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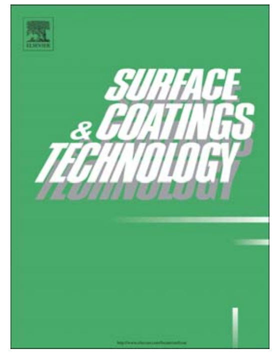

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Focused ion beam optical patterning of ta-C films

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Abstract

Optical contrast formation by Ga^+ ion implantation has been made use of for focused ion beam (FIB) writing of nano-scale optical patterns in tetrahedral amorphous carbon (ta-C). UV-VIS optical spectroscopy results with Ga^+ broad-beam ion implantation have shown a significant shift of the optical absorption edge to lower photon energies as obtained from optical transmission measurements of ta-C samples, implanted with Ga^+ at ion energy E = 20 keV and ion fluences D = $3\times10^{14}\div3\times10^{15}$ cm^{-2}. 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). The obtained optical contrast (between implanted and unimplanted film material) could be made use of in the area of high-density optical data storage using computer controlled focused Ga^+ ion beams. The underlying structural modifications, induced by the Ga^+ ion bombardment, have been investigated by x-ray photo-electron spectroscopy (XPS) and transmission electron microscopy (TEM). Focused ion beam (FIB) implanted patterns in ta-C samples, obtained with a fluence of 5×10^{15} cm^{-2}, are also presented.

Keywords: Tetrahedral amorphous carbon; Focused ion beams; Optical data storage.

Abstract code: (given by the Organizing Committee)

1. Introduction

Carbon-based materials, and in particular tetrahedral amorphous carbon (ta-C), have attracted recently great interest from both scientific and industrial perspectives. 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 bandgap material – silicon carbide (SiC) – for uses in nano-scale optical data storage using focused ion beams techniques, where SiC films have found useful applications in recent years. Near-field techniques (e.g. scanning near-field optical microscopy (SNOM)) are used to access for reading such nano-scale optical data [4-9].

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 [6]. It is expected, that a similar mechanism of the carbon bonds transformations would result when applying ion bombardment with different ions, e.g. 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. Such investigations have been performed and presented here for the first time. 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 in other wide-bandgap materials like a-SiC:H [10].

In the present study, in addition to the optical characterisation performed, the underlying structural modification, induced by the Ga^+ ion bombardment, has been investigated by x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM), while some prototyping has been pursued by FIB patterning of complex optical images.

2. Experiment (or Materials and methods)

Samples of 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 (a schematic diagram presented in Fig.1). With the FCVA technique, the plasma stream is steered through a magnetic filter, so that to eliminate neutral particles generated at the cathode, and directed towards the substrate. At the filter exit, the fully ionized plasma, consisting of carbon ions and electrons, streams towards the substrate, which is kept at room temperature during deposition as controlled by a thermocouple attached to the substrate holder. The films were deposited with an arc current of 120 A under floating conditions. The size of the cathodic arc target area for uniform film deposition was ~2cm×2cm, where the sample substrates were positioned. A Bruker Dimension Icon AFM and a Dektak profilometer were used to estimate the film thickness.

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 μA/cm^2, the ion energy was E=20 keV, and the ion doses used were D=3.10^{14} ÷ D=3.10^{15} cm^{-2}. Water cooling system for the sample holder was used to maintain room temperature during the implantation process. SRIM simmulation programme [11] was used to determine the projected range Rp ~ 17 nm and ΔRp ~ 4 nm for Ga^+ implanted ions into the ta-C film samples (d = 40 nm). The Ga^+ focused ion beam (FIB) patterning was performed with NVision 40 Crossbeam System (Zeiss) using 1, 10, 80 pA Ga^+, 30 keV.

Optical transmission T and absolute specular reflection R was measured with a Cary 5E spectrophotometer at normal light incidence in the range 400÷1200 nm. Optical constants of the films were determined by the (TR) methods using Newton–Raphson iterative technique [12] and derivative free flexible Nelder–Mead simplex technique [13].

