

Vibrational spectroscopy of Ga⁺ ion implanted ta-C films

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Abstract. In the present work, low energy Ga⁺ ion beam implantation was used for the structural and optical properties modification of tetrahedral amorphous carbon (ta-C) thin films, using gallium (Ga⁺) as the ion species. Thin film samples (d~40nm) of ta-C, deposited by filtered cathodic vacuum arc (FCVA), have been implanted with Ga⁺ at ion energy E = 20 keV and ion doses D=3.10¹⁴÷3.10¹⁵ cm⁻². The Ga⁺ ion beam induced structural modification of the implanted material results in a considerable change of its optical properties, displayed in a significant shift of the optical absorption edge to lower photon energies as obtained from optical transmission measurements. This shift is accompanied by a considerable increase of the absorption coefficient (photo-darkening effect) in the measured photon energy range (0.5÷3.0 eV). These effects could be attributed both to additional defect introduction and increased graphitisation, as well as to accompanying formation of bonds between the implanted ions and the host atoms of the target, as confirmed by infra-red (IR) and Raman measurements. The optical contrast thus obtained (between implanted and unimplanted film material) could be made use of for information archiving, in the area of high-density optical data storage, while using focused Ga⁺ ion beams.

1. Introduction

Thin film materials of tetrahedral amorphous carbon (ta-C) have attracted great interest for a long time from both scientific and industrial perspectives. The term tetrahedral is used to describe amorphous carbon films with a large percentage of *sp*³ bonding (up to 87%). The films are manufactured using a variety of techniques, including filtered cathodic vacuum arc (FCVA), pulsed laser deposition (PLD) and mass selected ion beam deposition (MSIBD) [1-4]. The high *sp*³ content in the films results in unique properties that include extreme hardness (~70 GPa), chemical inertness, high electrical resistivity, and wide optical band gap [5–7]. Other important factors which make the films an attractive material for coatings include a smooth surface and low friction, thermal stability and transparency over a wide spectral range. These properties also offer advantages as compared to another wide optical bandgap material – silicon carbide (SiC) – for uses in nano-scale optical data recording for archival information storage using focused ion beams (FIB) techniques, where SiC thin films have found useful applications recently [8-15].



In the case of polycrystalline silicon carbide (pc-SiC) thin films, ion bombardment is used to amorphise areas of the films by computer operated FIB systems, thus creating useful optical contrast between non-irradiated polycrystalline areas and the irradiated amorphous areas, which can be further used for nano-scale optical data recording for archival information storage [8-10]. In the case of hydrogenated amorphous silicon carbide (a-SiC:H) films, computer operated FIB systems are used to both introduce irradiation defects and additionally chemically modify the amorphous structure of the films, thus reducing their optical bandgap in even a more effective manner for the useful creation of optical contrast between implanted and non-implanted areas of the film material for applications in nano-scale optical data recording [11-15].

In both polycrystalline and amorphous SiC film materials, a considerable part in the creation of useful optical contrast between irradiated and non-irradiated areas of the films is played by the transformation of substantial part of the present diamond-like (sp³) carbon bonds, before the irradiation, into graphite-like (sp²) carbon bonds, as a result of it [10,15]. It is expected, that a similar mechanism of the carbon bonds transformation would result when applying ion bombardment with different ions, e.g. nitrogen (N⁺) and gallium (Ga⁺) ions, in the case of ta-C films, so that to achieve useful optical contrast between irradiated and non-irradiated areas of the films. The use of gallium as the ion implanted species is particularly attractive since it is available in standard focused ion beam (FIB) machines, and in addition has been shown to be capable of generating large optical contrasts [16]. The underlying structural modification, induced by the N⁺ and Ga⁺ ion bombardment, has been investigated by Raman and infra-red (IR) spectroscopy measurements.

2. Experimental

Thin ta-C films (d~40 nm) were deposited on c-Si (100) substrates using a commercial FCVA system (Commonwealth Scientific Corporation). Carbon plasma is produced from the arc spot on the cathode, 99.999% pure graphite in high vacuum. Cathodic arcs are prolific generators of highly ionized carbon plasmas. With the FCVA technique, the plasma stream is steered through a magnetic filter to eliminate neutral particles generated at the cathode. At the filter exit, the fully ionized plasma, consisting of carbon ions and electrons, streams towards the substrate. The films were deposited at room temperature with an arc current of 120 A under floating conditions.

