



# Long-term H-release of hard and intermediate between hard and soft amorphous carbon evidenced by in situ Raman microscopy under isothermal heating

C. Pardanaud<sup>a,\*</sup>, C. Martin<sup>a</sup>, G. Giacometti<sup>a</sup>, P. Roubin<sup>a</sup>, B. Pégourié<sup>b</sup>, C. Hopf<sup>c</sup>, T. Schwarz-Selinger<sup>c</sup>, W. Jacob<sup>c</sup>, J.G. Buijnsters<sup>d</sup>

<sup>a</sup> Aix-Marseille Université, CNRS, PIIM UMR 7345, 13397 Marseille cedex 20, France

<sup>b</sup> CEA, IRFM, 13108 Saint-Paul-lez-Durance, France

<sup>c</sup> Max-Planck-Institut für Plasmaphysik, EURATOM Association, Boltzmannstr. 2, 85748 Garching, Germany

<sup>d</sup> Department MTM, Katholieke Universiteit Leuven, Kasteelpark Arenberg 44, B-3001 Leuven, Belgium

## ARTICLE INFO

### Article history:

Received 14 March 2013

Received in revised form 3 May 2013

Accepted 7 May 2013

Available online 23 May 2013

### Keywords:

Amorphous hydrogenated carbon

Raman spectroscopy

Hydrogen retention

Long-term hydrogen release

## ABSTRACT

We study the kinetics of the H release from plasma-deposited hydrogenated amorphous carbon films under isothermal heating at 450, 500 and 600 °C for long times up to several days using in situ Raman microscopy. Four Raman parameters are analyzed. They allow the identification of different processes such as the carbon network reorganization and the H release from  $sp^3$  or  $sp^2$  carbon atoms and the corresponding timescales. Carbon reorganization with aromatization and loss of  $sp^3$  hybridization occurs first in 100 min at 500 °C. The final organization is similar at all investigated temperatures. Full H release from  $sp^3$  carbon occurs on a longer timescale of about 10 h while H release from  $sp^2$  carbon atoms is only partial, even after several days. All these processes occur more rapidly with higher initial H content, in agreement with what is known about the stability of these types of films. A quantitative analysis of these kinetics studies gives valuable information about the microscopic processes at the origin of the H release through the determination of activation energies.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Raman spectroscopy is a powerful tool to rapidly characterize C-based materials that contain  $sp^2$  carbon atoms ( $C(sp^2)$ ). Interpreting the 1000–1800  $cm^{-1}$  spectral region gives information on the carbon organization (aromatization). Because the Raman cross section for  $C(sp^3)$  is one to two orders of magnitude lower than that of  $C(sp^2)$ , two bands due to  $C(sp^2)$  dominate this spectral range even when samples contain only a few percent of  $C(sp^2)$ . They are the well-known G and D bands [1]. They contain information on disorder such as the size of aromatic domains, the  $C(sp^2)/C(sp^3)$  ratio for amorphous carbons (a-C), and the H content for hydrogenated carbons (a-C:H) [1–3]. Raman parameters generally used to probe the bonding structure are: the width and the position of the G and D bands, denoted  $\Gamma_{G,D}$  and  $\sigma_{G,D}$  respectively, the height ratio of these two bands,  $H_D/H_G$ , and if applicable, the  $m/H_G$  parameter with  $m$  being the slope of the photoluminescence background calculated between 800 and 2000  $cm^{-1}$ . In the case of heat-treated a-C:H films for which the H content varied from 2 to 30 at.%, we have recently obtained a linear relation between  $\log_{10}(m/H_G)$  and the H content ( $H/H + C = 25 + 9 \log_{10}(m/H_G)$ ) [4], similar to what was previously

obtained for as-deposited samples for which the H content varied from 20 to 47 at. % [5,6]. We have emphasized that  $m/H_G$  is sensitive not only to the H content, but also to defect passivation [7,8], possibly by H migration, and we also found that  $m/H_G$  is due only to H bonded to  $C(sp^3)$ . In addition we have obtained a linear relation between  $H_D/H_G$  and the H content ( $H/H + C = 0.54 - 0.53 H_D/H_G$ ), independent of whether the H is bonded to  $C(sp^2)$  or to  $C(sp^3)$ .  $H_D/H_G$  can thus be used to probe the total H content in the range from 2 to 30 at.%. Conversely, we have shown that the  $\Gamma_G$  and the  $\sigma_G$  parameters are sensitive mainly to the structural changes such as the re-organization leading to a larger aromatization and the loss of  $C(sp^3)$  induced by heating.