The XPS studies were performed on ESALAB MkII system with Al Kα radiation (1486.6 eV) and total instrumental resolution of ~1 eV. The pressure in the chamber was 1 x 10^{-8} Pa. The binding energy (BE) for the C1s line of the adventitious carbon was assumed at 285.0 eV. The C1s spectra of both unimplanted and Ga^+ implanted films were fitted by corresponding to the different carbon bonds components (peaks). Surface concentrations of elements were evaluated from integrated peak areas after Shirley-type background subtraction using theoretical Scofield's photoionization cross-section [14]. The accuracy of the measured BE was around 0.2 eV.

The chemical composition, the state of the elements in the Ga^+ implanted ta-C films surfaces and different structures were studied using transmission electron microscopy (TEM) measurements. The TEM experiment was carried out with High Resolution Scanning Transmission Electron Microscope JEOL JEM 2100, with 200 keV energy.

3. Results and discussion

The optical transmission (T) and reflectivity (R) measurements results for unimplanted and gallium implanted ta-C samples are presented in Fig. 2a and Fig. 2b, respectively. The absorption coefficient of the layers α was determined according to the equation:

$$\alpha = \frac{1}{d}\ln[\frac{(1-R_f(\lambda))^2}{T_f}]$$

where d is the layer thickness, T_f and R_f are the transmittance and reflectance of the layer [15]. T_f and R_f are obtained from the measured transmittance T and reflectance R data, corrected for the contribution of the glass substrate [16]. The obtained results for the dispersion curves of the absorption coefficient α in the measured wavelength range for the ta-C films are shown in Fig. 2c.

It could be clearly observed in Fig.2a that the untreated sample has higher transmittance which drops down with the fluence increase for the Ga^+ implanted samples. This effect can be explained by increased absorption (Fig.2c), resulting from the bandgap decrease due to increasing number of defects and graphitisation, as well as by increased reflection (Fig.2b) from the Ga^+ colloids formed (more information for this is given in the TEM measurements section).

The chemical composition and state of the elements on the ta-C films surfaces with and without Ga^+ ion implantation were studied using X-ray photoelectron spectroscopy (XPS). In the Fig. 3a and Fig. 3b are presented the C1s spectra of as deposited ta-C film and Ga^+ implanted ta-C films, respectively. The C1s spectra of both ta-C films are fitted by four components (peaks). The peaks at 284.6eV and 285.4 eV we associate to the C-C bond in sp2 and sp3 configuration. These observations are consistent with those reported elsewhere [17, 18].The sp2 to sp3 ratio of ta-C films can be determined from the relative intensities of the curve fitted XPS C1s spectra. The other peaks are attributed to C-O, C=O and O-C=O bonds [19].

The sp3/sp2 ration of the ta-C films is calculated to be 1.24.

Implantation of ta-C by Ga^+ ions caused change in the shape of the C1s peak. This shape is typical for increased graphite bonds. The C1s spectrum was fitted with four peaks again and some peaks are also associated with the existence of different oxygen groups on the surface. It is obvious from these results that the Ga^+ ions convert the sp3 to sp2 type carbon. This effect increases with the fluence and the higher Ga^+ fluence caused almost complete transformation of sp3 type carbon to sp2, which is also supported by the results shown in Table 1 (GL% - shows the Gaussian - Lorentzian sum of the peak used in the fit; 0 % for Gaussian and 100% for Lorentzian).

In Fig.4 and Fig.5 are shown the TEM images of ta-C films modified by Ga^+ ion implantation with different fluences. According to D.E.Hole et al. [20] gallium does not form any stable bonds with carbon and it is bonding with itself only, forming gallium colloids with amorphous structure. The most widespread size of the Ga colloids in Fig .4 is in the range from 6 nm to 8 nm, while the sizes vary from 4 nm to 16 nm, as seen in the histogram therein.