Ion implantation of N⁺ and Ga⁺ was carried out at room temperature (RT) using a commercial broad-beam ion implanter. The ion-beam intensity was I~2 μA/cm², the ion energy was E=20 keV, and the ion doses used were D=3.10¹⁴ ÷ D=3.10¹⁵ cm⁻². SRIM simulation program [17] was used to determine the projected range Rp ~ 29 nm and the straggling ΔRp ~ 10 nm, for N⁺, and Rp ~ 17 nm and ΔRp ~ 4 nm, for Ga⁺, implanted ions into the ta-C film samples (d ~ 40 nm).

The structural modifications of the ta-C films by the N⁺ and Ga⁺ ion implantation were monitored by Raman and Infrared (IR) spectroscopy. The Raman spectra were obtained using a LabRAM HR Visible (Horiba Jobin- Yvon) Raman spectrometer. An objective X50 was used both to focus the incident laser beam onto the pellets surface into a spot with a diameter about 2μm and to collect the scattered light. The used excitation was He-Ne 633 nm laser line. To avoid overheating the measurements were performed with a reduced laser power of 0.6 mW.

Fourier Transform Infrared (FTIR) spectroscopy measurements were done by Shimadzu FTIR Spectrophotometer IRPrestige-21 in the spectral range 350-4000 cm⁻¹ in reflectance mode (specular reflectance attachment), Al mirror. The samples were measured in absorbance

3. Results and discussion

3.1. Raman measurements

We have obtained and compared Raman measurement results for ta-C films implanted with Ga⁺ ions at doses D₁=3x10¹⁴ ions/cm² and D₂=3x10¹⁵ ions/cm², and an unimplanted film was used like a reference sample. The analyzed spectrum range was from 100 cm⁻¹ to 3500 cm⁻¹ and the part 1000 ÷ 2200 cm⁻¹ was studied as the spectrum responsible for the film's scattering.

In figure 1 the comparison is depicted between Raman band intensities of three samples. It is well manifested that the spectrum band of the unimplanted sample is rather less in intensity than the band's intensities of the implanted samples. The Raman shift is calculated so that to be interpreted and compared with other science sources.

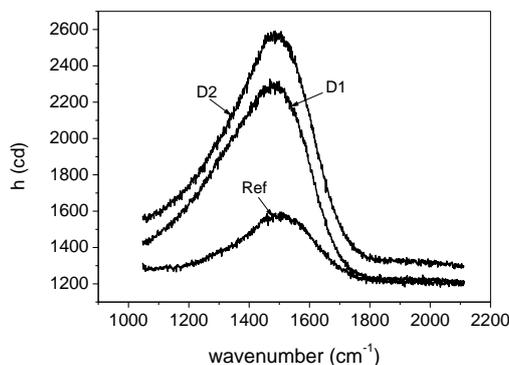


Figure 1. Raman spectra of ta-C films: unimplanted (Ref.), Ga⁺ implanted with a dose D1=3.10¹⁴ cm⁻² (D1) and Ga⁺ implanted with a dose D2=3.10¹⁵ cm⁻² (D2).

Direct information from the intensity measurements could not be given but changes in the ratio between I_D/I_G, the intensities of the D and G peaks in the Raman spectra [18], could bring same useful information about changed graphite-like bonded structures in the films. For that reason, in order to determine the values of I_D and I_G bands and to compare their intensities, the options of Origin 8.1 programme were used to deconvolute and to separate D and G peak. With the further option to calculate more precisely the intensity values, the most common Raman spectra fitting method was used, which is employing two Gaussian peaks with linear background subtraction.

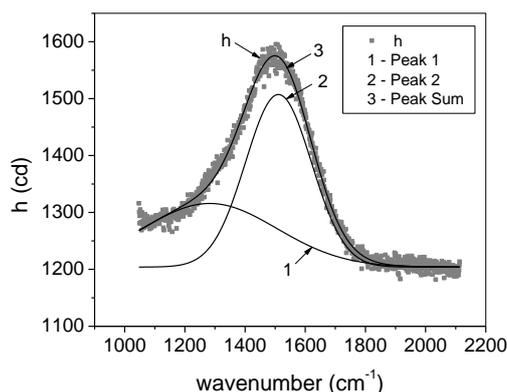


Figure 2. Deconvoluted Raman spectrum for reference sample.

