Structural modification of Ga^+ and N^+ ion implanted ta-C films

M Berova[1], M Sandulov[1], T Tsvetkova[1,4], D Karashanova[2], R Boettger[3] and L Bischoff[3]

[1]Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
[2]Acad. J. Malinovski Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Acad. G. Bontchev Str., Bl. 109, 1113 Sofia, Bulgaria
[3]Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, POB 510119, 01314 Dresden, Germany

E-mail: tsvet@issp.bas.bg

Abstract. Thin-film samples (d ~ 40 nm) of tetrahedral amorphous carbon (ta-C) deposited by filtered cathodic vacuum arc (FCVA) were implanted with Ga^+ at ion energy E = 20 keV and ion fluences $D = 3\times10^{14}\div3\times10^{15}$ cm^{-2} and N^+ with the same energy and a dose $D = 3\times10^{14}$ cm^{-2}. The Ga^+ ion beam induced a structural modification of the implanted material. This resulted in a considerable change of its structural properties, manifested as the formation of a new phase under non-equilibrium conditions, which could be accompanied by considerable changes in the ta-C films optical properties. The N^+ implantation also resulted in a modification of the surface structure. These effects were explored using transmission (TEM) and scanning (SEM) electron microscopy.

1. Introduction

In recent years, carbon-based materials, and in particular tetrahedral amorphous carbon (ta-C), have attracted great interest from both scientific and industrial points of view. The term tetrahedral is used to describe amorphous carbon films with a large percentage of sp3 bonding. The high sp3 content in the films results in unique properties [1-3]. These properties also offer advantages as compared to another wide-optical-band gap material – silicon carbide (SiC) – for uses in nano-scale optical data storage using focused ion beams techniques, where SiC films have recently found useful applications [4-9].

In both polycrystalline and amorphous SiC film materials, a considerable role in the creation of a useful optical contrast between irradiated and non-irradiated areas of the films is played by the transformation of a substantial part of the present diamond-like (sp3) carbon bonds, before the irradiation, into graphite-like (sp2) carbon bonds, as a result of it [6]. It is expected that a similar mechanism of 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 a useful optical contrast would be achieved between irradiated and non-irradiated areas of the films. The use of

[4] To whom any correspondence should be addressed.

gallium as an 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 [10,11]. The implantation of N^+ leads to the formation of crystals on the sample surface. The underlying structural modification, induced by the N^+ and Ga^+ ion bombardment, was investigated by transmission (TEM) and scanning (SEM) electron microscopy measurements.

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. The 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 $I \sim 2\ \mu A/cm^2$, the ion energy was $E = 20$ keV, and the ion fluencies used were $D = 3\times10^{14} \div 3\times10^{15}\ cm^{-2}$ for the Ga^+-implanted, and $D = 3\times10^{14}\ cm^{-2}$ for the N^+-implanted samples. The SRIM simulation program [12] was used to determine the projected range Rp ~ 29 nm and the struggle ΔRp ~ 10 nm, for the N^+, and Rp ~ 17 nm and ΔRp ~ 4 nm, for the Ga^+ implanted ions into the ta-C film samples (d = 40 nm).

The chemical composition and state of the elements in the ta-C films surfaces with and without N^+ ions, as well as in the case of Ga^+ implantation, were studied using transmission electron microscopy (TEM) and scanning electron microscopy (SEM) measurements. The TEM experiment was carried out on a JEOL JEM 2100 high-resolution scanning transmission electron microscope with 200 keV energy and a height of 25 cm between the objective and projector lenses. The SEM experiment was conducted using a Philips 515 scanning electron microscope.

3. Results and discussion

3.1. Analysis and treatment of TEM images

Below, TEM images are presented of ta-C films before (figure 1) and after implantation with different elements and doses of ions (N^+ ions for figure 2 and Ga^+ ions for figure 3).

