

Surface characterisation of Ga⁺ ion implanted ta-C thin films

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Abstract. Samples of thin film (d~40nm) tetrahedral amorphous carbon (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 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. 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 graphitization, as well as due to Ga colloids formation, as confirmed by electron microscopy analysis. Further nano-scale structural and electronic properties characterisation of the Ga⁺ implanted films has been carried out here using conductive atomic force microscopy (C-AFM) measurements. The observed properties modification results from the high concentration of introduced Ga⁺ atoms, which is of the order of those for the host element. The obtained optical contrast (between implanted and unimplanted film material) could be made use of in the area of high-density optical data storage by using focused Ga⁺ ion beams.

1. Introduction

Pure carbon can occur in many forms reflected by the nearest neighbour bonds, and by midrange and long-range ordering of the solid. Different forms of carbon are being exploited in newly engineered applications. The most well-known forms of elemental carbon found in nature are graphite and diamond. Besides the crystalline forms, amorphous form of carbon has been found to be having a lot of technological applications. The properties of these amorphous carbons sensitively depend on the relative concentration of *sp*³ and *sp*² hybridized carbons. The resulting amorphous materials are variously referred to as tetrahedral amorphous carbon (*ta*-C), amorphous carbon (*a*-C), hydrogenated amorphous carbon (*a*-C:H), amorphous conducting carbon (*a*-CC), etc. The term tetrahedral is used to describe amorphous carbon films with a large percentage of *sp*³ bonding (up to 87%). 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 [1–3].

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 [4–10].



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 a very 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 [11-13].

In the 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 [14-20]. It is expected, that a similar mechanism of the carbon bonds transformation would result when applying ion bombardment with different ions, e.g. gallium ions (Ga⁺), in ta-C films, so that to achieve 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.

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 Ga⁺ was carried out at room temperature (RT) using a commercial broad-beam ion implanter. The ion-beam intensity was $I \sim 2 \mu\text{A}/\text{cm}^2$, the ion energy was $E=20 \text{ keV}$, and the ion fluencies used were $D1=3.10^{14}$ and $D2=3.10^{15} \text{ cm}^{-2}$. The SRIM simulation program [21] was used to define the projected range $R_p \sim 17 \text{ nm}$ and the straggles $\Delta R_p \sim 4 \text{ nm}$ for the Ga⁺ implanted ions into the ta-C film samples ($d = 40 \text{ nm}$).

Conductive atomic force microscopy (C-AFM) measurements were carried out using scanning probe microscopy (MFP-3DTM, Asylum Research, Oxford Instruments) operating in contact mode. A Ti/Ir coated silicon probes (ASYELECO1) with a resonant frequency of 70 kHz and spring constant of 2 Nm^{-1} were employed. A bias of +5 V was applied to the sample surface during measurements.

3. Results and discussion

The surface morphology of pristine and gallium implanted ta-C samples was studied using AFM measurements in contact mode. In figure 1a, figure 1b and figure 1c are displayed the morphology changes of the ta-C samples with the gallium implantation. In general, the pristine films are homogeneous over large areas of the substrate (figure 1a). Figures 1b and 1c are showing roughness increase with the gallium fluence increase, particularly well expressed for the case with the highest gallium fluence (figure 1c). Presumably, this is due to the high concentration of the introduced Ga⁺ atoms, which is of the order of those for the host element. The change of the structures could lead also to changes in the optical properties, which effect is a subject of some other publications of ours [22, 23].

The surface electrical conductivity change is presented in figure 1d, figure 1e and figure 1f, where the gallium fluence increase leads to apparent increase of the measured electrical conductivity. This is assumed to be due to the presence of electrically conductive graphitic nano-clusters, which are interconnected and grow with the gallium fluence. The conductivity increase is however limited as the graphitic clusters are limited in size with the growth of gallium metal colloids which also increase in size and concentration with the gallium fluence as reported in previous publications of ours [24, 25]. These graphitic clusters, though limited in size, are further increased in concentration and are redistributed with the gallium fluence increase (figure 3 and figure 4).