The G and D peaks are due to sp² sites only. The G peak is due to the bond stretching of all pairs of sp² atoms in both rings and chains. The D peak is due to the breathing modes of sp² rings. In figures 2, 3 and 4 are represented deconvoluted Raman spectra of the unimplanted ta-C film, and those for the implanted with Ga⁺ ions films, with doses D₁ and D₂, respectively, so that to reveal more information about the structure of the films. For the ta-C film implanted with D₁, I_D=525 cd and I_G=954,4 cd while for the sample implanted with the higher D₂ dose I_D=561 cd and I_G=756 cd. The ratios were calculated

as follows: $I_D/I_G=0.74$, $I_D/I_G=0.56$ and $I_D/I_G=0.37$, for the implanted samples with doses D_2 and D_1 and the unimplanted sample, respectively. The tendency for growth of this ratio in ta-C films is in accordance with other scientific literary sources and it is believed that the arising of this effect is due to increasing of sp^2 sites in chains and their decreasing in rings while disordering increases. The lower ratio I_D/I_G in combination with high G peak is a sufficient condition to confirm higher sp^3 in the film.

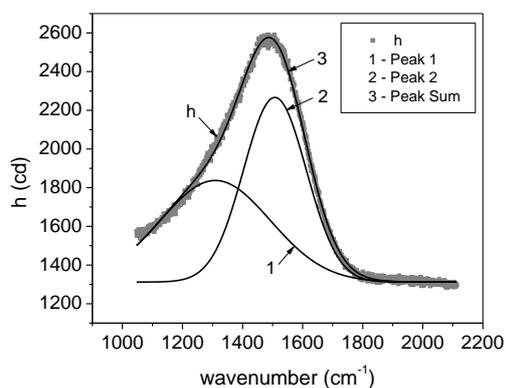


Figure 3. Deconvoluted Raman spectrum for Ga^+ implanted ta-C sample, $D_1=3.10^{14} \text{ cm}^{-2}$.

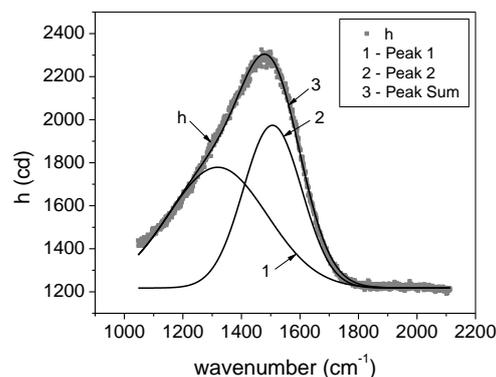


Figure 4. Deconvoluted Raman spectrum for Ga^+ implanted ta-C sample, $D_2=3.10^{15} \text{ cm}^{-2}$.

The values of the FWHM (full width at half maximum) for the G and D peak, $FWHM_G$ and $FWHM_D$, were obtained for the three kinds of samples. The values of $FWHM_G$ for the unimplanted and the implanted samples with D_1 and D_2 are $219,35 \text{ cm}^{-1}$, $209,45 \text{ cm}^{-1}$ and $199,92 \text{ cm}^{-1}$, respectively. A tendency is observed for decreasing of $FWHM_G$ values while applying ion implantation and its influence is increasing with the dose. This implies a decrease of the sp^3 content and an increase of sp^2 clustering areas, while disordering increases. The ion beam induced structural modification is also related to a slight shift in the G peak frequency, demonstrated as a position shift of the G band towards lower wavenumbers with the increase of the implantation dose (figures 2,3 and 4).

3.2. Infrared Spectra

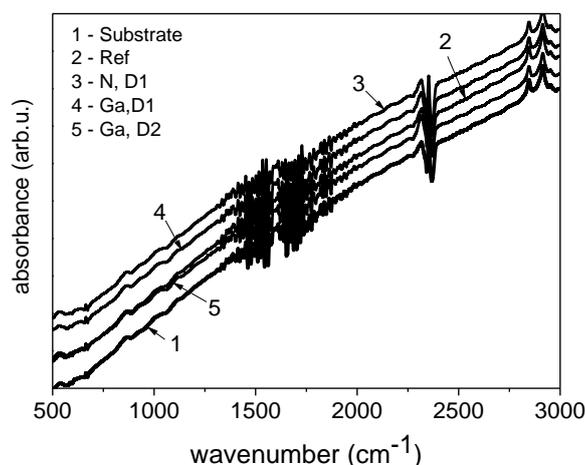


Figure 5. IR spectra of ta-C films: substrate (1), unimplanted (Ref), N^+ implanted with a dose $D_1=3.10^{14} \text{ cm}^{-2}$ (N, D1) Ga^+ implanted with a dose $D_1=3.10^{14} \text{ cm}^{-2}$ (Ga, D1) and Ga^+ implanted with a dose $D_2=3.10^{15} \text{ cm}^{-2}$ (Ga, D2).

