Maria BEROVA[1], Maksim SANDULOV[1], Tania TSVETKOVA[1], Ivalina AVRAMOVA[2], Roman BOETTGER[3], Lothar BISCHOFF[3]

Bulgarian Academy of Sciences, Bulgaria (1), Institute General and Inorganic Chemistry, Bulgaria (2), Helmholtz-Zentrum Dresden-Rossendorf, Germany (3)

doi:10.15199/48.2016.08.16

X-Ray Photoelectron Study of Ion Implanted Tetrahedral Carbon

Abstract. *Samples of thin film (d~40nm) tetrahedral amorphous carbon (ta-C), deposited by filtered cathodic vacuum arc (FCVA), have been implanted with N^+ and Ga^+ at ion energy E = 20 keV and ion fluences D = 3.10^{14}÷3.10^{15} cm^{-2}. This results in optical properties modification, best manifested by a significant shift of the optical absorption edge to lower photon energies, which 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 graphitization, as confirmed by X-ray photo-electron spectroscopy (XPS) measurements. The non-implanted films show the expected variety of carbon-carbon chemical bonds: three- and fourfold coordinated carbon, while the X-ray results show that ion implantation leads to the introduction of additional disorder in the films. The X-ray photoelectron spectra of the implanted films show that, in addition to the already mentioned changes, the ion bombardment results in an increase of the threefold coordinated as compared to the fourfold coordinated carbon bonds, i.e. increased graphitization of the carbon content in the films. These structural modifications, due to the ion implantation, are the reasons for the observed changes in the optical properties of the films, which could be made use of in the area of high-density optical data storage using focused Ga^+ ion beams.*

Streszczenie. *Próbki cienkiej folii (d~40nm) tetraedrycznego amorficznego węgla (ta-C), napylanego za pomocą przefiltrowanego katodowego łuku próżniowego (FCVA), zaimplantowano N^+ oraz Ga^+ z energią jonów E = 20 keV oraz dawkami jonowymi D = 3.10^{14}÷3.10^{15} cm^{-2}. Skutkuje to zmianą właściwości optycznych, szczególnie znacznym przesunięciem optycznej krawędzi absorpcji do poziomu niższych energii fotonów, czemu towarzyszy znaczny wzrost wartości współczynnika absorpcji (efekt foto-zaciemnienia) dla zakresu energii fotonów (0.5÷3.0 eV). Efekty te mogą być przypisane zarówno do wprowadzania dodatkowych defektów jak i zwiększonej grafityzacji, co potwierdzono metodą rentgenowskiej spektroskopii foto-elektronowej (XPS). Folie nieimplantowane demonstrują oczekiwaną różnorodność wiązań chemicznych węgiel-węgiel: trzy I czterokrotnie skoordynowanego węgla, podczas gdy wyniki badań rentgenowskich wykazali, że implantacja jonowa prowadzi do wprowadzenia dodatkowych zaburzeń w foliach. Rentgenowskie widma fotoelektronowe implantowanych folii wykazują, że dodatkowo do wcześniej wspominanych zmian dochodzi wzrost trzykrotnie skoordynowanej krawędzi w wyniku bombardowania jonowego w porównaniu do czterokrotnie skoordynowanej krawędzi węgla, oznacza to wzrost grafityzacji zawartości węgla w foliach. Takie zmiany strukturowe, ze względu na implantację jonową, są rezultatem obserwowanych zmian właściwości optycznych próbek, które mogłyby być wykorzystywane do optycznego przechowywania danych za pomocą skupionych wiązek jonowych Ga^+. (**Rentgenowskie badania fotoelektronowe węgla tetraedralnego poddanego implantacji jonowej**).*

Słowa kluczowe: tetraedryczny amorficzny węgiel; skupione wiązki jonów; optyczne przechowywanie danych.
Keywords: tetrahedral amorphous carbon; focused ion beams; optical data storage.

Introduction

Carbon-based materials, and in particular 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 [5–8]. 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 [9-15].

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 [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 [12-15].

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 [11]. 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 [16,17].