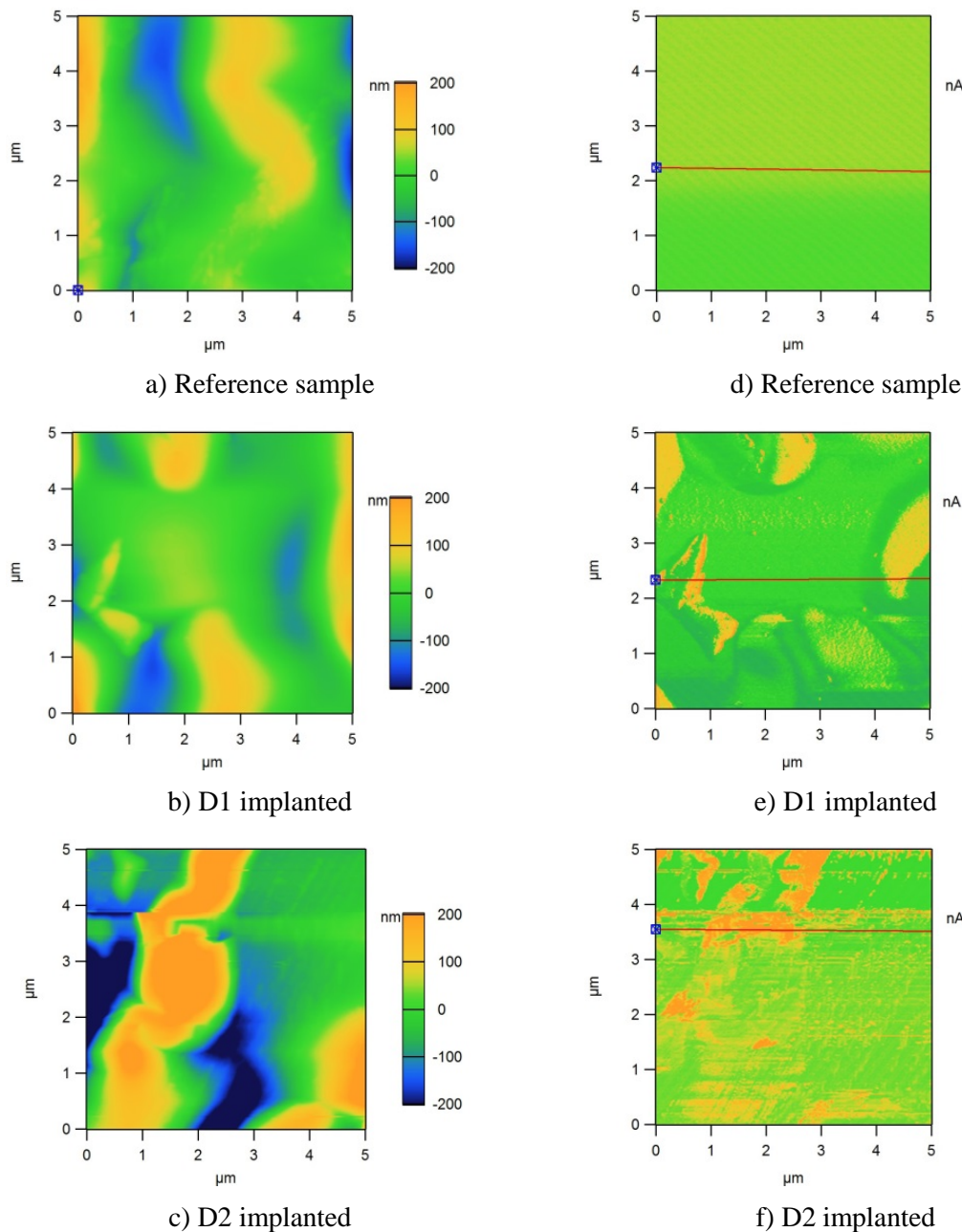


Figure 1. C-AFM images of topography: a) reference sample, b) D1 implanted and c) D2 implanted; and corresponding current: d) reference sample, e) D1 implanted and f) D2 implanted.

In the following figures, figure 2, figure 3 and figure 4, are displayed the three-dimensional current images, the current sections across the lines designated in the two-dimensional current images in figure 1 (figure 1d, figure 1e and figure 1f) and current histograms from 5x5 μm area, for the reference sample, the D1 sample and the D2 sample (figure 2, figure 3 and figure 4, respectively). Apparently, the electrical conductivity increases already for the lower gallium implantation fluence (D1), with only redistribution of the charge resulting from the higher gallium fluence (D2) and hardly noticeable any increase of current. As pointed out earlier, the conductivity increase appears limited as the graphitic clusters are eventually disrupted by the gallium colloids that increase in size and concentration with the fluence.

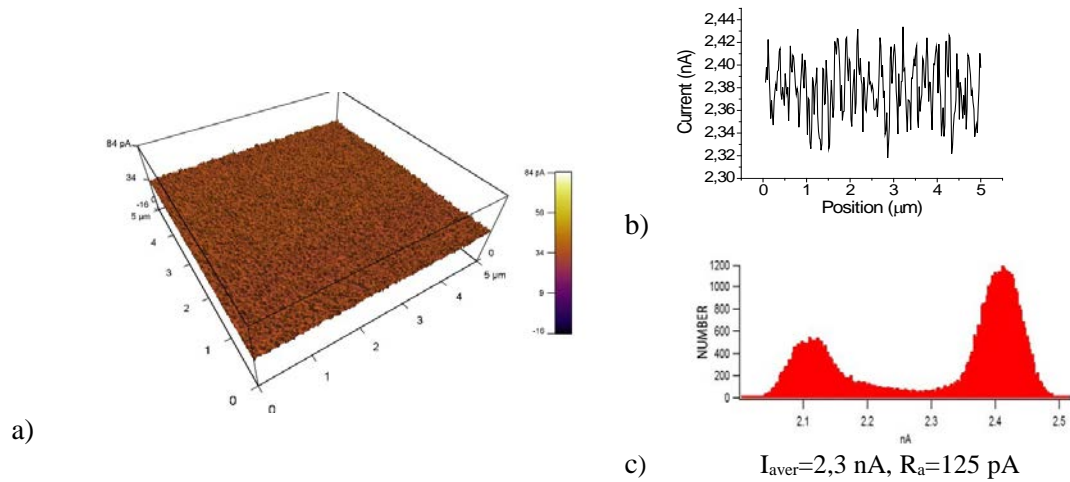


Figure 2. Current image (a), current section across the line in figures 1d (b) and current hystogram from 5x5 μm area (c) for reference sample (I_{aver} – mean value of current; R_a – average deviation).