Figure 1 presents a TEM image of a clear ta-C film without any implantation impact. On the surface, one can see a few little dark spots, which are identified as a graphite-like fraction in an amorphous carbon matrix.

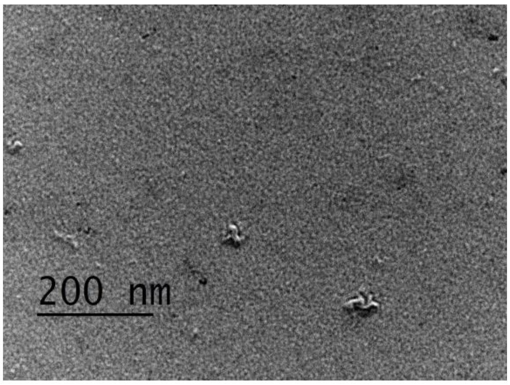


Figure 1. TEM image presenting area of a clear ta-C film without any implantation effects.

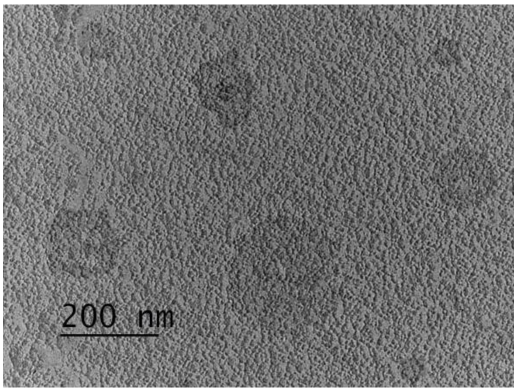


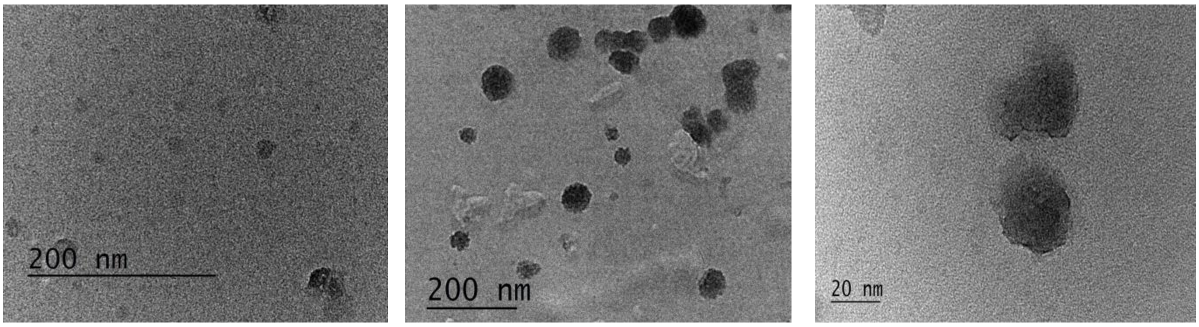
Figure 2. TEM image of area of a N^+-implanted ta-C film with a dose $D1 = 3\times10^{14}\ cm^{-2}$.

Figure 2 shows a TEM image of a ta-C film after N^+ ion implantation effect of a dose $D1 = 3\times10^{14}$cm^{-2}. It is noticed that the dark spots are larger compared with those in the film without any implantation effect. It could be presumed that the implantation effects contribute to clustering of the graphite fraction.

Using selected-area electron-diffraction (SAED) microscopy for the N^+ implanted sample, electron-beam diffraction images were obtained from these darker spots. The result showed that they were crystals in the amorphous carbon.

In the case of Ga^+ implanted ta-C films, the TEM images revealed gallium precipitates in the form of approximately spherical colloids (figure 3). The SAED patterns indicated that they were amorphous gallium.

The size of these colloids clearly increases with the Ga^+ ion dose (figure 3a and figure 3b). These results are in good agreement with previous results of TEM analysis of Ga^+-implanted float glass samples [13]. Figure 3c is a zoomed area from Figure 3b, where one can see that the inclusions look like droplets in the layer. In the next section we will discuss further the nature of these colloids.