To obtain more information on the different processes involved under heating we investigate here the long-term kinetics of the isothermal hydrogen release from a-C:H films with initial  $H/H + C$  ratios of 0.29, 0.32 and 0.37 at temperatures of 450 °C, 500 and 600 °C by means of in situ Raman microscopy. We show how the evolution kinetics provide valuable information on the H release processes and emphasize the role of the initial structure and H-content on these processes.

## 2. Experimental

Plasma-deposited hydrogenated amorphous carbon films, a-C:H, with  $H/H + C \sim 0.29, 0.32$  and  $0.37$  (DC self bias of  $-300, -200$  and

\* Corresponding author.

E-mail address: [cedric.pardanaud@univ-amu.fr](mailto:cedric.pardanaud@univ-amu.fr) (C. Pardanaud).

–100 V, respectively), and a thickness of  $e \sim 0.20 \mu\text{m}$  (see ref. [9] for details on the deposition method) were studied together with a thicker film with  $\text{H}/\text{H} + \text{C} = 0.32$  (applied substrate bias: –200 V) and a thickness of  $e \sim 1 \mu\text{m}$  (see ref. [5] for details on the deposition method). The 0.29 and 0.32 films are hard films while the 0.37 film is intermediate between a hard and a soft film [9,10]. Note that the thick film has a larger  $\text{C}(\text{sp}^3)$  content than the three thin films: this is indicated by its G band position at  $1540 \text{ cm}^{-1}$  instead of  $1522 \text{ cm}^{-1}$  for the thin films, their G band widths being similar (see Fig. 9 in [2]). The samples with the as-deposited films were cut into several pieces, each piece being heated under argon flow in a cell at 1.5 bar with a linear ramp of  $150 \text{ }^\circ\text{C min}^{-1}$  to reach the working temperature. Time zero was taken at the end of the ramp. Temperatures 450, 500 and  $600 \text{ }^\circ\text{C}$  were studied.

Raman spectra were obtained using a Horiba-Jobin-Yvon HR LabRAM apparatus (laser wavelength:  $\lambda_L = 514.5 \text{ nm}$ , 50X objective, numerical aperture of 0.5 leading to a laser focus diameter of  $2.5 \mu\text{m}$ , resolution  $\sim 1 \text{ cm}^{-1}$ ). The laser power was chosen to have a good signal/noise ratio and/or to prevent damages and three values were tested, 0.01, 0.1 and 1 mW, corresponding to power densities from  $2 \times 10^2$  to  $2 \times 10^4 \text{ J cm}^{-2} \text{ s}^{-1}$ . Unless otherwise stated, spectra were recorded in situ at the working temperature. The cell was a commercial LINKAM TS1500, argon was Alphagaz 2 (99.9995% purity, Air Liquid Company). The Raman parameters analyzed were the G band wavenumber,  $\sigma_G$ , the G band full-width at half-maximum,  $\Gamma_G$ , the relative height of the G and D bands,  $\text{H}_D/\text{H}_G$ , and the  $\text{m}/\text{H}_G$  parameter. Heights were measured on the raw data after the linear baseline calculated between 800 and  $2000 \text{ cm}^{-1}$  (slope  $m$ ) was subtracted. In that case,  $\text{H}_D$  was therefore measured at its apparent maximum, except when the D band maximum was not sufficiently well defined (i.e. for the as-deposited sample). In the latter case  $\text{H}_D$  was taken at  $1370 \text{ cm}^{-1}$ . All these parameters are presented in Fig. 1.

