigated bias range. At higher pressures N_H first decreases with increasing bias, indicating that ion bombardment related effects (sputtering, outdiffusion) dominate over hydrogen incorporation. Then it remains constant, indicating that a dynamic equilibrium is reached between hydrogen incorporation and loss.

When the D values corresponding to films deposited at various pressure and substrate bias are plotted as a function of N_H a general trend emerges (figure not shown): the deposition rate decreases when the hydrogen content increases. The low deposition rate D ($D \sim 100$ Å/min) observed at low pressure (0.1 mTorr) is attributed to the predominance of the passivation of dangling bonds by hydrogen radicals. At higher pressure (≥ 0.5 mTorr) the growth rate is significantly higher ($300 \leq D \leq 500$ Å/min) because of a higher hydrogen desorption rate. At 0.9 mTorr the substrate current density is about the same as at 0.1 mTorr (figure 1). Yet, the deposition rate observed at 0.9 mTorr is higher than at 0.1 mTorr. The effect is attributed to a lower hydrogen incorporation rate at 0.9 mTorr. This is consistent with the observation of a relatively high concentration of hydrogen radicals within the plasma at low pressure [10] where the electron temperature is higher [2]. It is not possible to reach the deposition rate ≥ 50 nm/min when incorporating more than $\sim 23\%$ of hydrogen. The lowest N_H value obtained using C_2H_2 as precursor is close to 20%. This limit is believed to be correlated to the amount of hydrogen within the reactor.

The film microstructure and physical properties depend closely on the hydrogen content. Figure 5 shows the film density ρ as a function of N_H . The denser films are those which exhibit the lowest N_H values. Figure 6 shows the evolution of ρ as a function of V_0 for several plasma pressures. For the films deposited at $P > 0.1$ mTorr ρ first increases with $|V_0|$, reaches a maximum and then decreases. The increase in the density is known to correspond to an increase in the hybridisation ratio [2-3]. The maximum density is reached when the carbon atoms carried by $(C_2H_x)^+$ ions undergo a subplantation process with an energy of ~ 150 eV. This energy corresponds to highest sp^3 hybridisation [13].

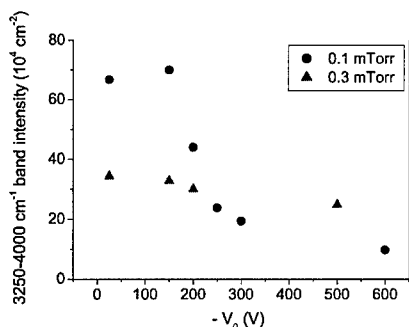


Figure 7. 3250-4000 cm^{-1} IR band intensity as a function of the substrate bias for two plasma pressures.

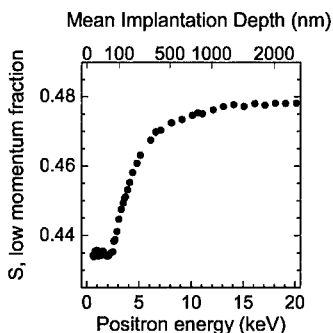


Figure 8. S parameter as a function of the positron beam energy for a film deposited at $P=0.1$ mTorr and with $V_0=-80$ V.

To shed more light on the hydrogen incorporation the films were analysed using FTIR spectroscopy. Figure 7 shows the evolution of the 3250-4000 cm^{-1} IR band intensity I_{OH} as a function of V_0 for films deposited at 0.1 and 0.3 mTorr. This band is known to contain OH, NH and NH_2 sub-bands [11]. The peak related to the H_2 vibration mode near 4135 cm^{-1} was not detectable in the present experimental conditions. The observed decrease in the intensity of the stretching band can not be unambiguously correlated to a decrease in the amount of hydrogen bound to the carbon network. Such plots should be taken with caution since the signal detected depends on the optical film properties which vary as a function of the process parameters. For $|V_0| < 200$ V I_{OH} is greater at 0.1 mTorr than at 0.3 mTorr. According to [4, 12] this result indicates that the oxygen and nitrogen absorption is greater for the lower density films than for denser films. The difference in density between films deposited at 0.1 and 0.3 mTorr (FIG.6) is qualitatively visible in the different shape of the CH stretching bands (not shown). Whatever the pressure used, the $\text{C}(\text{sp}^3)\text{H}_2$ and $\text{C}(\text{sp}^3)\text{H}$ modes seem to increase linearly with bias while the relative intensity of the Csp^3H_3 mode decreases.

One of the consequences of the ion energy transfer via elastic collisions is the production of vacancies. Positron Doppler broadening spectroscopy has been used to access the film porosity. The low momentum parameter S corresponding to the energy window 511 $[-0.71; +0.71]$ keV centred at the positron annihilation peak is very sensitive to the presence of voids acting as positron trapping sites. The parameter S increases when open volumes are present in the material. To investigate the depth dependence of S, the $S(E)$ curve was recorded as a function of the positron beam energy E within the range from 0.5 to 20 keV. The $S(E)$ curve corresponding to a film deposited at low pressure (~ 0.1 mTorr) with $V_0 = -80$ V is shown in FIG. 8. The constant S value corresponding to the a-C:H layer ($S = 0.4344$) suggests that the film is homogeneous with respect to the porosity. The high S value indicates that the positron effective diffusion length is relatively short. The corresponding positron trapping rate is attributed to the presence of open volumes in the structure. We note that the size of the pores is small enough to make them undetectable by TEM. SRIM-2000 simulations show that the number of vacancies per C^+ ion increases almost linearly from ~ 0.3 to ~ 7.7 when the ion energy increases from 25 to 300 eV. However as shown in figure 4, N_{H} remains constant when the substrate bias is increased above $|V_0| > 150$ V. Consequently the porosity and the hydrogen content are not correlated.

CONCLUSIONS

- We have provided experimental evidence that the hydrogen incorporation within DECR plasma deposited (t)a-C:H films results from the competition between chemisorption, subplantation and ion bombardment enhanced desorption.
- We have demonstrated that the increase in the hydrogen incorporation leads to a decrease in the film density and deposition rate.
- We have shown that plasma deposited (t)a-C:H films are porous. The porosity and the hydrogen content are not correlated.
- We have confirmed earlier observations that absorption of oxygen and nitrogen increases when the density of the films decreases.

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