

## Ion implantation induced modification of ta-C films

M Sandulov, M Berova and T Tsvetkova\*

Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko  
Chaussee, 1784 Sofia, Bulgaria

\*E-mail: tania\_tsvetkova@yahoo.co.uk

**Abstract.** Thin film samples ( $d \sim 40\text{nm}$ ) of tetrahedral amorphous carbon (ta-C), deposited by filtered cathodic vacuum arc (FCVA), have been implanted with  $\text{N}^+$  at ion energy  $E = 20\text{keV}$  and ion dose  $D = 3.10^{14}\text{cm}^{-2}$ . The induced structural modification of the implanted material results in a considerable change of its optical properties, best manifested by 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 ( $0.5\div 3.0\text{eV}$ ). These effects could be attributed both to additional defect introduction and increased graphitization, as confirmed by 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 ion nano-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 ( $\sim 70\text{GPa}$ ), chemical inertness, high electrical resistivity, and wide optical band gap [5-8]. 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 [9-16].

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 [9-11]. 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 [12-16].



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 (sp<sup>3</sup>) carbon bonds, before the irradiation, into graphite-like (sp<sup>2</sup>) carbon bonds, as a result of it [11,16]. It is expected, that a similar mechanism of the carbon bonds transformation would result when applying ion bombardment with different ions, e.g. nitrogen ions (N<sup>+</sup>), in ta-C films, so that to achieve useful optical contrast between irradiated and non-irradiated areas of the films as reported in a previous publication [17], which could possibly be of interest for further uses in archival information storage.

## 2. Experimental

Thin ta-C films (d~40 nm) were deposited on Corning glass 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.

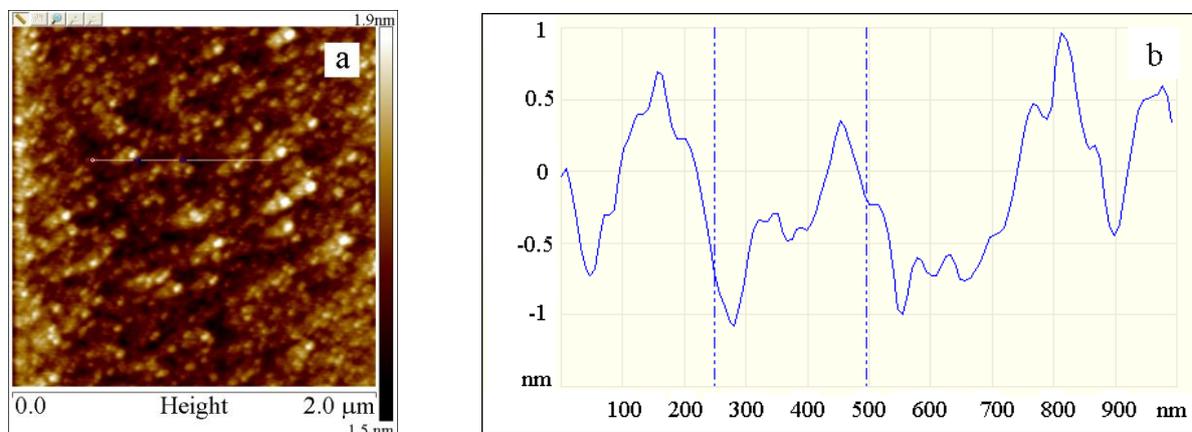
Ion implantation of N<sup>+</sup> was carried out at room temperature (RT) using a commercial broad-beam ion implanter. The ion-beam intensity was I~2 μA/cm<sup>2</sup>, the ion energy was E=20 keV, and the ion dose used was D=3.10<sup>14</sup> cm<sup>-2</sup>. SRIM simulation programme [18] was used to determine the projected range R<sub>p</sub> = 29 nm and the straggle ΔR<sub>p</sub> = 10 nm of the implanted N<sup>+</sup> ions into the ta-C film samples (d = 40 nm).

Atomic force microscope (AFM) - Dimension 3000 Digital Instruments - was used to analyze the topography of the N<sup>+</sup> ion implanted samples.

The structural modifications of the ta-C films by the N<sup>+</sup> ion implantation were monitored by Raman spectroscopy using Horiba Jobin-Yvon LabRam confocal Raman microscope fitted with an argon ion laser. The spectra were taken using a 100× objective lens, an excitation wavelength (λ) of 532 nm and a spot size of ~ 0.70 μm at 10% of total laser power. The laser exposure time was 30 s and the collected spectra were averaged three times with a dwell time of 1 s.

