



## Hard diamond-like layers produced during DIII-D tokamak operations

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### Abstract

Measurement of the hardness of carbon films, obtained by the exposure of a graphite sample to the tokamak divertor plasma and the deposition of the eroded material on Si substrates, has shown the unexpected result that their hardness was very high. The hardness was about 10-20 GPa, which is close to the hardness of sapphire. We have studied the structural and optical properties of these films by Raman and infrared spectroscopy. The Raman spectra are consistent with a high hardness. The graphite-like Raman band at  $1515\text{ cm}^{-1}$  is down-shifted, which indicates the presence of both  $sp^2$  and  $sp^3$  bonds in the cross-linked structure of the films which is typical for hard carbon films. From the transmission spectra it is found that the band-gap absorption edge is not lower than that of Si. Infrared spectra show a triplet around  $2900\text{ cm}^{-1}$ , which is assigned to the CH stretching modes. © 1998 Published by Elsevier Science B.V.

### 1. Introduction

Carbon based materials are widely used to protect the first wall and to decrease the impurity fluxed into the plasma of tokamaks. Due to erosion during the plasma-wall interaction, the redeposition layers form on plasma-facing elements of the tokamak vessel [1]. These layers can possess absolutely different physical and chemical properties in comparison to the original surfaces. Hydrogen isotope retention in such layers is an issue of great importance due to tokamak fuel recycling and radiation safety. That is why it is very necessary to study the structure and other properties of these deposition layers.

This Letter is devoted to the investigation of carbon films deposited onto an Si substrate used as a collector of sputtered material during the exposure of a graphite sample to the DIII-D divertor plasma.

Spectroscopic techniques such as Raman scattering and infrared spectroscopy were used to investigate the film. These methods allow one to characterize the composition, microstructure and the degree of order in films. Raman spectroscopy can provide information on the changes in the local bonding in carbon films [2,3]. Infrared spectroscopy is a very sensitive method for studying the impurities in carbon films. In particular, it is of great importance for our films to detect the presence of H isotopes. The presence of H (D) atoms bonded chemically with carbon atoms should

give the characteristic bands in infrared spectra. The study of the band-gap absorption edge may give additional information about the film structure. The film mechanical properties (hardness) were measured too.

## 2. Experimental procedure

The exposure of the ATG graphite sample was provided by the DIMES (Divertor Material Evaluation System) mechanism, which allows installation of samples in the DIII-D divertor region during a few discharges or even only one shot. The graphite sample, arranged to receive a parallel heat flux on a small region of the surface, was exposed to about 600 ms of the outer strike point plasma. The graphite sample was constructed to collect the ablated material directed downward into a trapping zone onto an Si disc collector. The average heat flux onto the graphite sample during the exposure was about  $200 \text{ W/cm}^2$ , implying a parallel heat flux of the order of  $10 \text{ W/cm}^2$ . The divertor electron density was  $2.5 \cdot 10^{20} \text{ m}^{-3}$ , and the electron temperature was about 60 eV. We suppose the surface temperature on the Si collector disc was around room temperature.

Raman spectra were studied by means of a home-made multichannel spectrometer with triple monochromatization and the 514.5 nm excitation with a power density of about  $50 \text{ W/cm}^2$ . The infrared spectra were detected with a BOMEM DA3.002 spectrometer in the  $500\text{-}20000 \text{ cm}^{-1}$  region.

Hardness measurements on a submicron scale were performed using the NanoScan measurement system, based upon the principles of scanning force microscopy [4]. The hardness of a number of crystals (quartz, topaz, garnet, sapphire, cubic  $\text{ZrO}_2$ , cubic BN) was measured using both our system and a standard tester PMT-3 by the Vickers indenter test. The results of these techniques were the same within experimental error (7%).

## 3. Experimental results and discussion

The thickness of the obtained film was evaluated by the interferometry method and was found to be about

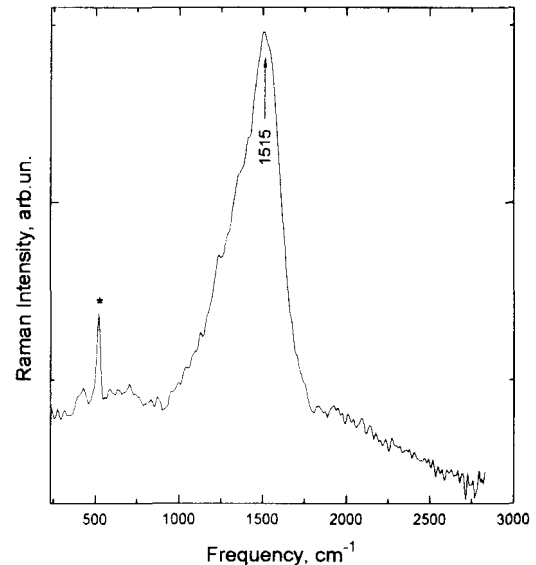


Fig. 1. Raman spectra of the carbon film on Si, (\*) the Raman band from the Si substrate.

$0.3 \mu\text{m}$  in the thickest part and about  $0.04 \mu\text{m}$  in the thinnest region.