In Fig. 5 it could be clearly observed that the colloids are becoming larger with the fluence, which is seen from the histogram where the average size varies from about 15 nm to 65 nm. The boundaries of the particles remain distinct and roundly in shape, which is an evidence for the creation of new Ga phase without nucleus, for that reason they could have amorphous structure and spherical shape. The increased size of the gallium colloids with the dose affect the optical reflectivity of the samples, thus decreasing the transmittance and improving the optical contrast.

In Fig. 6 are shown the produced contrasting images in the optical wavelength range by gallium focused ion beam implantation. It should be noted that these are basic investigations and prototyping, as FIB is a serial technique which is not able to fabricate large memory capacities. These are some first results showing the ability for optical data recording in ta-C films by FIB processing. Noting the potential of the FIB technique, i.e. down to below 10 nm size features of produced patterns, further experiments are planned to fabricate next nano-scale optical images, for the reading of which scanning near-field optical microscopy (SNOM) will be needed.

4. Conclusion

The results described in the present work have shown that choosing relatively low Ga^{+} ion fluences and energies 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, while also accompanied by emerging fraction of gallium colloids formation. The optical transmission change, which is the basic mechanism of forming optical contrast images as reading is performed in transmission mode, is due to both optical transmission and reflectivity change combined. The increase of the absorption coefficient (α) is shown to reach over 50% change in magnitude in the measured wavelenght range, which may be sufficient to fulfill the requirements for optical contrast needed for applications in optical data storage, bearing in mind also the reflectance increase, as the optical data reading is carried out with scanning optical near-field microscopy (SNOM) in transmittance mode. The increased reflectance is due to the increased size of the gallium colloids with the ion dose. The obtained results, given the potential of the FIB technique, could be of use in nano-scale optical data storage using focused ion beams techniques.

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Figure captions

Fig. 1. Schematic diagram of a FCVA system

Fig. 2. Optical transmittance (a), reflectance (b) and absorption coefficient (c) spectra of ta-Ca for a reference sample and implanted samples with Ga^+ ions with fluences D1=3.10^{14}cm^{-2} and D2=3.10^{15}cm^{-2}

Fig. 3: C1s peak for unimplanted samples (a) and Ga^+ implanted samples with a fluence $D_2 = 3.10^{15}$ cm^{-2} (b)

Fig. 4: TEM image of an area of Ga^+ implanted ta-C film with fluence $3x10^{14}$ ions/cm^2 and histogram of the distribution of gallium colloids by size in this area

Fig. 5: TEM image of an area of Ga^+ implanted ta-C film with fluence $3x10^{15}$ ions/cm^2 and histogram of the distribution of gallium colloids by size in this area

Fig. 6: Contrast images and dependence of absorbance of implanted areas on Ga^+ fluences (squares 10 x 10 µm^2): 1e14, 5e14, 1e15, 5e15, 1e16, 5e16 cm^{-2}

Table 1: C1s peak position and area for unimplanted and Ga^+ implanted samples.