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

## 3. Results and discussion



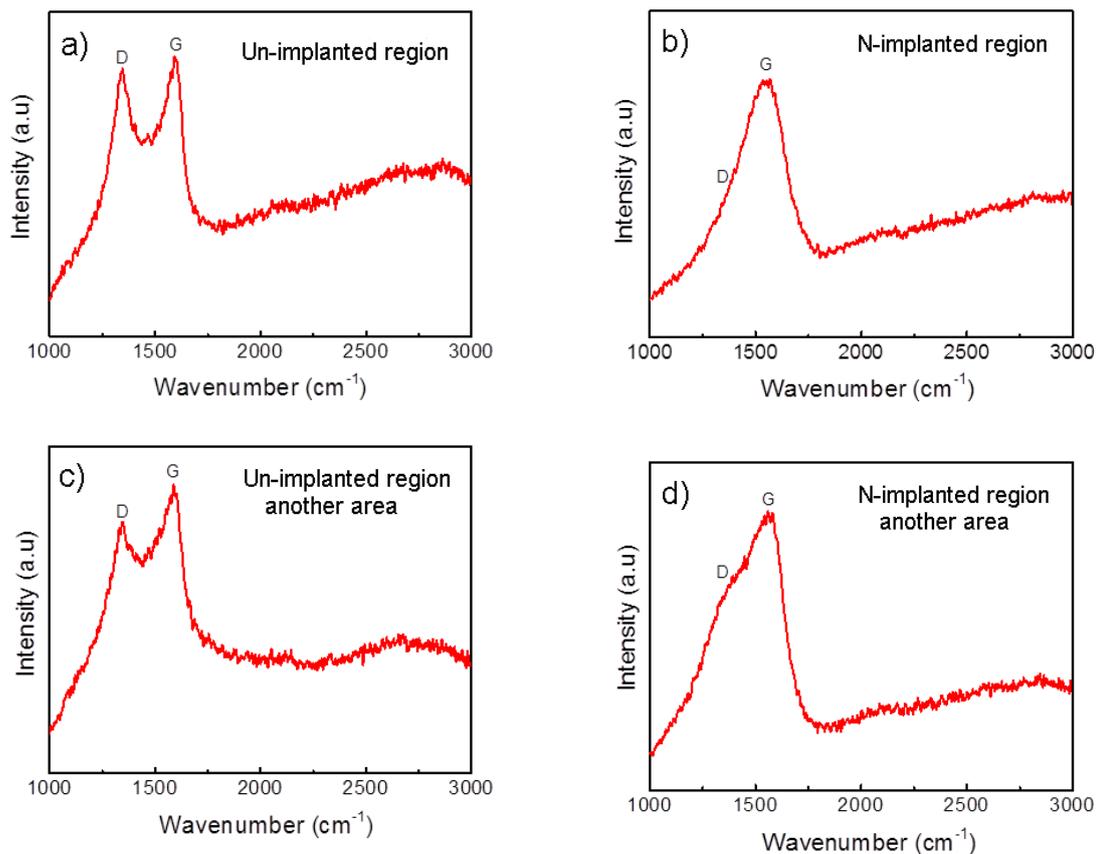
**Figure 1.** AFM results on N<sup>+</sup> ion implanted ta-C sample: (a) Topography image; (b) RMS roughness is less than 2nm at different areas of the samples.

**3.1. AFM spectroscopy results on ta-C samples implanted with  $N^+$  broad-beam implantation** The  $N^+$  ion implanted samples topography was studied by AFM spectroscopy both before and after the ion implantation. In both cases surface roughness (RMS) is less than 2 nm, as shown in figure 1 above.

**3.2. Raman spectroscopy results on ta-C samples implanted with  $N^+$  broad-beam implantation**

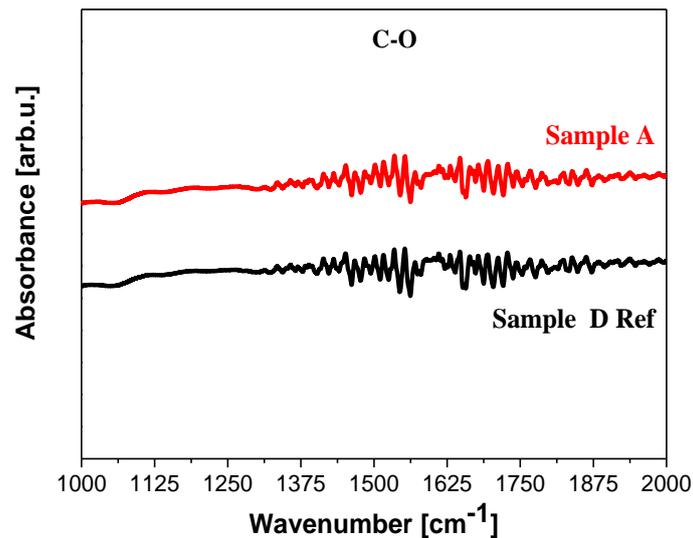
The useful optical contrast, between irradiated and non-irradiated areas of the films, which was reported in a previous publication [17], which could possibly be of interest for further uses in archival information storage, is expected to be resulting from the ion beam induced structural modification leading to increased optical absorption in the visible range of the spectrum.