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^+ and Ga^+ was carried out at room temperature (RT) using a commercial broad-beam ion implanter. The ion-beam intensity was I~2 μA/cm^2, the ion energy was E=20 keV, and the ion fluences used were D=3.10^{14} ÷ D=3.10^{15} cm^{-2}. SRIM simulation program [12] was used to determine the projected range Rp ~ 29 nm and the range struggling 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 chemical composition and state of the elements on the DLC films surfaces with and without of N^+ ions as well as Ga^+ implantation were studied using X-ray photoelectron spectroscopy (XPS). The XPS studies were performed on Axis Supra with monochromatic Al K_α radiation (1486.6 eV) and total instrumental resolution of ~0.5 eV.

Results and discussion

On the Figure 1 are shown the C1s spectra of as deposited ta-C film, and N^+ and Ga^+ implanted ta-C films, with equal ion fluences. The C1s spectrum of the reference ta-C film has its typical shape, which is in agreement with previously reported results [19]. This peak could be fitted with 4 components. The first two of them situated around 284.4 eV and 285.0 eV are associated to the C-C bond in sp2 and sp3 configuration. The other component having higher binding energy will be related to existence of C-O bond over the surface of the ta-C film (see Figure 4).

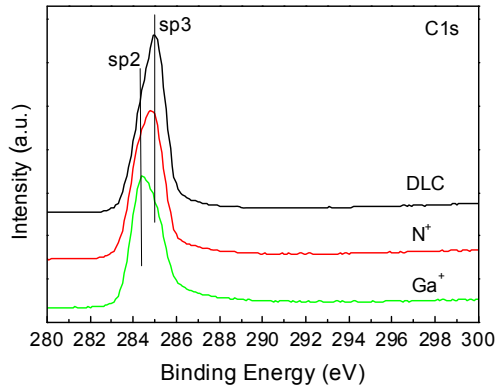

Fig.1. C1s spectra for unimplanted and N^+ and Ga^+ implanted samples with a fluence D1 = 3.1014 cm^{-2}

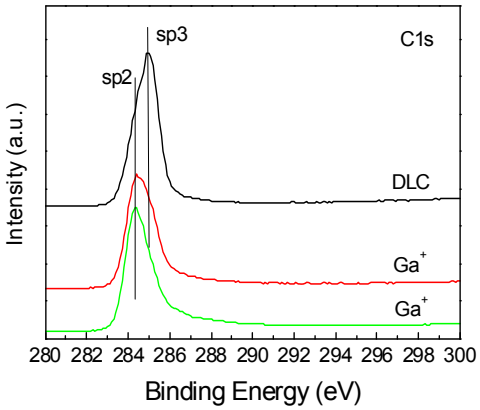

Fig.2. C1s spectra for unimplanted and Ga^+ implanted samples with D_1 = 3.10^{14} cm^{-2} and D_2 = 3.10^{15} cm^{-2}

Implantation of ta-C films by N^+ and Ga^+ ions with equal fluences caused change in the shape of the C1s peak. Implantation of N^+ and Ga^+ caused transformation of sp3 to sp2 type carbon. The degree of graphitization is higher in the ta-C films as a result of the Ga^+ implantation. Small quantity of nitrogen was detected in all investigated films and the binding energy of N1s peak is typical for N-C-O bond (spectra not shown here).

On the next Figure 2 are presented the C1s spectra of as deposited ta-C film and Ga^+ implanted ta-C films with two different fluences. It is obvious from the results that the Ga^+ ions convert the sp3 to sp2 type carbon. On the Figure 3 and Figure 4 are presented the deconvoluted C1s spectra of as deposited ta-C film and Ga^+ implanted ta-C films, respectively. It is obvious from the results that the Ga^+ ions convert the sp3 to sp2 type carbon. The higher Ga^+ fluence caused almost complete transformation of sp3 type carbon to sp2, which is also supported by the data presented in the following Table (GL% - shows the Gaussian - Lorentzian sum of the peak used in the fit; 0 % for Gaussian and 100% for Lorentzian):