(a) (b) (c)

Figure 3. TEM image of an area of Ga^+-implanted ta-C film: a) dose $D2 = 3\times10^{14}$cm^{-2}; b) dose $D2 = 3\times10^{15}$cm^{-2}; c) dose $D2 = 3\times10^{15}$cm^{-2} at higher magnification.

3.2. Analysis and treatment of the SEM images

A SEM image taken from the surface of the unimplanted ta-C film is given in figure 4. In comparison with the reference sample, the N^+ implanted ta-C layer is highly damaged with randomly located formations on the surface (figure 5). In the magnified image in figure 6, it is seen that the formations are small crystals (figure 6).

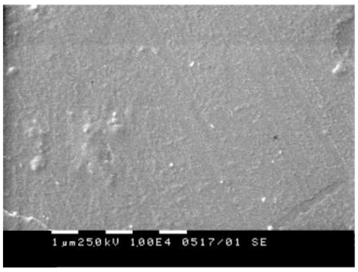


Figure 4. SEM image of an unimplanted ta-C film, electron-beam energy 25 kV, magnification 5000.

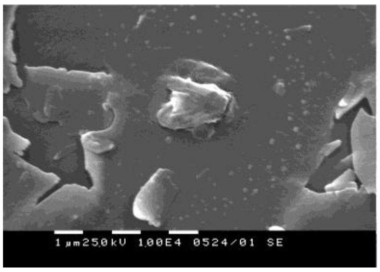


Figure 5. SEM image of a ta-C film implanted with N^+, $D1 = 3\times10^{14}$ cm^{-2}, electron-beam energy 25 kV, magnification 10000.

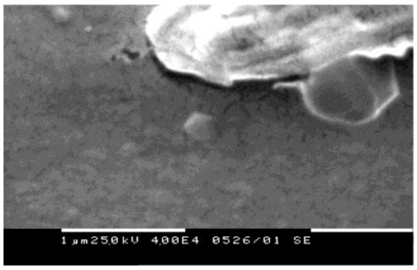


Figure 6. SEM image of a ta-C film implanted with N^+, $D1 = 3\times10^{14}$ cm^{-2}, electron-beam energy 25 kV, magnification 40000.

We also compared two samples implanted with Ga^+ with different doses: $D_1 = 3\times10^{14}$ cm^{-2} and $D_2 = 3\times10^{15}$ cm^{-2} with the same reference sample as above (figure 4). In figure 7, the image of sample D_1 shows that there are a few convexities. In figure 8 one can see that the sample implanted with the second dose shows an increase of the inclusions.

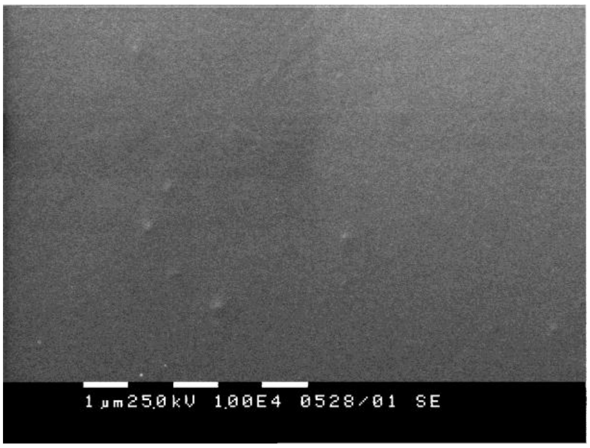


Figure 7. ta-C film implanted with Ga^+, $D_1 = 3\times10^{14}$ cm^{-2}.