The possible mechanism is presumed to be that the nitrogen ion irradiation, with relatively low doses ( $D \sim 3 \times 10^{14} \text{ cm}^{-2}$ ), induces structural modifications by increased defects introduction and converting  $sp^3$ -bonded carbons into  $sp^2$ -bonded ones in ta-C films, as confirmed by the Raman results shown in figure 2. The Raman spectra show a distinctive change after the  $N^+$  implantation, namely the ratios of D and G bands [ $I(D)/I(G)$ ] decreases drastically, so that in some cases is leading to complete disappearance of the D band. The D peak arises from aromatic rings.  $I(D)/I(G)$  will increase with increasing disorder in graphite with the presence of such rings. However, for more disorder, clusters decrease in number become smaller and more distorted, until they open up [19]. Analysis of the G band enhancement implies clustering of the  $sp^2$ -bonded carbon aromatic rings with implanting N ions.



**Figure 2.** Raman results on ta-C samples: unimplanted (a,c) and  $N^+$  ion implanted (b,d).

**3.3. Infra-red (IR) spectroscopy results on ta-C samples implanted with  $N^+$  broad-beam implantation**  
The ion-implanted ta-C samples with  $N^+$  broad-beam implantation with a dose  $D = 3 \times 10^{14} \text{ cm}^{-2}$  were studied by infra-red (IR) spectroscopy in the range  $1000\text{--}2000 \text{ cm}^{-1}$ , where C-C bond vibrations are expected at about  $1358\text{--}1569 \text{ cm}^{-1}$  [20]. The obtained IR spectroscopy results are displayed in figure 3, where the  $sp^2$  C-configuration at  $\sim 1550 \text{ cm}^{-1}$  is shown to be slightly increasing as a result of the  $N^+$  ion implantation, confirming the Raman data presented in figure 2.



**Figure 3.** IR results on ta-C samples: unimplanted (D) and  $N^+$  ion implanted (A).

#### 4. Conclusion

$N^+$  broad-beam ion implantation in ta-C samples was carried out at room temperature at a relatively low dose, which has been shown previously to lead to a useful optical contrast between irradiated and non-irradiated areas of the films, which could possibly be of interest for further uses in archival information storage. This optical contrast has been confirmed to be resulting from the ion beam induced structural modification, including increased defect introduction and enhanced graphitisation, i.e.  $sp^3$  to  $sp^2$  conversion of the C-C bonds, leading to increased optical absorption in the visible range of the spectrum.

#### Acknowledgements

The authors would like to thank Dr. K. Nagareddy from the University of Exeter, UK, for the help with the AFM and Raman measurements. The help of Dr. K. Gesheva from the Bulgarian Academy of Sciences, Bulgaria, with the measurement of the IR spectra is also gratefully acknowledged.

#### References

- [1] McKenzie D, Muller D and Pailthorpe B A 1991 *Phys. Rev. Lett.* **67** 773
- [2] Fallon P J, Veerasamy VS, Davis CA, Robertson J, Amaratunga G A J, Milne W I and Koskinen J 1993 *Phys. Rev. B* **48** 4777
- [3] Friedmann T A, McCarty KF, Barbour J C, Siegal M P and Dibble D C 1996 *Appl. Phys. Lett.* **68** 1643
- [4] Lifshitz Y, Kasi S R and Rabalais J W 1989 *Phys. Rev. Lett.* **62** 1290
- [5] Silva S R P, Xu S, Tay B K, Tan H S, Scheibe H J, Chhowalla M and Milne W I 1996, *Thin Solid Films* **290–291** 317

- [6] Veerasamy V S, Yuan J, Amaratunga G, Milne W I, Gilkes K W R, Weiler M and Brown L  
*Phys. Rev. B* 1993 **48** 17954
- [7] Robertson J 1991 *Solid State Chem.* **21** 199
- [8] Xu S, Flynn D, Tay B K, Prawer S, Nugent K W, Silva S R P, Lifshitz Y and Milne W I 1997  
*Philos. Mag. B* **76** 351
- [9] Ruttensperger B, Krötz G, Müller G, Derst G and Kalbitzer S 1991 *J. Non-Cryst. Solids* **137-138** 635
- [10] Müller G 1993 *Nucl Instrum Methods B* **80-81** 957
- [11] Kalbitzer S 2004 *Nucl Instrum Methods B* **218** 343
- [12] 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 207-2018
- [13] Tsvetkova T, Takahashi S, Zayats A, Dawson P, Turner R, Bischoff L, Angelov O and Dimova-Malinovska D 2005 *Vacuum* **79** 94
- [14] Tsvetkova T, Takahashi S, Zayats A, Dawson P, Turner R, Bischoff L, Angelov O and Dimova-Malinovska D 2005 *Vacuum* **79** 100
- [15] 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
- [16] Tsvetkova T, Sellin P, Carius R, Dimova-Malinovska D and Angelov O 2007 *J. Optoelect. Adv. Mater.* **9** 375
- [17] Sandulov M, Berova M, Tsvetkova T and Zuk J 2014 *Acta Physica Polonica* in press  
Ziegler J F, Biersack J P 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