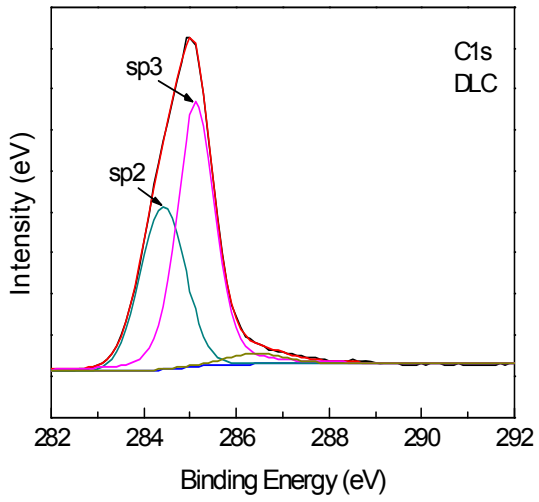

Fig.3. Deconvoluted C1s spectrum for unimplanted samples

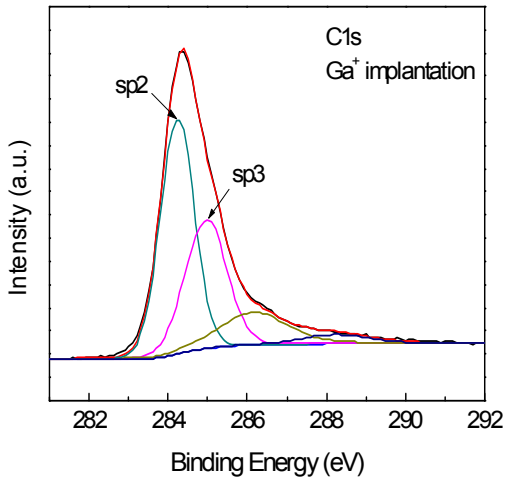

Fig.4. Deconvoluted C1s spectrum for Ga^+ implanted samples with a fluence D_2 = 3.10^{15} cm^{-2}

Table: C1s peak position and area for unimplanted and Ga^+ implanted samples.

C1s Unimplanted ta-C				
Peak	Position (eV)	Area	FWHM (eV)	%GL (%)
0	284.400	24227,290	1.142	0
1	285.123	37737,990	0.968	28
3	286.450	2278,163	1.500	24
C1s Implanted ta-C with Ga^+, D2				
Peak	Position (eV)	Area	FWHM (eV)	%GL (%)
0	284.224	28104,160	1.015	3
1	284.944	19102,700	1.250	6
3	286.136	8750,891	2.000	35
2	288,220	2264,289	2.000	20

Conclusion

The obtained results in the present work have shown that choosing relatively low N^+ and Ga^+ ion fluences $D = 3.10^{14} \div 3.10^{15}$ cm^{-2} and ion beam energy E ~ 20 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. The related increase of the absorption coefficient (α) in the visible wavelength range is over 50% change [20], which is sufficient to fulfill the requirements for optical contrast needed for applications in optical data recording and archival information storage, given also the contribution of the reflectivity increase to the transmission decrease, as the transmission mode is used for the data reading of the stored optical information.

The authors would like to thank the group of Prof. S. Kitova for the samples preparation and characterisation. The authors would also like to thank the staff of the ion beam center at the Helmholtz-Zentrum Dresden-Rossendorf e.V., a member of the Helmholtz Association, for performing the ion implantation.

Authors: *T.Tsvetkova, Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria, tsvet@issp.bas.bg,* M.Berova, *Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria, mberova@issp.bas.bg,* M.Sandulov, , *Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria, msandulov@issp.bas.bg,* I.Avramova, *Institute General and Inorganic Chemistry Acad.G.Bonchev Str., 1113 Sofia, Bulgaria,* iva@svr.igic.bas.bg, R.Boettger, *[3]Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, P.O.B. 51 01 19, 01314 Dresden, Germany* , r.boettger@hzdr.de, L.Bischoff, *[3]Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, P.O.B. 51 01 19, 01314 Dresden, Germany,* l.bischoff@hzdr.de
The correspondence address is: *tsvet@issp.bas.bg*.

REFERENCES

[1] McKenzie D.R., Muller D., Pailthorpe B.A., Compressive-stress-induced formation of thin-film tetrahedral amorphous carbon , *Phys. Rev. Lett.* 67, 773 (1991).

[2] Fallon P.J., Veerasamy V.S., Davis C.A., Robertson J., Amaratunga G.A.J., Milne W.I., Koskinen J., Properties of filtered-ion-beam-deposited diamondlike carbon as a function of ion energy, *Phys. Rev. B* 48, 4777 (1993).

