RAMAN ANALYSES OF HOPG EXPOSED TO HELIUM OR HYDROGEN PLASMA: APPLICATION TO MAGNETIC FUSION

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Introduction

The fusion reaction involving deuterium and tritium is considered for energy production in future. One way to obtain energy from this reaction is to confine magnetically on a long time D+T plasma and to heat it to ignition, using machines called tokamaks. The ITER project, located in France, has been designed in this context.

To evacuate fusion ashes (helium nuclei) from the plasma core, magnetic lines have to drive them to the walls before they are neutralized and pumped. Then, undesirable plasma wall interactions occur: physical and/or chemical erosion (ion energies ranging from a few tenths to a few hundreds of eV), transport in the machine, chemical reactions during transport and deposition. Nowadays, most of the tokamaks' walls that are exposed to the highest flux of particles are made in graphitic carbon materials.

To better understand carbon deposition formation due to interaction of plasma with graphitic walls, we have re-visited HOPG irradiated with He [1] and H_2 ions in a laboratory plasma reactor. The structural modifications have been studied by varying the kinetic energies (E_K) of the impinging ions from 80 to 800 eV, using both Raman and Transmission Electronic Microscopies. This extended abstract focuses on the analysis of the Raman spectra obtained.

Raman spectroscopy is routinely used to characterize C-based materials, from nanocrystalline graphite (nc-G) to amorphous carbons (a-C, a-C:H, ta-C:H, ta-C). This fast and non-destructive technique probes structural [2] and bonding properties by interpreting the 1000 - 1800 cm^{-1} region, dominated by the well known G and D bands caused by sp^2 carbon atoms. The G band is due to the bond stretching of both aromatic and aliphatic C-C pairs, whereas the D band (sometimes associated to a D' band) is due to the breathing of aromatic rings. This D band exists only when there is "disorder" in the case of nc-G materials [1], whereas this band disappears for ta-C materials which are majoritarily composed of sp^3 carbon [3]. Spectra of amorphous carbons and nc-G are clearly distinct [4]: G and D bands are much broader for a-C (width, denoted hereafter Γ_G, ~ 80 - 200 cm^{-1}) than for nc-G (Γ_G ~ 15 - 80 cm^{-1}). The other Raman parameters used in the what follows are the relative height H_D/H_G, and the G band position σ_G.

Experimental

HOPG samples were exposed during 15 minutes to hydrogen and helium plasma (≈ 10^{15} cm^{-2} s^{-1}) using the PHISIS set up [5]. The dominant ion in the hydrogen plasma is H_2^+ (≈ 70% of the total ion amount with 0.2 Pa, 100 W) [6].

Raman spectra were recorded using a Horiba-Jobin-Yvon HR LabRAM apparatus (λ_L=514.5 nm with a x100). The laser power was kept less than ~1mW/μm^2 to prevent damages. Spectra were recorded with various exposure times to check that samples do not evolve under laser irradiation.

Results and Discussion

Fig. 1.a displays the Raman spectrum of HOPG samples bombarded by He plasma with kinetic energies varying between 80 and 800 eV compared to virgin HOPG. The virgin HOPG displays only the G band at 1582 cm^{-1}, with Γ_G ≈ 15 cm^{-1}. For the lowest kinetic energy, a thin band appears at 1360 cm^{-1} and is still visible at 800 eV. For increasing energies a broad contribution at 1500 cm^{-1}, with a shoulder at 1200 cm^{-1} appears. Another shoulder is also present at 1600 cm^{-1}. For each kinetic energy, we decompose in three components the overall Raman spectrum: the HOPG substrate component (G band), a nc-G component (G/D bands) and a amorphous component (G/D bands).

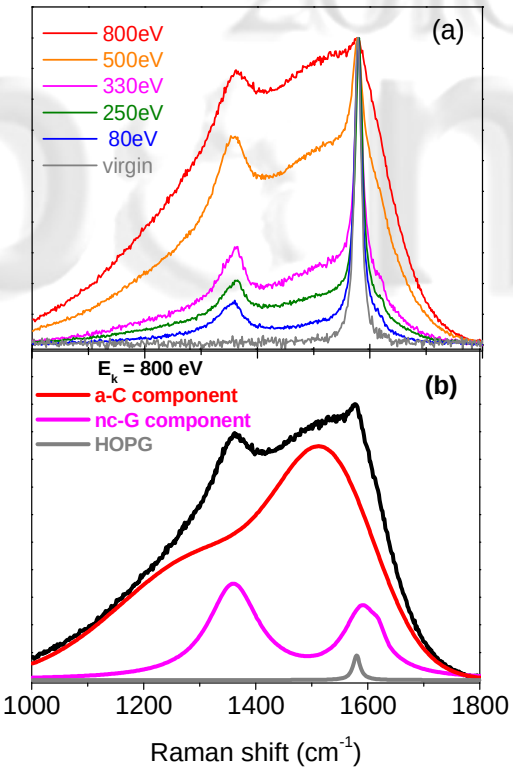

Fig. 1 Raman spectrum of HOPG bombarded by a He plasma with (a) E_K = 80-800 eV, (b) Fit of the 800 eV plasma.

