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# OPTICAL CONTRAST FORMATION IN ta-C FILMS BY ION IMPLANTATION

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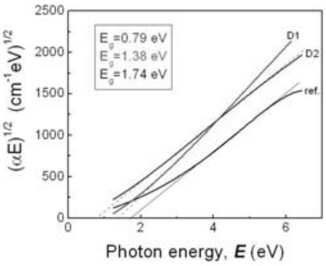
Tetrahedral amorphous carbon (ta-C) thin films (d ~ 40 nm), deposited by filtered cathodic vacuum arc (FCVA) method, have been implanted with $Ga^+$ ions with energy 20 keV and ion fluences $3x10^{14}$ and $3x10^{15}$ $cm^{-2}$. The implantation induced modification of the films structure is reflected in a considerable change of their optical properties, best manifested by a significant shift of the optical absorption edge to lower photon energies as obtained from optical measurements. This shift is accompanied by a considerable increase of the absorption coefficient in the photon energy range (0.5 ÷ 3.0 eV). The observed effects could be attributed both to additional defect generation and increased graphitization, as well as by gallium colloids formation. The optical contrast thus obtained (between implanted and unimplanted film material) could be of use in the area of high-density optical data storage using focused $Ga^+$ ion beams.



## INTRODUCTION

Thin films of amorphous carbon (a-C) also referred to as diamond like carbon (DLC), have received considerable attention due to their intrinsic highly attractive properties. Amorphous carbon (a-C) is a disordered phase of carbon without long-range order, containing carbon atoms mostly in graphite-like sp2 and diamond-like sp3 hybridization sites. Depending on the relative concentrations of sp2- or sp3- hybridized carbon, a-C has shown excellent physical properties such as high hardness, low friction coefficient, chemical inertness, relatively high thermal conductivity, and optical transparency.[1] 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.[5–9] 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.[10-17]

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

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for archival information storage.[10-12] 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.[13-17]

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.[12, 17] It is expected, that a similar mechanism of the carbon bonds transformation would result when applying ion bombardment with different ions, *e.g.* gallium ($Ga^+$) 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. In order to explore such possibilities, optical properties characterization of $Ga^+$ implanted films has been performed using optical spectroscopy and ellipsometric measurements.

## RESULTS AND DISCUSSION

### 1. Spectrophotometric measurements of $Ga^+$ implanted ta-C films

In Figs. 1a,b the optical transmittance (T) and reflectance (R) measurements of the unimplanted and $Ga^+$ implanted samples of ta-C films on glass substrates are presented in the range of 400÷1200 nm. The absorbance (A) values presented in Fig. 1c were calculated as A=1-(T+R).

It could be clearly observed in Fig. 1a that the untreated sample has higher transmittance which drops down with the increase of the $Ga^+$ fluence in the implanted samples. This effect can be explained by increased reflection (Fig. 1b) from the $Ga^+$ colloids formed. The latter has been proved and visualized on our TEM and SEM micrographs.[18] Absorption enhancement (Fig. 1c) is an evidence for additional structural changes most probably due to introduction of $Ga^+$ colloid clusters and generation of defects by the implantation process.

### 2. Ellipsometric measurements of $Ga^+$ implanted ta-C films

In order to elucidate the optical constants of refractive index n, extinction coefficient k and the films thickness from the ellipsometric data, a two-layer optical model was used to represent the sample consisting of a silicon substrate, silicon native oxide layer as a first layer and an alpha-C layer as a second layer. The thickness of the deposited ta-C films, further in the optical model denoted as DLC layer, was determined in the 700 - 1000 nm transparent range using the Cauchy model. The best fits were achieved with a mean square error (MSE) quite below10. Then the film thickness was fixed and further in the whole studied spectral range the dielectric function of the DLC layer was parameterized by B-spline model and, after that with General oscillator model including one Tauc-Lorentz oscillator.[19] For the fits made in the whole measured spectrum, the MSE values were around 10. The calculated parameters were obtained with accuracy as follows: for the film thickness it was ±0.2 nm, while for the *n* and *k* values it was ±0.0005. The results from the fitting procedures are illustrated for the sample D2 in Fig. 2, where the experimental and theoretical $\Psi$ and $\Delta$ data are given at different angles of incidence.