### 3. Results and discussion

Fig. 1 displays Raman spectra of the a-C:H film ( $e = 0.2 \mu\text{m}$ ,  $\text{H}/\text{H} + \text{C} = 0.32$ ), as deposited at room temperature and after 4, 45 and 500 min at  $500 \text{ }^\circ\text{C}$ . The Raman spectrum of the as-deposited film is composed of the underlying silicon wafer signature at  $520 \text{ cm}^{-1}$ , a G band at  $1522 \text{ cm}^{-1}$ , and a broad shoulder at  $\sim 1200 - 1400 \text{ cm}^{-1}$  containing the D band. When the sample is heated, the silicon signature diminishes because the a-C:H becomes more absorbent [11,12]. The photoluminescence background significantly increases, due to the defect passivation (and the quenching of non-radiative relaxation

processes [4,6]) before it starts decreasing as hydrogen is released. The G band narrows and slightly blueshifts, as previously observed in [4,13]. The D band also narrows and its height increases. According to previous studies [2,13,14], these evolutions reveal the organization of the material, i.e. a loss of  $\text{C}(\text{sp}^3)$  and increasing aromatization. When the heating time increases, the Raman spectra keep changing: the G and D bands become more clearly distinguishable,  $\text{H}_D/\text{H}_G$  increases and  $\text{m}/\text{H}_G$  decreases. A long timescale process thus occurs, which we investigate in more detail below.

Fig. 2 displays the isothermal evolution with time up to 800 min of  $\sigma_G$ ,  $\Gamma_G$ ,  $\text{m}/\text{H}_G$  and  $\text{H}_D/\text{H}_G$  at  $500 \text{ }^\circ\text{C}$  at the three laser powers, 0.01, 0.1 and 1 mW for the a-C:H film ( $e = 0.2 \mu\text{m}$ ,  $\text{H}/\text{H} + \text{C} = 0.32$ ). No significant effect of the laser power is observed, indicating that no additional heating due to the laser irradiation is induced even at 1 mW, contrary to what was measured in [15] for thinner (15 nm) films. Fig. 2a and b displays a similar isothermal evolution for  $\Gamma_G$  and  $\sigma_G$ , reaching plateaus in  $\sim 100 \text{ min}$ .  $\Gamma_G$  is at  $180 \text{ cm}^{-1}$  for the as-deposited film and the plateau at  $500 \text{ }^\circ\text{C}$  is at  $85 \text{ cm}^{-1}$ .  $\sigma_G$  is at  $1522 \text{ cm}^{-1}$  for the as-deposited film and the plateau at  $500 \text{ }^\circ\text{C}$  is at  $1580 \text{ cm}^{-1}$ . These evolutions suggest that at  $500 \text{ }^\circ\text{C}$ , the film gets rapidly more organized (in typically 100 min) and that this organization then does not significantly evolve. Conversely, Fig. 2c and d show that for  $\text{m}/\text{H}_G$  and  $\text{H}_D/\text{H}_G$  this rapid evolution is followed by a slow and roughly linear change (decrease for  $\text{m}/\text{H}_G$  and increase for  $\text{H}_D/\text{H}_G$ ).  $\text{H}_D/\text{H}_G$  and  $\text{m}/\text{H}_G$  are both correlated with the H content [4]. We thus interpret these evolutions as due to the isothermal H release, with a first phase occurring rapidly together with structural changes (within about 100 min), followed by a second phase occurring on a longer timescale.

To test the spatial homogeneity of heating-induced changes, we map the film at room temperature after heating at  $500 \text{ }^\circ\text{C}$  for 800 min, in a  $\sim 35 \times 35 \mu\text{m}^2$  area, much larger than the  $5 \mu\text{m}^2$  area of the laser spot, with the 0.01 mW laser power. Histograms obtained by analyzing the maps of the four parameters,  $\sigma_G$ ,  $\Gamma_G$ ,  $\text{m}/\text{H}_G$  and  $\text{H}_D/\text{H}_G$  are displayed in Fig. 3. Their widths are small ( $\sigma_G = 1601 \pm 2 \text{ cm}^{-1}$ ,  $\Gamma_G = 76 \pm 4 \text{ cm}^{-1}$ ,  $\text{m}/\text{H}_G = 0.25 \pm 0.09 \mu\text{m}$  and  $\text{H}_D/\text{H}_G = 0.77 \pm 0.02$ ), indicating that the sample is uniform, both in structure and in composition. The values obtained for  $\Gamma_G$ ,  $\text{m}/\text{H}_G$  and  $\text{H}_D/\text{H}_G$  at the end of the 800 min heating at  $500 \text{ }^\circ\text{C}$  fall in this range, confirming that the spot irradiated by the laser is not more heated than the other parts of the sample. Conversely,  $\sigma_G$  is at  $1580 \text{ cm}^{-1}$  at the end of the heating process, significantly outside the histogram values, and this is due to a reversible temperature effect due to multi-phonon interactions, similarly to what was found for graphite or graphene [16]. We have checked that the effect was reversible by varying alternately the temperature between room temperature and  $500 \text{ }^\circ\text{C}$ .

