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Modes of Hydrogen Incorporation in Hydrogenated Amorphous Carbon (a-C:H), Modifications with Annealing Temperature (*)

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Abstract. — In order to obtain more information about the nature of the hydrogen bonding and the thermal stability of a-C:H films, we have studied two different types of films labeled I and II deposited in a d.c. multipolar plasma system from pure methane at substrate bias equal to -40 and -600 V respectively. A combination of several complementary techniques has been carried out on the samples in their as-deposited state as well as after isochronal annealing cycles at increasing temperatures up to 650 °C. The results clearly indicate that the two types of samples have very different H bonding and microstructure in their as-deposited state. They also behave differently upon annealing and still exhibit quite different microstructures and H bonding configurations up to high annealing temperature.

1. Introduction

Contrarily to hydrogenated amorphous silicon films in which only sp^3 Si atoms are present, in a-C:H samples carbon can take either sp^3 (like in diamond) or sp^2 (like in graphite) electronic configurations. The hydrogen incorporated in the film is known to control the respective proportion of sp^2 and sp^3 sites. These two parameters are found to be deeply dependent on the method and the conditions of deposition, especially the impact energy of the film-forming species during growth. It is also clearly established that the balance between the sp^2 and sp^3 hybridizations of the C atoms and the amount of H present in the samples are of crucial importance for the electronic and mechanical properties of the amorphous films [1, 2].

The aim of this paper is to contribute to a better understanding of H incorporation and its influence on the microstructure of the material. We thus present a detailed study performed on

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two types of films deposited by the d.c. multipolar plasma method at different substrate bias. Using infrared absorption (I.R.) measurements, we characterize all the samples in their as-deposited state and after successive annealing cycles at increasing temperatures. These results are discussed as a whole and are correlated with those obtained from optical transmission, photothermal deflexion spectroscopy (PDS), and conductivity experiments.

2. Experimental Details

Two series of a-C:H, labeled I and II, 0.6–0.7 μm thick, were prepared from pure methane in a d.c. multipolar plasma system at a substrate temperature of about 50 °C. The substrate bias was equal to –40 and –600 V for series I and II respectively. As previously reported [3], this important parameter determines the impact energy of the film-forming particles and consequently strongly influences the amount of H incorporated in the films as well as their microstructure. The films were deposited simultaneously on crystalline silicon and quartz substrates.

The total H content was checked by Elastic Recoil Detection Analysis (ERDA) measurements. The H bonding was studied by I.R. experiments over a large frequency range, from 500 to 4000 cm^{-1} . A combination of optical transmission and PDS measurements was carried out over the 0.7–2.5 eV spectral range, in order to determine the optical gap E_{04} as well as the refractive index n at 2 μm and the film thickness d . These experiments were completed by dark electrical conductivity measurements performed at room temperature in coplanar configuration. All these experiments were applied to the two types of samples in their as-deposited state and after annealing steps at increasing temperatures. The annealing cycles were performed in a quartz tube evacuated to 10^{-6} Torr, using a heating rate of about 20 °C/min, and isochronal annealing times of 30 min.

3. Results and Discussion

We present in Figures 1a and 1b typical I.R. spectra in the C–H stretching region obtained in the as-deposited state for series I and series II respectively. The absorption bands were decomposed into Gaussian components which correspond to the different possible vibrational modes of the C–H bonds [4, 5]. The total integrated intensity of the whole stretching band is larger by about a factor 5 for series I, indicating the presence in this series of much higher bonded H content than in series II, in qualitative agreement with the ERDA data. This result is consistent with the fact that the amount of H incorporated in the films decreases as the negative bias increases in absolute magnitude, as previously reported [3, 6].

In the frequency range below 3000 cm^{-1} , which corresponds to the contribution of H bonded to sp^3 -C sites, Figure 1 suggests that in both series, H is present in CH_3 groups (sub-bands at 2870 and 2960 cm^{-1}) as well as in CH_2 units (sub-bands at 2855 and 2920 cm^{-1}). In the frequency range above 3000 cm^{-1} , which is assigned to H bonded to sp^2 -C sites, Figure 1 indicates that the fraction of H bonded to these sites is much more important for series II, approximately 23% of the total bonded H compared to 7% only in series I. Moreover, it can be seen that H is incorporated as olefinic chains (sub-band around 3000 cm^{-1}) and aromatic rings (sub-band around 3050 cm^{-1}) in series II, while only olefinic configurations are present in series I. Although oscillator strength effects may influence the intensity of the I.R. absorption bands, H is therefore bonded preferentially to sp^3 -C sites. This tends to show that deposition conditions which lead to the incorporation of large H content favour the formation of sp^3 -C sites [1, 7] (series I). This difference between the two types of films is confirmed by the I.R. spectra in the low frequency range (below 1800 cm^{-1}). In series II one observes a well defined