The optical constants refractive index n and extinction coefficient k of the studied samples are summarized in Fig. 3. As it can be seen, the refractive index dispersion of the unimplanted sample (Fig. 3a) follows the normal behavior, while it changes with the $Ga^+$ ions implantation. By increasing the $Ga^+$, the k values become larger and the absorption edge moves toward longer wavelengths. All these changes suggest that implantation with $Ga^+$ ions causes structural modification in the amorphous carbon matrix.

It is suggested that implantation causes partial transformation of the present diamond-like (sp3) carbon bonds into graphite-like (sp2) carbon bonds and, thus it strongly affects the bandgap energy $E_g$ value. By analyzing the spectral dependence of the absorption coefficient $\alpha$ and using the Tauc's expression[20] with assumption of indirect type electron transition, the energy band gap values were evaluated. For this purpose, the $\alpha$ values were calculated from the k values ($\alpha=4\pi k/\lambda$) presented in Fig. 3b and the Tauc plots[20] of $(\alpha E)^{1/2}$ versus photon energy E were built (Fig. 4). Extrapolating the linear part of the curves toward zero absorption, the interception with the photon energy E axis provided the Eg values. The obtained bandgap energies as a function of implanted ion fluence are presented in Fig. 5. Apparently, the rearrangement of hybridization sites in the amorphous C matrix leads to enhanced graphitization, pronounced in a drop of $E_g$ value from 1.74 eV of reference film to 0.8 eV of the implanted films with larger $Ga^+$ ion fluence equal to $3x10^{15}$ $cm^{-2}$.

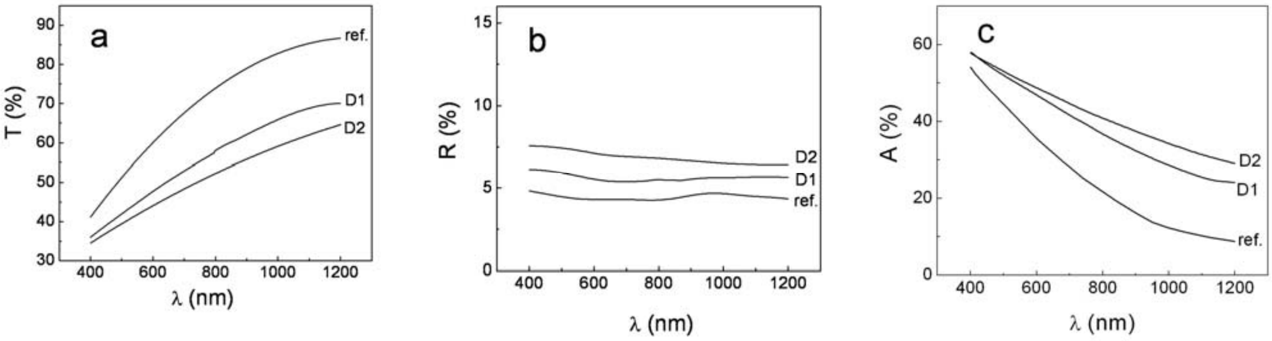

Fig. 1 – Optical transmittance T (a), reflectance R (b) and absorbance A (c) spectra of ta-Ca for the reference sample and samples D1 and D2, implanted with $Ga^+$ ions with fluences of $3x10^{14}$ $cm^{-2}$ and $3x10^{15}$ $cm^{-2}$, respectively.