We have measured the infrared spectra in reflectance mode in the spectral range 350-3000 cm^{-1} for ta-C film samples without implantation (reference), ta-C implanted with N^+ ions with dose 3.10^{14} ions/ cm^2 , ta-C implanted with Ga^+ ions with dose 3.10^{14} ions/ cm^2 and ta-C implanted with Ga^+ dose 3.10^{15} ions/ cm^2 (figure 5).

In figure 5 are seen the following lines: 1490 cm^{-1} , 1550 cm^{-1} , 1630 cm^{-1} , 1560 cm^{-1} , 2375 cm^{-1} . The lines are due at: 1490 cm^{-1} , 1550 cm^{-1} , 1630 cm^{-1} - C-C stretch (in ring), 2375 cm^{-1} -C(triple bond)C- stretch or C(triple bond)N- stretch, 2800-2900 cm^{-1} is due to air contamination and is a CO_2 line. We observe that triple bonds have higher absorption than aromatic bonds. The film is near the standard for diamond-like carbon (DLC) films: 80% sp^3 and 20% sp^2 . There is small growth of the absorption as a result of the implantation.

The graphics of figure 6 shows the increase of absorption of the ta-C films after N^+ and Ga^+ ion implantation as compared with the Si substrate. In figure 7 there is a line for which the wavenumber corresponds to that of observed gallium compounds - around 660 cm^{-1} [19, 20]. In figure 8 there are lines around 1100 cm^{-1} and 1250 cm^{-1} which are due C-H or C-N stretching bonds [21]. The growth of the absorption is more visible in figures 7 and 8 than in figure 5, and we can conclude that absorption of the N^+ implanted sample is higher than the reference sample, while the decrease of the absorption of the Ga^+ ion implanted ta-C films (which is even greater with the Ga^+ dose increase), as compared with the N^+ implanted one, is presumably due to the gallium colloids formation and their growth resulting in increased light scattering [22].

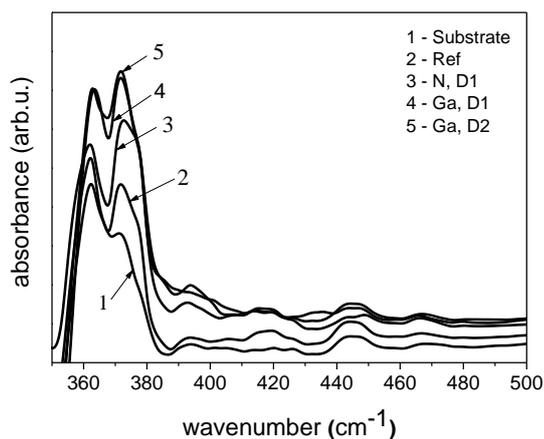


Figure 6. IR spectra of ta-C films: substrate (1), unimplanted (Ref), N^+ implanted with a dose $\text{D1}=3.10^{14}$ cm^{-2} (N, D1) Ga^+ implanted with a dose $\text{D1}=3.10^{14}$ cm^{-2} (Ga, D1) and Ga^+ implanted with a dose $\text{D2}=3.10^{15}$ cm^{-2} (Ga, D2).

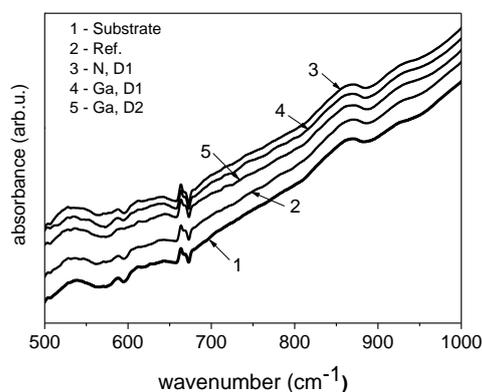


Figure 7. IR spectra of ta-C films: substrate (1), unimplanted (Ref), N^+ implanted with a dose $\text{D1}=3.10^{14}$ cm^{-2} (N, D1) Ga^+ implanted with a dose $\text{D1}=3.10^{14}$ cm^{-2} (Ga, D1) and Ga^+ implanted with a dose $\text{D2}=3.10^{15}$ cm^{-2} (Ga, D2).