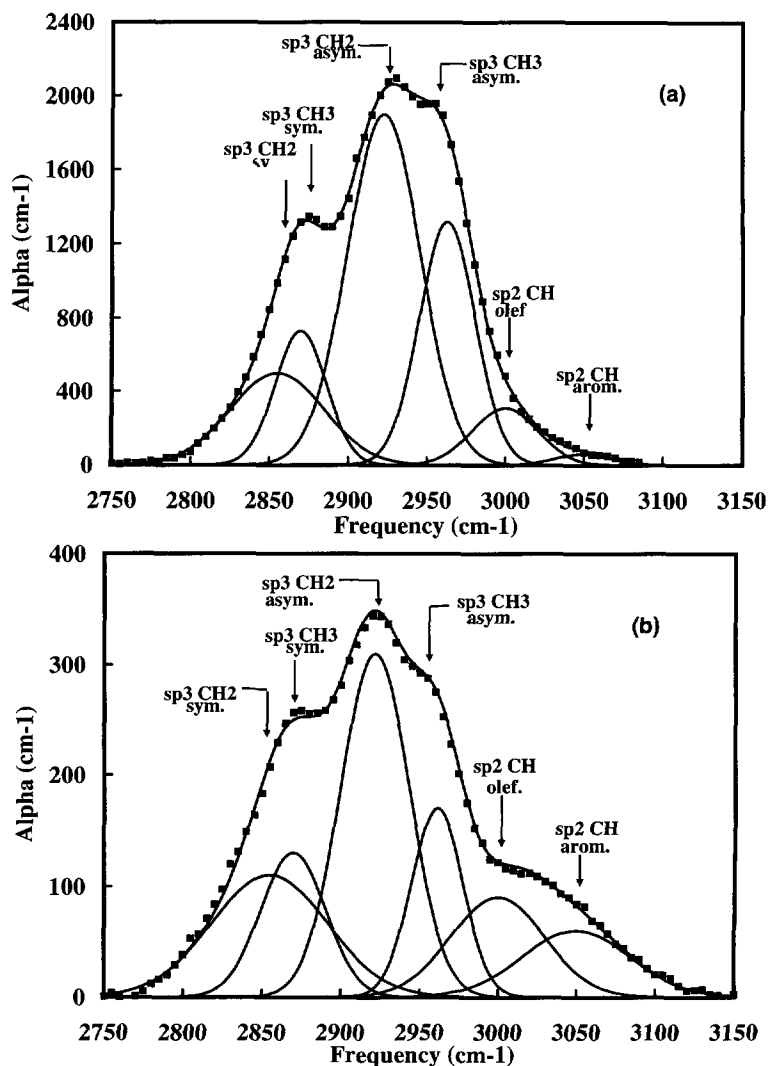


Fig. 1. — Typical I.R. absorption bands in the C-H stretching modes for series I(a) and series II(b) samples in their as-deposited state; the positions of the different gaussian components corresponding to the different CH_x groups are indicated on the figure.

band centred around 1580 cm^{-1} and absorption peaks below 900 cm^{-1} . The first band corresponds to $\text{C}=\text{C}$ double bond stretching modes [4,5], which confirms that this series contains a large fraction of $\text{sp}^2\text{-C}$ sites bonded to H or to other C atoms in various configurations. The bands below 900 cm^{-1} are related to out-of-plane deformation vibrations of aromatic $\text{sp}^2\text{-CH}$ groups, in agreement with the presence of aromatic rings in this series (C-H stretching band at 3050 cm^{-1}). Both features are on the contrary hardly detectable in the I.R. spectra of series I, which in turn exhibits a well defined strong doublet at $1375\text{--}1455\text{ cm}^{-1}$, as well as two additional broad bands centred around 1700 and 1060 cm^{-1} which are observable only in this series. The doublet is characteristic of the presence of an important concentration of $\text{sp}^3\text{-CH}_3$ units, there must also be some contribution to the 1455 cm^{-1} component from $\text{sp}^3\text{-CH}_2$ groups [8,10]. This is an additional indication that in series I, H is essentially bonded to $\text{sp}^3\text{-C}$ sites. This

doublet must be present in series II which also contains a large proportion of sp^3 -CH₃ groups, but it is almost completely buried into a wide and intense absorption band (1000–1500 cm^{-1}) which may be assigned to vibrations of the highly connected C skeleton [8–10]