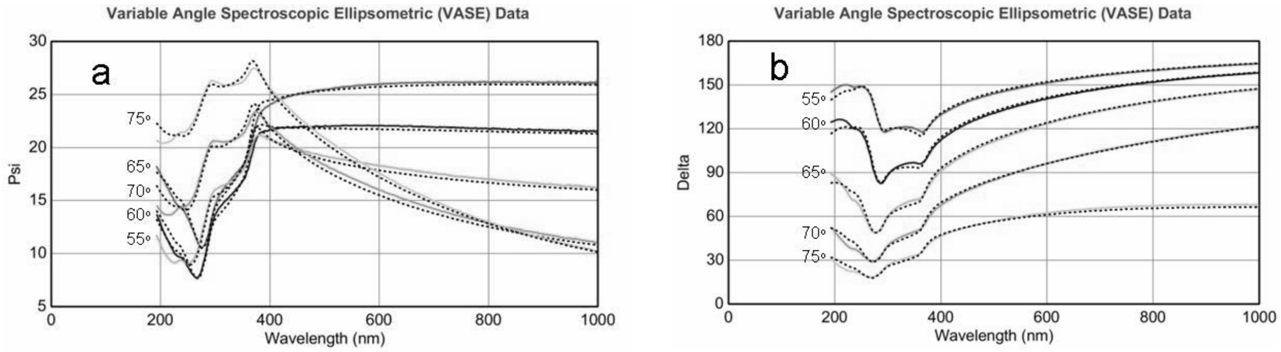

Fig. 2 – Experimental (solid lines) and theoretical (dash lines) wavelength dependences of the ellipsometric angles Ψ and Δ (MSE=12) for sample D2, implanted with $Ga^+$ ions with fluence of $3x10^{15}$ $cm^{-2}$.

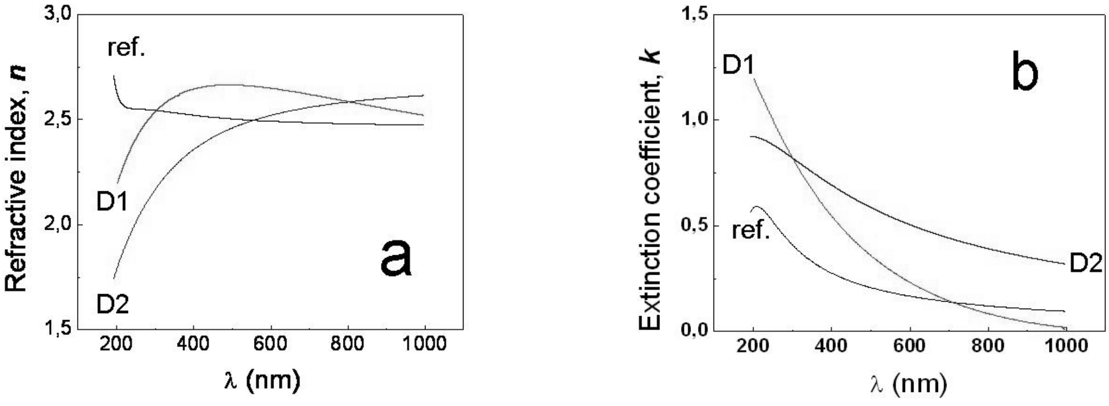

Fig. 3 – Dispersion curves of the refractive index (a) and extinction coefficient (b) of the reference sample and samples D1 and D2, implanted with $Ga^+$ ions with fluences of $3x10^{14}$ $cm^{-2}$ and $3x10^{15}$ $cm^{-2}$, respectively.

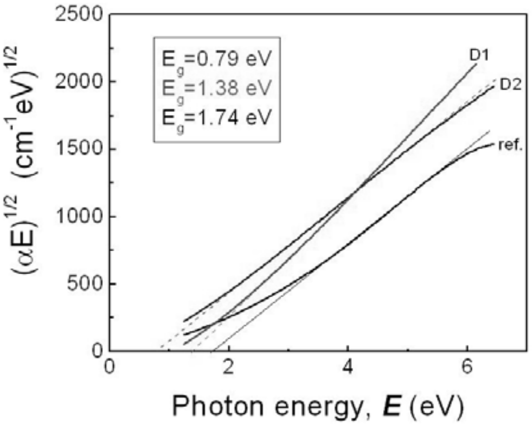

Fig. 4 – Plots $(\alpha E)^{1/2}$ vs. photon energy E for the reference sample and samples D1 and D2, implanted with $Ga^+$ ions with fluences of $3x10^{14}cm^{-2}$ and $3x10^{15}cm^{-2}$, respectively.