The Raman spectrum of our carbon film is shown in Fig. 1. The spectrum was accompanied by a strong photoluminescence. The spectrum shows an intense band at  $1515 \text{ cm}^{-1}$  with a low-frequency shoulder that is similar to that associated with the amorphous carbon [5]. This band is very broad and its width exceeds  $300 \text{ cm}^{-1}$ , which indicates an amorphous structure of the film. The position of this band is noticeably lower than that of graphite with  $\text{sp}^2$  bonding ( $1580 \text{ cm}^{-1}$ ) and higher than that of diamond with  $\text{sp}^3$  bonding ( $1333 \text{ cm}^{-1}$ ). The peak at  $1515 \text{ cm}^{-1}$  is down-shifted relative to the graphite band peak location, thus we can conclude that the microstructure of the film consists of both  $\text{sp}^2$ - and  $\text{sp}^3$ -bonded carbon atoms and the film may be called diamond-like [2,3].

Weak broad bands in the  $400\text{-}800 \text{ cm}^{-1}$  region and near  $2000 \text{ cm}^{-1}$  are also seen in Fig. 1. If features in the  $400\text{-}800 \text{ cm}^{-1}$  region are usually seen in Raman spectra of carbon films [6], then a broad band near  $2000 \text{ cm}^{-1}$  may be assigned to either sum bands or a contribution of allene-type fragments ( $\text{C} = \text{C} = \text{C}$ ).

Since the film contains a noticeable quantity of  $\text{sp}^3$ -bonded carbon atoms, it was interesting to study the band-gap absorption edge of the system. It is known that the

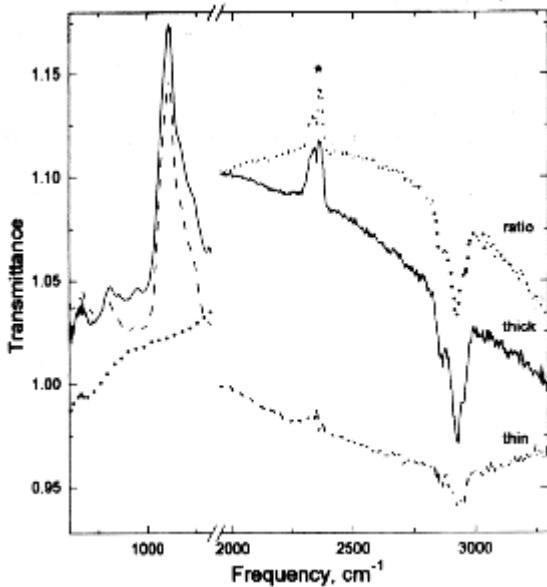


Fig. 2. Infrared transmission spectra of the thin and thick carbon films on Si and their ratio; (\*) infrared bands of CO<sub>2</sub> from air.

absorption edge is not seen in graphite, it is near 5 eV in diamond, it lies in an intermediate region in diamond-like films and depends on the content of sp<sup>3</sup> bonds. We measured the transmission of the film through the silicon substrate and found that it is entirely defined by the absorption of silicon. Although we could not measure the absorption edge of the film accurately, we have found that the optical gap  $E_g$  of the film is at least not lower than that of silicon ( $E_g \approx 1.18$  eV). Earlier, such a large optical gap in diamond-like films has been observed only in laser-deposited films [7]. From the reflectivity spectrum data, we have evaluated the refraction index in the near IR region to be 1.9 and the thickness was of the order of a few thousands of angstroms.

Fig. 2 shows the transmission spectra of the thin and thick films on the same Si substrate in the infrared region, as well as the ratio of these spectra. A triplet of bands at 2856, 2921 and 2952 cm<sup>-1</sup> is seen in the 2000-3000 cm<sup>-1</sup> region, where we could expect bands corresponding to CH or CD bonds. These bands originate from the stretching mode of the CH bond in the sp<sup>3</sup> configuration, on the CH, CH<sub>2</sub> and CH<sub>3</sub> sites [8].

Apart from the triplet, one can see an intense band at 1100 cm<sup>-1</sup> in spectra of both thin and thick films in Fig. 2. Since this band is absent in the ratio of these spectra (Fig. 2), we assume that it is related to the silicon substrate. It is known [9] that the 1100 cm<sup>-1</sup> band may be associated with the bulk and surface SiO vibrations. Its appearance in spectra (Fig. 2) is due to an increase of transmission at 1100 cm<sup>-1</sup> which indicates a depletion of oxygen in the surface layer of silicon. Perhaps, the depletion of oxygen atoms in the Si surface layer is initiated by interaction with H isotope fluxes during the tokamak discharge.

Since all spectroscopic data indicated a diamond-like structure of the film, it was reasonable to expect that the hardness would be higher than those in graphite. The film hardness was measured and found to be really higher than in graphite, which has a hardness of about 0.1 GPa. The value of the film hardness strongly changed in various positions of the surface. The hardness varied from 10 GPa to 20 GPa, which was close to those in diamond-like hydrogenated films or in sapphire. Note that the hardness of diamond is about 100 GPa, while sapphire has a hardness of about 14 GPa. Probably, the high hardness of the film is caused by the formation of a cross-linked structure, typical for hard carbon based materials.

#### 4. Conclusions

The deposition layers obtained in the DII-D tokamak were investigated using IR and Raman spectroscopy, the film hardness was also measured.

It is shown that the film has a diamond-like structure and a hardness, typical for rather hard surfaces, for example, sapphire. It is reasonable to continue the study of such layers, produced under tokamak conditions and increasing the temperature of the substrate during the deposition.

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