The additional 1700 and 1060 cm^{-1} bands observed in series I clearly suggest a high contamination by oxygen and water (C = O, C–O bond stretching modes), and can be related to a wide band appearing around 3450 cm^{-1} (O–H groups). This result indicates that the samples of series I present a strong open porosity, which is in agreement with the very low value, about 1.54, obtained for the refractive index n . On the contrary, for series II n is about 1.92, suggesting that these samples are already more dense. The “polymeric” character of series I also explains the quite high value of its optical gap $E_{04} = 3.3$ eV. Series II also exhibits a high value for $E_{04} = 2.9$ eV, which is much higher than the value expected for films having a smaller H content and a larger concentration of sp^2 -C sites [8, 11]. This can be explained by the fact that E_{04} was determined from optical transmission measurements on samples deposited on quartz substrates; these substrates being insulators, contrarily to the slightly doped c-Si substrates used for the I.R. measurements, they might not be at the same effective potential as the c-Si substrates for strong negative bias (–600 V), which certainly leads to a different deposited material.

The effect of annealing on the C–H bonding is illustrated in Figures 2a and 2b by the modifications of the I.R. spectra in the C–H stretching frequency range obtained for series I and series II after each annealing step respectively. For series I, the contribution of the C–H bonds on sp^3 -C sites (below 3000 cm^{-1}) first decreases moderately at 200 °C and 300 °C, then more abruptly at 400 °C and 500 °C. The H release from the C–H bonds therefore starts at a temperature as low as 200 °C. A surprising result is however obtained at and above 400 °C, where the contribution of the C–H bonds on sp^2 -C sites in aromatic configurations (3050 cm^{-1}) starts to increase, suggesting that sp^3 -C sites are transformed into sp^2 -C sites without losing their H, and that aromatic rings are formed, both as a result of this process and at the expenses of sp^2 -CH olefinic configurations which are almost completely eliminated at 500 °C. At this annealing temperature there is still an important concentration of H bonded to sp^3 -C sites in CH₂ and CH₃ groups and to sp^2 -C sites in aromatic configurations. For series II, the absorption bands below 3000 cm^{-1} are almost unchanged up to 300 °C, suggesting a higher thermal stability of these samples. Then the H fraction bonded to sp^3 -C sites starts to decrease slowly at 400 °C and almost vanishes at 500 °C. On the other hand, the olefinic sp^2 -CH configurations are partially eliminated at 400 °C, and at 500 °C only the contribution of aromatic sp^2 -CH groups is still observable, with about the same intensity.

We observed the expected trends in the values of the optical gap E_{04} (obtained from PDS) which decrease as the H content decreases. Furthermore, as H evolves out, the films of both series become more dense. This is clearly evidenced by the increase of the n value and the decrease of the d value (obtained from the optical transmission) as the annealing temperature increases. However, the samples of series II remain more compact than those of series I.

Another important difference in the annealing behaviour between series I and series II is deduced from the variations with annealing temperature of the room temperature electrical conductivity σ . It stays almost constant up to 400 °C for series I and 500 °C for series II. It then increases slowly up to 550 °C and abruptly at higher temperature up to 650 °C (by about 4 orders of magnitude), for series I, while for series II, it increases rapidly and continuously up to 650 °C (by about 7 orders of magnitude). These results suggest that in series II the C network is then strongly connected with a high proportion of sp^2 -C sites, possibly organized in graphitic clusters [12].

