Laser-induced modification of hydrogenated amorphous carbon films

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Abstract. Laser-induced modification of thin films of amorphous carbon (a-C:H) was investigated. The films have been deposited by DC PECVD on silicon substrates using different bias voltages: 1 kV, 1.5 kV, 2 kV, and 2.5 kV. Raman spectra of the films measured in a micro-Raman system at 633 nm with different laser power were recorded. It was observed an increased D-peak for laser power density of $10^{10}$ W/m$^2$ indicating modification of the film by the laser, which does not happen for smaller laser power. This modification is stronger in the films produced at higher bias voltages, which have stronger absorption at 633 nm. This observation suggests that laser modification of a-C:H films is due to thermal effects.

1. Introduction
Hydrogenated amorphous carbon films (a-C:H) possess interesting physical and chemical properties [1-3]. Therefore there is a lot of interest of their investigation and applications. The most common fabrication process for a-C:H films is plasma-enhanced chemical vapour deposition (PECVD). The macroscopic properties of the resulting a-C:H films depend on the deposition energy. Changing only the bias voltage in a DC PECVD system it is possible to change the microstructure and thus the optical properties of the fabricated films. In this way we succeeded in fabrication of solar absorber matched to the solar spectrum [4].

During our work on solar absorber we noticed that these films are easily modified by the laser irradiation during the Raman spectra measurements. Actually such effect was observed earlier [5]. In this paper we report laser-induced modification behavior of a-C:H films fabricated at different bias voltages in a DC PECVD system.

2. Experimental
Hydrogenated amorphous carbon films (a-C:H) were deposited in a DC plasma CVD reactor. Benzene diluted with argon was used in this process. The films were deposited on silicon substrates placed upon the water-cooled cathode. The metal vacuum chamber acted as anode. Benzene vapors were
obtained by boiling of benzene at constant temperature of 25°C. Before the film deposition the substrates were cleaned in acetone, ethanol and deionized water in ultrasonic bath followed by a 10 min Ar ion sputtering at 1 kV. Four series of samples were deposited at different bias voltages: 1 kV, 1.5 kV, 2 kV, and 2.5 kV.

Raman spectra of the samples were measured with a LabRAM HR spectrometer at 633 nm in the near backscattering geometry. The diameter of the laser spot on the sample is about 1 µm and the spectral resolution is 1 cm⁻¹. The laser power was 9 mW and set of filters were used in order to reduce the laser power on the sample surface.

3. Results

Figures 1÷4 show Raman spectra of the films deposited at different bias voltages. For each voltage two Raman spectra are given – one at full laser power of 9 mW and another one taken with 10% transmission filter. All films measured with this filter (i.e. at laser power 0.9 mW) showed no modification. This was concluded from measurements with filters with higher attenuation, which give practically the same Raman spectra as the spectra taken with 10% transmission filter. All samples – figures 1 ÷ 4 (deposited at 1 kV, 1.5 kV, 2 kV, and 2.5 kV) showed increased D-peak at the full laser power. This is an indication for increased graphitic clusters dimensions [6] caused by the laser power modification.

**Figure 1.** Raman spectra of a-C:H films deposited at 1 kV bias voltage and measured without filter (D0) and with 10% transmission filter (D2).

**Figure 2.** Raman spectra of a-C:H films deposited at 1.5 kV bias voltage and measured without filter (D0) and with 10% transmission filter (D2).
We were not able to determine the threshold laser power, where the modification starts for each film. However, it could be noticed that the films deposited at higher bias voltages were easier to modify. This is understandable because they have much higher absorption at this laser wavelength. Nevertheless an estimation using the laser spot diameter of $\sim 1 \mu m$ gives a laser power density of $10^{10}$ W/m$^2$, in good agreement with other published data [5].

![Image of Raman spectra](image)

**Figure 3.** Raman spectra of a-C:H films deposited at 2 kV bias voltage and measured without filter (D0) and with 10% transmission filter (D2).

**Figure 4.** Raman spectra of a-C:H films deposited at 2.5 kV bias voltage and measured without filter (D0) and with 10% transmission filter (D2).

### 4. Discussion

The parameters of the measured Raman peaks (position, width and their intensity ratio) were used for the characterization of the films. The interpretation and evaluation of the Raman spectra was first based on the decomposition of the curve into two components. Later decomposition into four peaks was also used. The Raman spectra of all our films measured at filtered (reduced) laser power showed a peak at 1510 cm$^{-1}$ typical for a hydrogenated amorphous carbon (a-C:H), which however, is different from the pure G-peak observed in graphite. We observed also the well-known peak at about 1360 cm$^{-1}$ referred to as the D-peak associated with in-plane vibrations and resulted from structural imperfections of the material. In all films the I(D)/I(G) ratio was about 1 or smaller. After Raman measurement at full laser power a significant increase in I(D)/I(G) ratio was observed for all samples (figure 5). The
increase in I(D)/I(G) is an evidence for the development of graphitization in the films. It was also found a shift in a G-peak position from 1510 to 1573 cm\(^{-1}\), an effect, which can be explained with the films becoming more graphite-like.