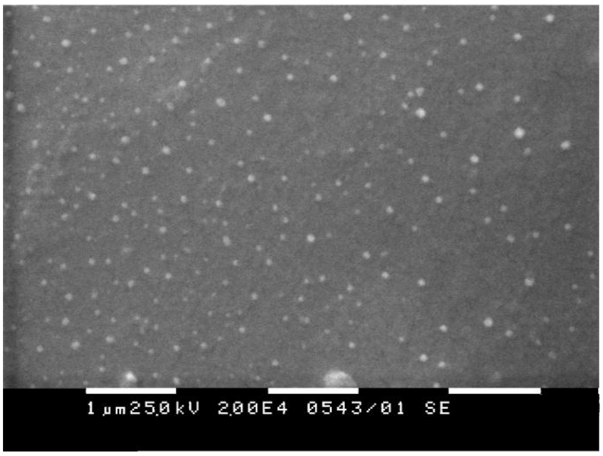


Figure 8. ta-C film implanted with Ga^+, $D_2 = 3\times10^{15}$ cm^{-2}.

Figure 9. ta-C film implanted with Ga^+, $D_1 = 3\times10^{14}$ cm^{-2}, electron beam energy 25 kV, magnification 20000.

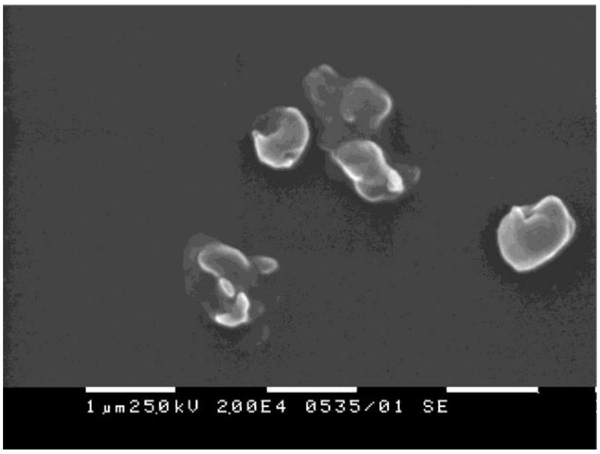


Figure 10. ta-C film implanted with Ga^+, $D_2 = 3\times10^{15}$ cm^{-2}, electron beam energy 25 kV, magnification 20000.

Figure 9 and figure 10 both show in greater detail at higher magnification the colloid nature of the Ga^+ inclusions at the two doses. This phenomenon is in good agreement with those observed by D.E. Hole, P.D. Townsend, J.D. Barton, L.C. Nistor, J. Van Landuyt [13] for Ga^+ implantation effects in float glass samples. The results of their experiment were obtained by TEM and RBS.

From the analysis of the distribution of the dark spots in the images of the TEM investigation, we can conclude that the number of dark areas is increasing with the dose of implantation with Ga^+ ions in a nonlinear way. The contrast of the dark spots (graphite in the case of N^+ and gallium precipitates in the case of Ga^+) rises after the implantation with a higher dose. The change of the structures could also lead to changes in the optical properties, which effect is a subject of others our publications [14, 15]. There is a difference between the sizes of the spots in the case of the N^+ and the Ga^+ implantation, caused by the different masses of the two ions (N^+ produces a larger size).

The TEM and SEM investigations of the N^+-implantation-induced structural modification in ta-C films are also very helpful in elucidating the role of this implantation in enhancing the resistive switching properties of ta-C films.

4. Conclusions

The present study of Ga^+- and N^+-implanted ta-C films revealed that there can be significant differences between the impact of various elements and their doses to the size and distribution of particles created by ion implantation. It was concluded that the TEM and SEM analyses conducted indicated the formation of new phases in both cases of implantation. Comparing the two types of elements, we can conclude that Ga^+ ions formed colloids with a more spherical shape and distinct boundaries than the clusters in the N^+ implanted samples. As the dose is increased, the Ga^+ colloids became bigger and their amount grew. In consequence, it is expected that these formations contribute to the changes observed in the optical properties of ta-C films, which can be used for optical data recording applications.

Acknowledgements

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