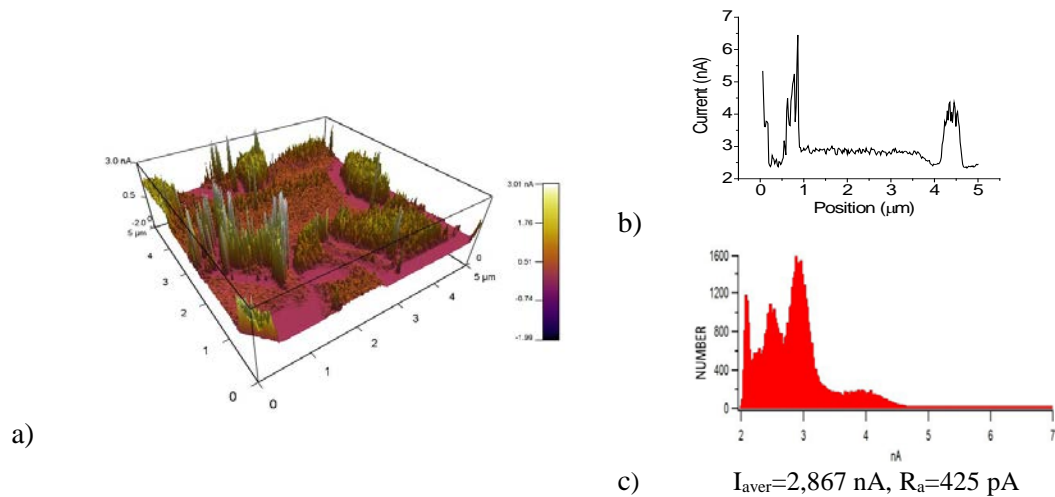


Figure 3. Current image (a), current section across the line in figures 1e (b) and current hystogram from 5x5 μm area (c) for D1 sample (I_{aver} – mean value of current; R_a – average deviation).

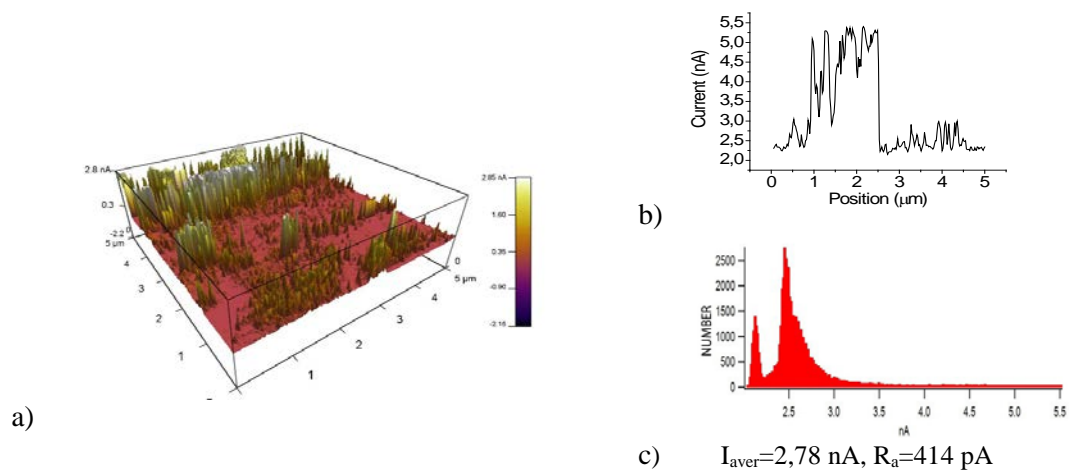


Figure 4. Current image (a), current section across the line in figures 1f (b) and current hystogram from 5x5 μm area (c) for D2 sample (I_{aver} – mean value of current; R_a – average deviation).

4. Conclusion

The obtained results in the present work have shown that ion implantation of ta-C thin films with Ga⁺ with relatively low ion fluence ($D = 3.10^{14} \text{ cm}^{-2}$) has no significant effect on the film surface morphology. However, higher fluences of Ga⁺ ion implantation (on the order of $D = 3.10^{15} \text{ cm}^{-2}$) in such films results in considerable modification of the surface structure and morphology changes of the implanted ta-C films. Simultaneously, the surface electrical conductivity of the gallium implanted ta-C samples increases, presumably due to the growth of graphitic clusters in the implanted areas, which increase in concentration with the gallium fluence. The observed properties modification results also from the high concentration of introduced Ga⁺ atoms, which is of the order of those for the host element. The change of the structures could lead also to changes in the optical properties, studied in earlier publications of ours, which effect could be made use of in high-density optical data storage.

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