These effects are probably due to the high absorption in the films inducing a very high local temperature, which cannot be dissipated quickly enough by the substrate, leading to graphitization and even to material ablation. The power dissipated by the substrate can be estimated by the simple thermal conductivity equation \( Q = kA(T_2-T_1)/d \), where \( k \) is the thermal conductivity of the silicon substrate, and \( A \) is the area of the laser spot. The temperature \( T_1 = 300 \) K is the room temperature and as \( T_2 \approx 4000 \) K sublimation temperature of graphite is used. Because the thermal conductivity of the silicon is temperature dependent a value of 98.9 W/(m.K) at 400 K was used. Thermal flux through the carbon was neglected since the thermal conductivity of amorphous carbon is small (about 0.2–0.3 W/m.K) [7]. Inserting these values an estimated power of about 1 mW was found which is in good agreement with the experimental data. Obviously even some mW of the laser power absorbed in the film cannot be dissipated by the substrate leading to temperature increase, graphitization and even to material ablation. We consider this laser power as threshold power above which the amorphous carbon will be modified. Of course the exposition time and the film thickness are also important, but we did not investigate their influences in details.

When no filter was used, we did not notice a reduced intensity of the spectrum of the films deposited at 1 kV, 1.5 kV and 2 kV, which could be possible explanation of laser ablation and reduction in the volume of scattering material in the irradiated area. Thus, it appears that this will happened at higher laser intensities. However, in the 2.5 kV sample one can notice such a reduction, i.e. laser ablation already occur.

Comparisons of the Raman spectra with those of thermally annealed samples [8, 9] suggest that the observed modification is primarily due to local temperature effects. In the annealing experiments as the temperature increased, the Raman spectra of annealed DLC films show a narrowing of the G – peak bandwidth and a G – peak position shift toward the graphitic peak at 1590 cm\(^{-1}\). Furthermore, increasing the annealing temperature increases the D-peak intensity and the intensity ratio I(D)/I(G). Similar effects could be observed in the samples modified by the Raman laser. In general, we can conclude that the increase of the bias voltages of our samples produces similar structural changes as the increase of annealing temperature. This can be explained by the increased absorption of these films at the laser wavelength. Although our results show decrease of D – peak and G – peak intensities with the bias voltages, Raman spectra of our films obtained with 1 – 1.5 kV and 2 – 2.5 kV are similar to those of in-situ annealed with atomic hydrogen DLC films at about 400°C and 700°C, respectively [9, 10].

As mentioned already decomposition into four peaks was also used. This was presented (figure 6 and figure 7) for films deposited at 2 kV and 2.5 kV. The main peaks are D-peak at about 1535 cm\(^{-1}\) - disorder peak, dependent on physical size of the sp\(^2\) aromatic domains and G - disorder peak (random-network clusters). Additional peaks: D‘ at 1220–1300 cm\(^{-1}\) and G\(_2\) at about 1585 cm\(^{-1}\) [8, 9] could be identified [8, 9]. D‘-disorder peak was also observed on the Raman spectrum of heavily ion-implanted highly oriented pyrolytic graphite [11]. G\(_2\) peak is ordered graphite [12].

5. Conclusions
Laser-induced modification of amorphous carbon (a-C:H) films during the Raman spectra measurements was investigated. Our results confirmed earlier observations that a film modification can occur if proper care is not taken when using Raman spectroscopy and as a result “real” Raman spectra of materials cannot be obtained. The threshold power density above which the amorphous carbon is modified was estimated to be about 10\(^{10}\) W/m\(^2\). This modification is stronger in the films produced at higher bias voltages, which have stronger absorption at laser wavelength 633 nm. Our observation suggests that laser-induced modification of a-C:H films is due to thermal effects.
**Figure 5.** Dependence of the ratio of D and G peak intensities on bias voltage before (D2) and after (D0) laser annealing.

**Figure 6.** Raman spectra of a-C:H films deposited at 2 kV bias voltage and measured without filter (D0) fitted with four peaks.

**Figure 7.** Raman spectra of a-C:H films deposited at 2.5 kV bias voltage and measured without filter (D0) fitted with four peaks.

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