Figures

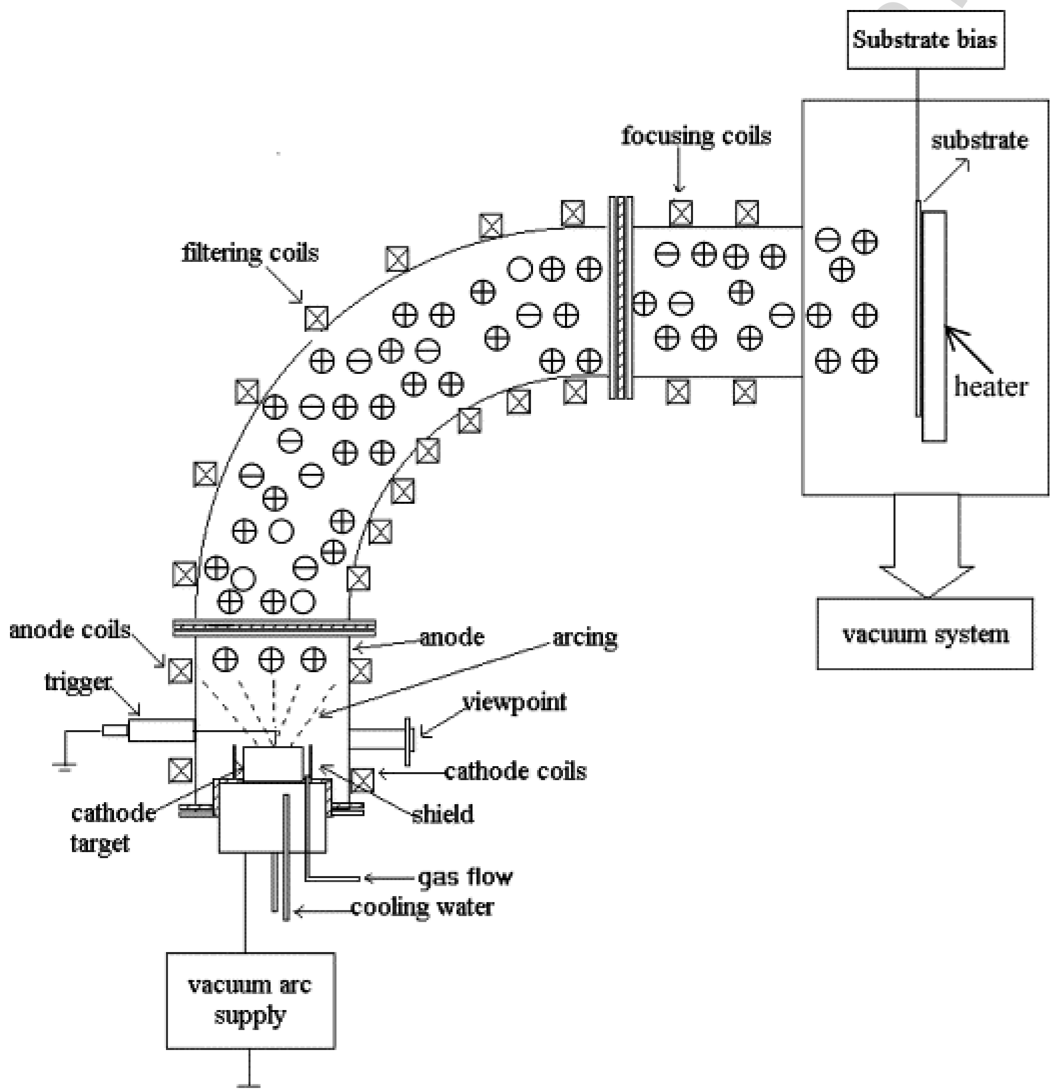

Fig.1

Figures

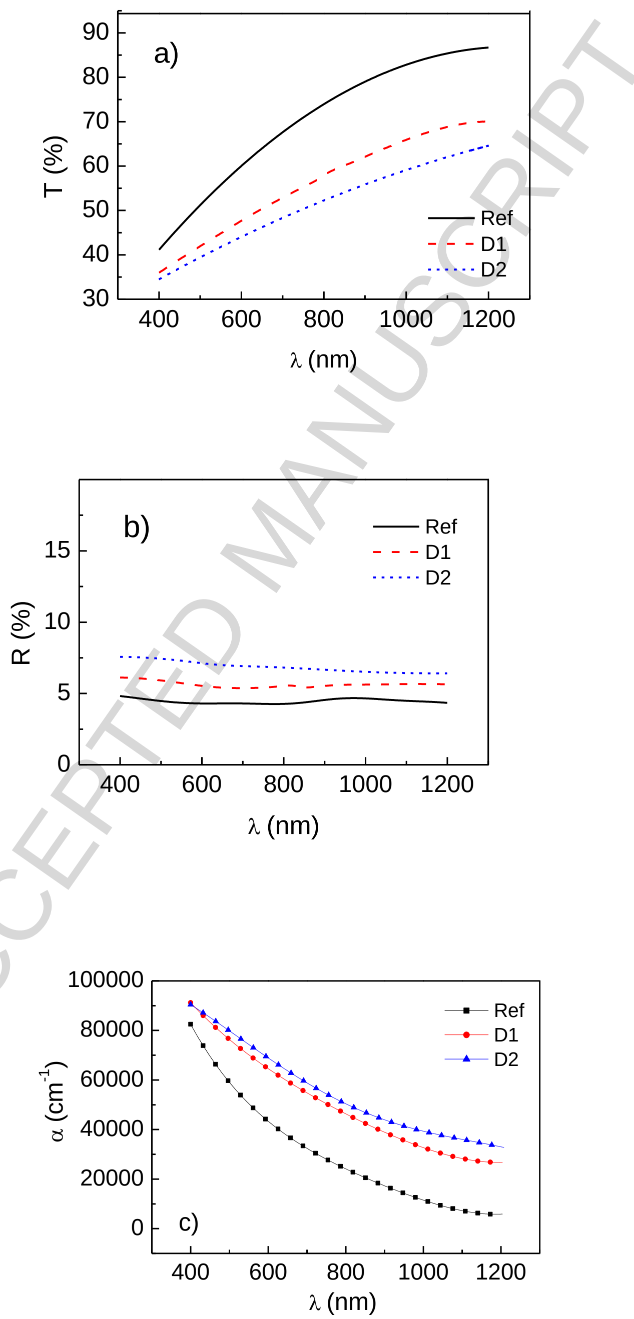

Fig.2

Figures

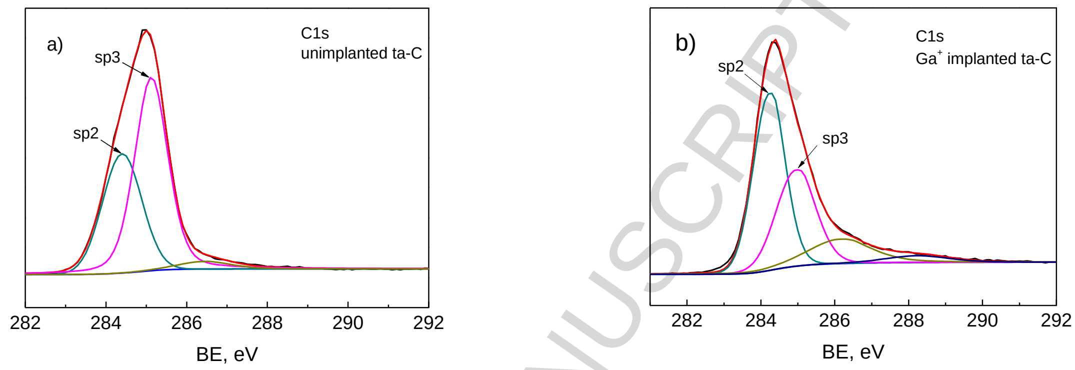

Fig.3

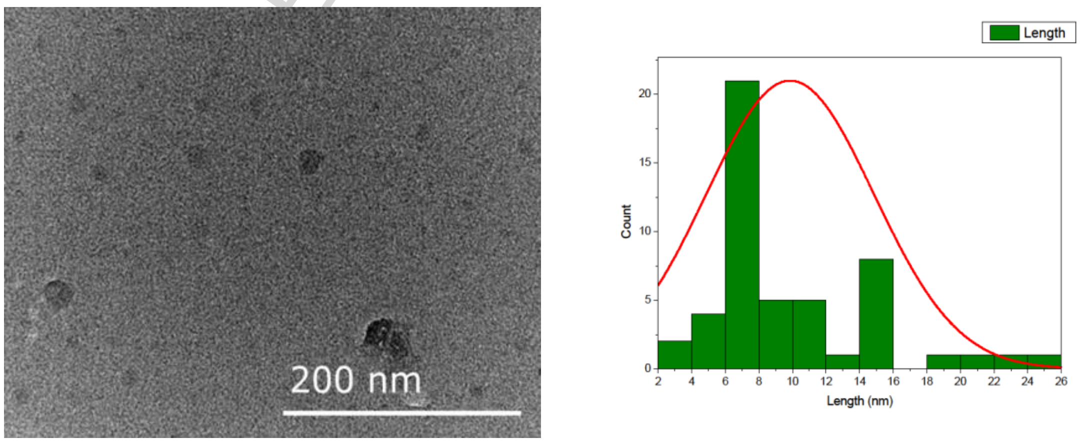

Fig.4

Figures

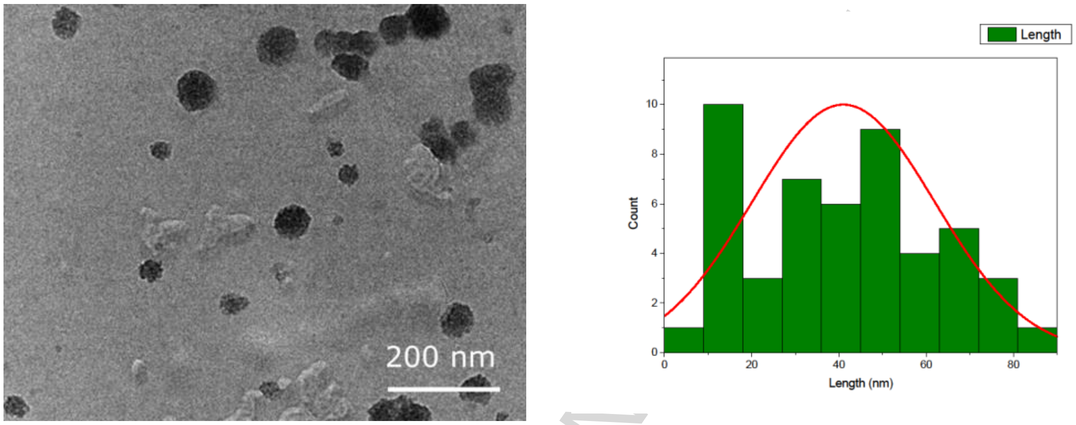