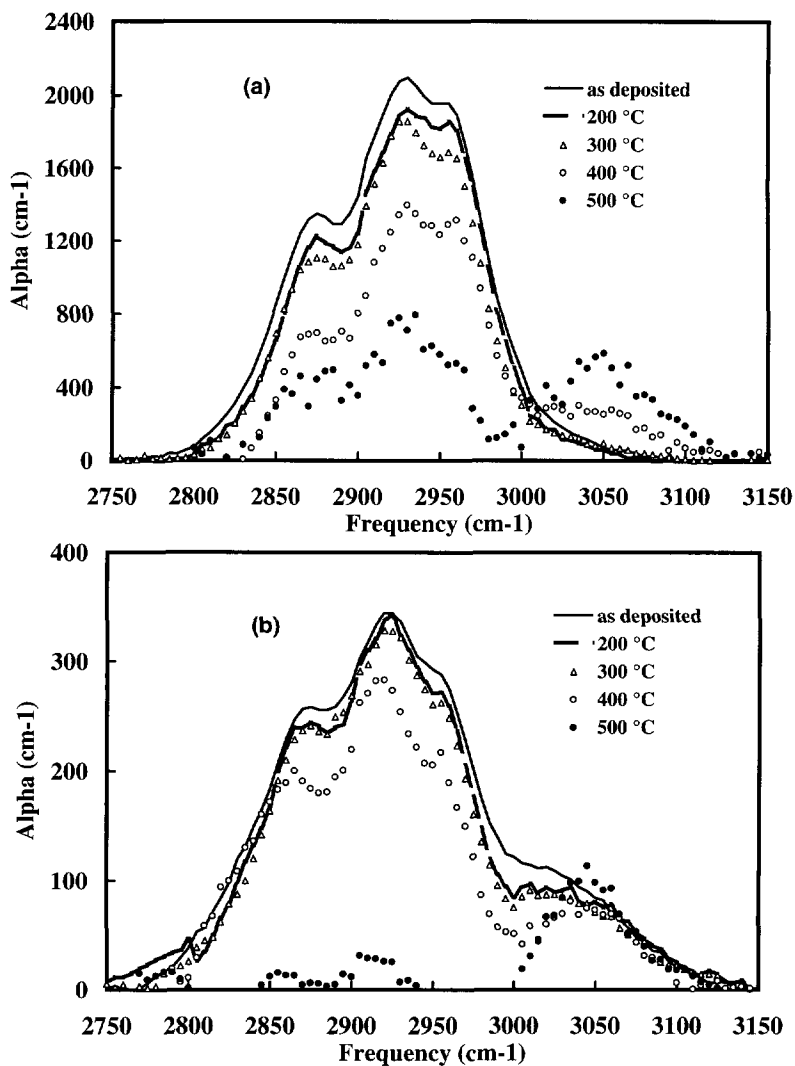


Fig 2. — Modifications of the different C-H stretching bands after each annealing step obtained for series I(a) and series II(b)

4. Conclusion

From this systematic study carried out on two series (I and II) of a-C:H films deposited respectively at -40 and -600 V in a d.c. multipolar plasma system using pure methane, we showed that in the as-deposited state the two types of samples exhibit very different H incorporation and microstructure. A high H content essentially bonded to sp^3 -C sites and a very small proportion of sp^2 -C sites essentially in olefinic configurations are present in the low bias series I, while the high negative bias series II contains a large proportion of non-hydrogenated as well as hydrogenated sp^2 -C sites in both olefinic and aromatic configurations, and a smaller H content bonded to sp^3 -C and sp^2 -C sites. Annealing also affects differently the two types of films. They still exhibit quite different H bonding and microstructures at

annealing temperature as high as 500 °C. At this temperature, series I retains a large H content bonded both to sp^3 and sp^2 (aromatic) C sites, while series II has a low H amount, bonded only to sp^2 -C sites in aromatic configurations. The release of H makes the two types of films more dense, with, however, a higher compactness for the samples of series II

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References

- [1] Robertson J., Amorphous carbon, *Adv. Phys.* **35** (1986) 317-374.
- [2] Tang X.M., Weber J., Baer Y., Muller C., Hanni W. and Hintermann E., Influence of hydrogen on the structure of amorphous carbon, *Phys. Rev B* **48** (1993) 10124-10128.
- [3] Perrière J., Siejka J., Enard J.P., Laurent A. and d'Heurle F.M., Low temperature plasma anodization of silicides, *Mat. Res. Sympos. Soc.* **38** (1984) 443-447.
- [4] Koidl P., Wild C., Dischler B., Wagner J. and Ransteiner R., Plasma deposition properties and structure of amorphous hydrogenated carbon films, *Mat. Sci. Forum* **52-53** (1989) 41-70.
- [5] Dischler B., Bubenzer A. and Koidl P., Bonding in hydrogenated carbon studied by optical spectroscopy, *Solid. State Com.* **48** (1983) 105-108.
- [6] Spousta J., Perrière J., Laurent A., Fogarassy E., Prevot B. and DE Umamo S., Laser induced modifications in a-C:H thin films, *Appl. Surf. Sci.* **69** (1993) 242-248.
- [7] Tersoff J., structural properties of sp^3 -bonded hydrogenated amorphous carbon, *Phys. Rev. B* **44** (1991) 12039-12042.
- [8] Bonouh Y., Thèye M.L., Dehbi-Alaoui A., Matthews and Stoquet J.P., Influence of annealing on the hydrogen bonding and the microstructure of diamondlike and polymerlike hydrogenated amorphous carbon films, *Phys. Rev. B* **51** (1995) 9597-9605.
- [9] Bellamy, The infrared Spectra of complex molecules, Vol. **2** (Chapman and Hall, London, 1975).
- [10] Lukins P.B., McKenzie D.R., Vassalo A.M. and Hann J.V., *Carbon* **31** (1993) 569.
- [11] Dixit P.N., Kumar S., Sarangi D. and Bhattacharyya R., Onset of photoconduction in hydrogenated amorphous carbon films prepared by asymmetric PECVD technique, *Solid State Com.* **90** (1994) 421-423.
- [12] Robertson J., Clustering and gap states in amorphous carbon, *Phil. Mag. Lett.* **57** (1988) 143-148.