Fig. 1.b displays the spectral decomposition of HOPG bombarded by He (with E_k = 800 eV). The thin 1582 cm^{-1} signature is due to the HOPG substrate that has not been

modified by the plasma. A ≈ 1590 cm^{-1} band (which is at the origin of the 1600 cm^{-1} shoulder) together with a ≈ 1360 cm^{-1} band form the G and D bands of the nc-G component (profiles are Lorentzian). A D' band has been added as it is known that the D band of nc-G carbons is always accompanied by a D' band at ≈ 1620 cm^{-1} [7]. A broad band, situated at 1525 cm^{-1} and its shoulder situated at ≈ 1320 cm^{-1} form the G and D bands of the a-C component (profiles are Gaussian). Γ_G, σ_G and H_D/H_G corresponding to this latter component are similar to the Raman parameters usually obtained for a-C.

For the 800 eV He plasma, H_D/H_G ≈ 1.7 for the nc-G component, which leads to an aromatic domain size of ≈ 2.6 nm according to the Tuinstra relation [2]. This size seems to be similar for the entire energy domain studied. At 800 eV H_D/H_G ≈ 0.54 for the a-C component, which leads to an aromatic size of ≈ 1 nm according to the Ferrari relation [4]. As displayed in fig. 1.a the a-C component is present even at 250 eV. Then from 250 to 800 eV, only the ratio of the a-C and nc-G components seems to vary. Note that aromatic sizes deduced for the 800 eV H_2 plasma are the same than for the 800 eV He plasma.

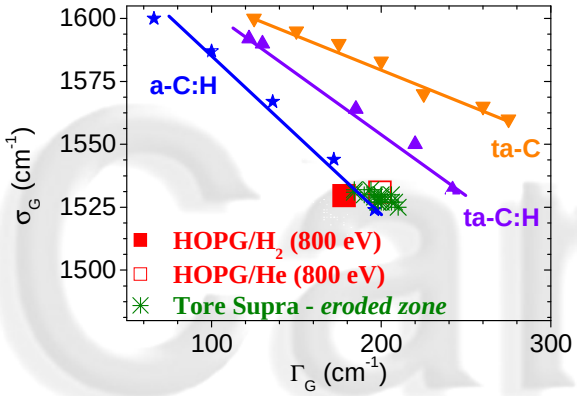

Fig. 2 σ_G versus Γ_G for a-C:H, ta-C, ta-C:H, TS deposits and HOPG submitted to a 800 eV He and H_2 plasma.

Fig. 2 displays the G band parameters (σ_G against Γ_G) of samples originating from the tokamak Tore Supra (deuterium plasma) and collected on the graphitic walls that have been submitted to the highest fluxes of ions in the device (called the *eroded zone* [8]) and of the a-C component involved in the bombardment of HOPG by 800 eV He and H_2 plasmas, compared to different kinds of carbon. The a-C:H, ta-C:H [9] and ta-C [10] were heat treated at different temperatures (highest temperatures reached: 450°C for a-C:H, 1000°C for ta-C:H and 1300°C for ta-C). The heat treatment reveals that the relation between σ_G and Γ_G is linear, and that each line is related to a kind of carbon. All the HOPG a-C components and Tore Supra G band parameters fall in the a-C:H region. Then, the nature of the impinging ion seems to not strongly affect the structure of the carbon. However, a linear background with a positive slope has been evidenced for the Tore Supra samples and the HOPG bombarded by H_2 whereas the background for He is flat. This linear background is due to luminescence [11] and is consistent with the formation of C-H bondings in the case of both Tore Supra samples and HOPG bombarded by H_2 plasma.

Note that in the same experimental conditions, Raman spectral intensities of a-C:H layers (thickness ≈ 200 nm) and HOPG bombarded by 800 eV plasma are of the same order of magnitude. This is surprising as the implantation depth in the material are lower than 15 (3) nm for 800 (80) eV He ions respectively, according to TRIM calculations [12].

Conclusions

We have studied with Raman microscopy the structure modification of HOPG by He and H_2 plasmas with different kinetic energy ions. We have shown that two kind of defects (nc-G and a-C components), that do not depend on the nature of the impinging ions, are created in the range E_k = 80-800 eV. We have also shown that luminescence effects, involving C-H bonding creation, take place for HOPG bombarded by H_2 whereas this luminescent effect does not occur for He plasma. D_2 bombardment together with heat treating effects on bombarded HOPG are planned to better identify the kind of defects that cause the a-C signature.

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