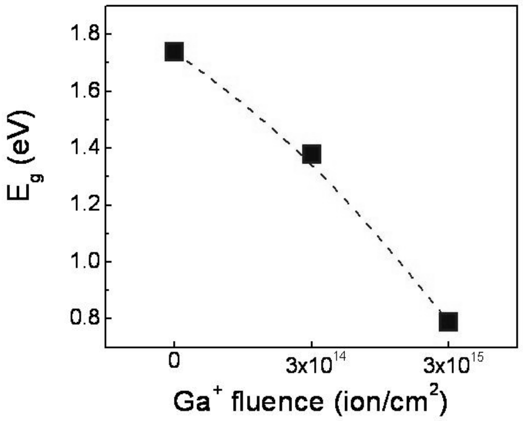

Fig. 5 – Optical band gap energy $E_g$ of the reference sample and implanted samples in dependence on the $Ga^+$ ions fluence, determined with an accuracy of ±0.05 eV.

## EXPERIMENTAL

Thin ta-C films (d~40 nm) were deposited on Corning glass and polished silicon 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~2 $\mu A/cm^2$, the ion energy was E=20 keV, and the ion fluencies used were $3x10^{14}$ and $3x10^{15}$ $cm^{-2}$. These samples were denoted further as D1 and D2, respectively. SRIM simulation program[21] was used to determine the projected range Rp ~ 17 nm and the struggle ΔRp ~ 4 nm for the $Ga^+$ implanted ions into a 40 nm thick ta-C film sample (Fig. 6).

Optical transmission T and absolute specular reflection R was measured on samples deposited on glass substrates with a Cary 5E spectrophotometer working in the range of 350-2500 nm and at normal light incidence. The optical constants of the films were determined by the (TR) methods using Newton–Raphson iterative technique[22] and derivative free flexible Nelder–Mead simplex technique.[23]

In addition, for extending the optical characterization and cross-checking the optical parameters, spectroscopic ellipsometric method was applied to the samples deposited on Si substrates. The measurements were carried out on a J.A. Woollam Co., Inc. M2000D rotating compensator spectroscopic ellipsometer with a CCD spectrometer with wavelength range from 193 to 1000 nm. Experimental data for the ellipsometric angles Ψ and Δ were taken at angles of light incidence 55°, 60°, 65°, 70° and 75° and they were modeled using the CompleteEASE Woollam Co., Inc. software.[19]

All optical measurements were performed at room temperature.

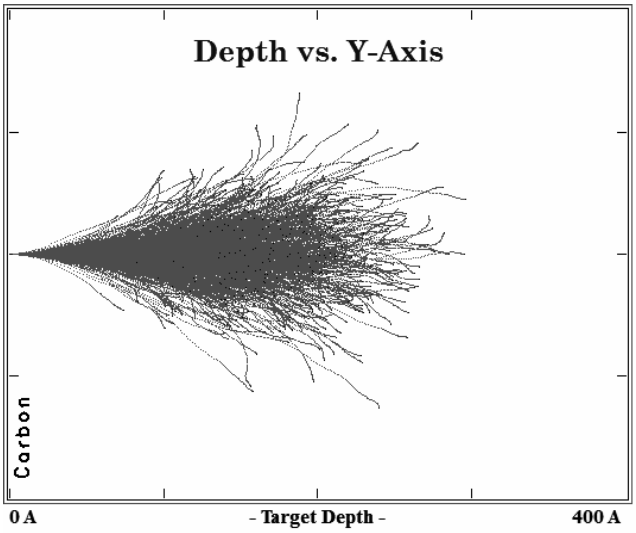

Fig. 6 – SRIM data for $Ga^+$ ions ranges in a 40 nm thick ta-C film. The energy of implanted ions was 20 keV.

## CONCLUSIONS

It has been established that implantation of ta-C thin films with moderate fluences ($3x10^{14}$ $cm^{-2}$ and $3x10^{15}$ $cm^{-2}$) of $Ga^+$ ions causes structural changes in the amorphous carbon matrix which reflects in the increased absorption, enhanced reflection and reduced band gap energy values. The observed changes of these optical parameters are attributed to formation of Ga colloid clusters, generation of defects and modification of the film structures through increasing graphitization with Ga+ ion fluence. The results obtained by the given technological procedures could be used for applications in high-density optical data storage and data archiving.

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