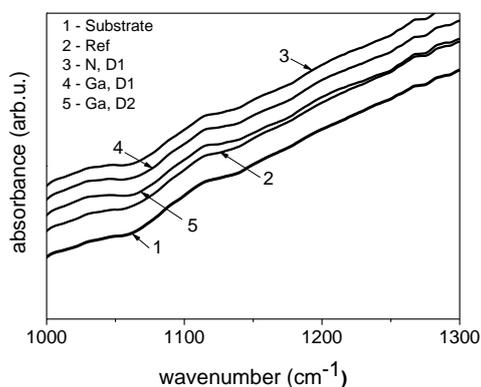


Figure 8. IR spectra of ta-C films: substrate (1), unimplanted (Ref), N^+ implanted with a dose $\text{D1}=3.10^{14}$ cm^{-2} (N, D1) Ga^+ implanted with a dose $\text{D1}=3.10^{14}$ cm^{-2} (Ga, D1) and Ga^+ implanted with a dose $\text{D2}=3.10^{15}$ cm^{-2} (Ga, D2).

4. Conclusion

The obtained results in the present work have shown that choosing relatively low N^+ and Ga^+ ion doses, $D=3.10^{14} \div D=3.10^{15} \text{ cm}^{-2}$, and ion energy, $E=20 \text{ keV}$, results in considerable modification of the structural and optical properties of the implanted ta-C films, indicating some increased graphitisation and assumed electronic properties modification, as shown by the Raman and IR spectroscopy results. The related increase of the absorption coefficient (α) in the visible wavelength range is sufficient in magnitude to fulfill the requirements for optical contrast needed for applications in optical data recording and archival information storage.

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References

- [1] McKenzie D, Muller D and Pailthorpe BA 1991 *Phys. Rev. Lett.* **67** 773
- [2] Fallon PJ, Veerasamy VS, Davis CA, Robertson J, Amaratunga GAJ, Milne WI and Koskinen J 1993 *Phys. Rev. B* **48**, 4777
- [3] Friedmann TA, McCarty KF, Barbour JC, Siegal MP and Dibble DC 1996 *Appl. Phys. Lett.* **68** 1643
- [4] Lifshitz Y, Kasi SR and Rabalais JW 1989 *Phys. Rev. Lett.* **62** 1290
- [5] Silva SRP, Xu S, Tay BK, Tan HS, Scheibe HJ, Chhowalla M and Milne WI 1996, *Thin Solid Films* **290–291** 317
- [6] Veerasamy VS, Yuan J, Amaratunga G, Milne WI, Gilkes KWR, Weiler M and Brown L *Phys. Rev. B* 1993 **48** 17954
- [7] Robertson J 1991 *Solid State Chem.* **21** 199
- [8] Ruttensperger B, Krötz G, Müller G, Derst G and Kalbitzer S 1991 *J. Non-Cryst. Solids* **137-138** 635
- [9] Müller G 1993 *Nucl Instrum Methods B* **80-81** 957
- [10] Kalbitzer S 2004 *Nucl Instrum Methods B* **218** 343
- [11] Tsvetkova T 1996 Ion Beam Modification of Amorphous Silicon-Carbon Alloys *Beam Processing of Advanced Materials*, ed J Singh, S Copley and J Mazumder (ASM International, Materials Park) pp 207-218
- [12] Tsvetkova T, Takahashi S, Zayats A, Dawson P, Turner R, Bischoff L, Angelov O and Dimova-Malinovska D 2005 *Vacuum* **79** 94
- [13] Tsvetkova T, Takahashi S, Zayats A, Dawson P, Turner R, Bischoff L, Angelov O and Dimova-Malinovska D 2005 *Vacuum* **79** 100
- [14] Takahashi S, Dawson P, Zayats AV, Bischoff L, Angelov O, Dimova-Malinovska D, Tsvetkova T and Townsend P 2007 *J. Phys. D: Appl Phys.* **40** 7492
- [15] Tsvetkova T, Sellin P, Carius R, Dimova-Malinovska D and Angelov O 2007 *J. Optoelect. Adv. Mater.* **9** 375
- [16] Bischoff L, Teichert J, Kitova S and Tsvetkova T 2003 *Vacuum* **69** 73
- [17] Ziegler JF, Biersack JP and Littmark U 1985 *The Stopping and Range of Ions in Matter* vol 1 (New York: Pergamon)
- [18] Ferrari A C and Robertson J 2000 *Physical Review B* **61** 14095
- [19] Ferrari A C, Rodil S E and Robertson J 2003 *Physical Review B* **67** 155306
- [20] Zhao Y, Frost R L, Yang J and Martens W N 2008 *J. Phys. Chem. C* **112** 3568.
- [21] Dwivedi N, Kumara S, Tripathia R K, Careyc J D, Malikb H. K. and Dalaia M K 2012 *Appl. Mater. Interfaces* **4** 5309
- [22] Berova M, Sandulov M, Tsvetkova T, Karashanova D, Boettger R and Bischoff L 2015 *J. Phys.: Conf. Ser.* in press