Fig. 4 is a plot similar to that of Fig. 2 to compare the isothermal evolutions of the three thin films ( $e = 0.2 \mu\text{m}$  and  $\text{H}/\text{H} + \text{C} = 0.29, 0.32$  and 0.37) at  $500 \text{ }^\circ\text{C}$  and that of the thick film ( $e = 1 \mu\text{m}$  and  $\text{H}/\text{H} + \text{C} = 0.32$ ) at  $450 \text{ }^\circ\text{C}$ . The laser power was 1 mW, except for the first 400 min at  $\text{H}/\text{H} + \text{C} = 0.29$  for which it was only 0.1 mW (as the spot was located at another place on the sample, the small jump in the data is due to the small width of the structure and H-content distribution, see Fig. 3). For all the Raman parameters at  $500 \text{ }^\circ\text{C}$  and for the first 100 min the faster the evolution the higher the initial H content. This is in agreement with what is known about the stability and the H desorption of this type of hydrogenated films [17–21], the higher the H content, the less stable is the film and the more rapid is the H desorption. For longer times, the plateaus reached by  $\sigma_G$  and  $\Gamma_G$  are almost independent of the initial H content, indicating that the structure of the film at  $500 \text{ }^\circ\text{C}$  is independent of the initial H content.  $\text{m}/\text{H}_G$  goes to zero for the three films at  $500 \text{ }^\circ\text{C}$  while  $\text{H}_D/\text{H}_G$  keeps slowly increasing along three distinct lines. As  $\text{H}_D/\text{H}_G$  depends on the total H content and  $\log_{10}(\text{m}/\text{H}_G)$  only on H bonded to  $\text{C}(\text{sp}^3)$ , this indicates that at this stage of the kinetics all remaining H is bonded to  $\text{C}(\text{sp}^2)$ . Furthermore, the remaining H content is higher for lower initial H content. The thick film evolution of  $\sigma_G$  and  $\Gamma_G$  and  $\text{m}/\text{H}_G$  at  $450 \text{ }^\circ\text{C}$  is intermediate between the thin films having the H

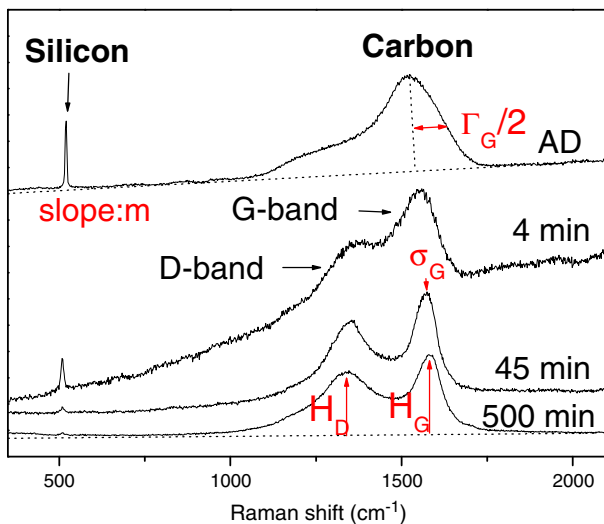


Fig. 1. Raman spectra of the a-C:H film ( $e = 0.2 \mu\text{m}$  and  $\text{H}/\text{H} + \text{C} = 0.32$ ) at room temperature, as deposited (AD) and at  $500 \text{ }^\circ\text{C}$  after 4, 45 and 500 min at  $500 \text{ }^\circ\text{C}$ .

Download English Version:

<https://daneshyari.com/en/article/700745>

Download Persian Version:

<https://daneshyari.com/article/700745>

[Daneshyari.com](https://daneshyari.com)