Fig.5

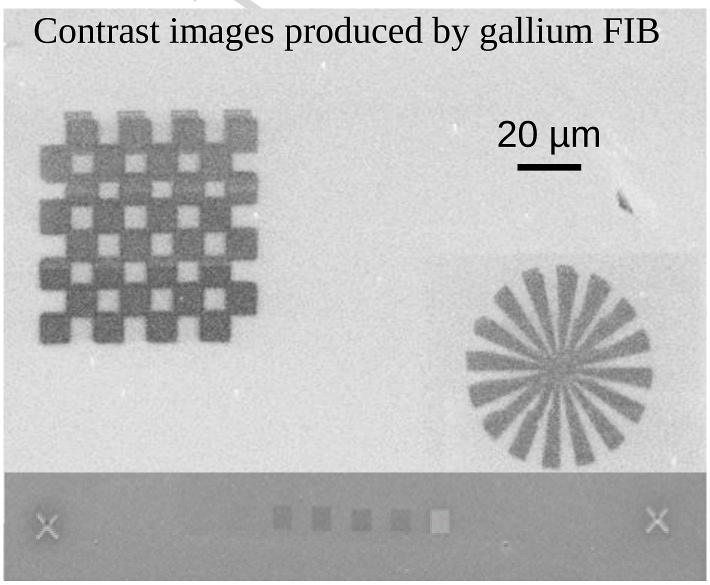

Fig.6

Table

Table 1: 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

Highlights

- Focused ion beam (FIB) application for nano-scale optical information storage
- Ga^+ FIB nano-scale optical patterning of wide bandgap tetrahedral amorphous carbon
- Ga^+ implantation results in optical absorption edge shift to lower photon energies
- XPS and TEM results show increased graphitisation and gallium colloids formation
- The optical data reading is carried out with optical near-field techniques (SNOM)