[3] Friedmann T.A., McCarty K.F., Barbour J.C., Siegal M.P., Dibble D.C., Thermal stability of amorphous carbon films grown by pulsed laser deposition, *Appl. Phys. Lett.* 68, 1643 (1996).

[4] Lifshitz Y., Kasi S.R., Rabalais J.W., Subplantation model for film growth from hyperthermal species: Application to diamond, *Phys. Rev. Lett.* 62, 1290 (1989).

[5] Silva S.R.P., Xu S., Tay B.K., Tan H.S., Scheibe H.J., Chhowalla M., Milne W.I., The structure of tetrahedral amorphous carbon thin films, *Thin Solid Films* 290–291, 317 (1996).

[6] Veerasamy V. S., Yuan J., Amaratunga G., Milne W. I., Gilkes K. W. R., Weiler M., Brown L.M., Nitrogen doping of highly tetrahedral amorphous carbon, *Phys. Rev. B* 48, 17954 (1993).

[7] J. Robertson, Hard amorphous (diamond-like) carbons, Prog. *Solid State Chem.* 21, 199 (1991).

[8] Xu S., Flynn D., Tay B.K., Prawer S., Nugent K.W., Silva S.R.P. , Lifshitz Y., Milne W.I., Mechanical properties and Raman spectra of tetrahedral amorphous carbon films with high sp3 fraction deposited using a filtered cathodic arc, *Philos. Mag. B* 76, 351 (1997).

[9] Ruttensperger B., Krötz G., Müller G., Derst G., Kalbitzer S., Crystalline-amorphous contrast formation in thermally crystallised SiC, *J Non-Cryst Solids* 137-138, 635 (1991).

[10] Müller G., The contribution of ion-beam techniques to the physics and technology of amorphous semiconductors, *Nucl Instrum Methods B* 80-81, 957 (1993).

[11] Kalbitzer S., Novel concepts for mass storage of archival data, *Nucl Instrum Methods B* 218, 343 (2004).

[12] Tsvetkova T., Ion beam modification of amorphous silicon-carbon alloys, in: *Beam Processing of Advanced Materials*, Eds. J. Singh, S. Copley, J. Mazumder, ASM International, Metals Park 1996, p. 207.

[13] Tsvetkova T., Takahashi S., Zayats A., Dawson P., Turner R., Bischoff L., Angelov O., Dimova-Malinovska D., Near-field optical mapping of ion-implanted patterns fabricated in amorphous silicon carbide, *Vacuum* 79, 94 (2005).

[14] Tsvetkova T., Takahashi S., Zayats A., Dawson P., Turner R., Bischoff L., Angelov O., Dimova-Malinovska D., Fabrication of nano-scale optical patterns in amorphous silicon carbide with focused ion beam writing, *Vacuum* 79, 100 (2005).

[15] Takahashi S., Dawson P., Zayats A.V., Bischoff L., Angelov O., Dimova-Malinovska D., Tsvetkova T., Townsend P.D., Optical contrast in ion-implanted amorphous silicon carbide nanostructures, *J Phys D: Appl Phys* 40, 7492 (2007).

[16] Bischoff L., Teichert J., Kitova S., Tsvetkova T., Optical pattern formation in a-SiC:H films by Ga^+ ion implantation, *Vacuum* 69, 73 (2003).

[17] Tsvetkova T., Angelov O., Sendova-Vassileva M., Dimova-Malinovska D., Bischoff L., Adriaenssens G.J., Grudzinski W., Zuk J., Structural and optical properties modification of a-SiC:H by Ga^+ ion implantation, *Vacuum* 70, 467 (2003).

[18] Ziegler J.F., Biersack J.P., Littmark U., *The Stopping and Range of Ions in Matter*, Vol.1, Pergamon, New York (1985).

[19] Yan X.B., Xu T., Yang S.R., Liu H.W.., Xue Q.J, Characterization of hydrogenated diamond-like carbon films electrochemically deposited on a silicon substrate, J. Phys. D: Appl. Phys. 37, 2416 (2004).

[20] Sandulov M., Berova M., Tsvetkova T., Zuk J., Ion beam induced darkening in tetrahedral amorphous carbon thin films, Acta Physica Polonica A, in press.