Thermal effects on the Ga\textsuperscript{+} ion beam induced structural modification of a-SiC:H

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Abstract. The effects of implantation temperature and post-implantation thermal annealing on the Ga\textsuperscript{+} ion beam induced optical contrast formation in hydrogenated silicon–carbon alloy (a-SiC:H) films and underlying structural modifications have been studied. The optical contrast formed (between implanted and unimplanted regions of the film material) has been made use of in the form of optical pattern formation by computer-operated Ga\textsuperscript{+}-focused ion beam. Possible applications of this effect in the area of submicron lithography and high-density optical data storage have been suggested with regard to the most widely spread focused micro-beam systems based on Ga\textsuperscript{+} liquid metal ion sources. The implanted samples were structurally analysed using vibrational spectroscopies, like Raman and infra-red (IR) spectroscopy, to define optimum implantation conditions. The precise role of implantation temperature effects, i.e. the target temperature during Ga\textsuperscript{+} ion irradiation, on the structural modification obtainable has been therefore a key part of this study. Appropriate post-implantation annealing treatments were also studied, since these are expected to offer further benefits in reducing the required ion dose and enhancing the optical contrast, thus increasing the cost-effectiveness of the method.

1. Introduction
The present work is concerned with a new approach to providing ultra-stable (>50 years), ultra-high density (>1Tbit/sq.in.) data storage for archival applications. We used ion-implantation to write nanoscale data into hydrogenated amorphous silicon carbide (a-SiC:H) films [1-7]. The role of implantation conditions on the Ga\textsuperscript{+} ion beam induced optical contrast formation in hydrogenated silicon–carbon alloy (a-SiC:H) films and underlying structural modifications have been studied, aiming to determine optimised conditions. The use of gallium as the ion implanted species is 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 [8,9]. The fact that Ga has a very low melting point (Tm= 29.8°C) and an unusual feature of volume contraction on melting are factors which favour Ga incorporation upon ion-implantation as dispersed clusters, or small nanoparticles. It was previously noted that Ga precipitation into nanoparticles can vary dramatically (in terms of particle size) with Ga concentration and small changes in surface implant temperature [10, 11]. The implanted samples were
structurally analysed using vibrational spectroscopies, like Raman and infra-red (IR) spectroscopy, to define optimum implantation conditions. The precise role of implantation temperature effects, i.e. the target temperature during Ga$^+$ ion irradiation, on the structural modification obtainable has been therefore a key part of this study. Appropriate post-implantation annealing treatments were also studied, since these are expected to offer further benefits in reducing the required ion dose and enhancing the optical contrast, thus increasing the cost-effectiveness of the bit-writing method.

Ga$^+$ broad-beam ion-implantation in a-Si$_{1-x}$C$_x$:H samples was carried out at different substrate temperatures and some of the implanted samples were annealed post-implantation at higher temperatures in vacuum. The expected benefit for the optical data storage method, which relies for readout on reduced optical transmission detected by scanning near-field optical microscopy (SNOM) [12,13], was that a lower implantation temperature would result in an increased amount of defects leading to an absorption increase, and hence further decrease in transmission (greater readout contrast). The expected effect of higher implantation temperatures, or high temperature post-implantation annealing, was that there would be an increase in the optical reflectivity and decrease in transmission due to Ga clusters coalescing into bigger Ga colloids.

2. Experimental

Wide bandgap a-Si$_{1-x}$C$_x$:H (x$_1$=0.18;x$_2$=0.35) thin film samples were deposited onto Corning glass substrates by RF (13.56 MHz) reactive magnetron sputtering. A composite target, composed of monocrystalline (100) silicon wafer with chips of pure graphite placed on it, was sputtered in an Ar-20%H$_2$ gas mixture. The film thickness, defined by Talystep profilometer and optical measurements, was ~200 nm. Rutherford backscattering spectrometry was used to define the carbon content (x) of the films.

Ga$^+$ ion implantation was performed at Helmholtz-Zentrum Dresden-Rossendorf. A range of samples have been processed at different substrate temperatures (typically from liquid nitrogen (LN$_2$) temperatures to around room temperature (RT), and also at a higher temperature $T=+50^\circ$C). Some of the RT implanted samples were further annealed at several different temperatures in vacuum. The Ga$^+$ ion-beam intensity was $I \sim 2$ µA/cm$^2$, the ion energy was $E = 30$ keV, and ion doses in the range $D = 10^{15} - 10^{17}$ ions.cm$^{-2}$ were used ($D_1$=1x10$^{15}$ cm$^{-2}$, $D_2$=5x10$^{15}$ cm$^{-2}$, $D_3$=2.5x10$^{16}$ cm$^{-2}$ and $D_4$=1.25x10$^{17}$ cm$^{-2}$ last dose only at RT). Furthermore, some additional samples were implanted with Ga$^+$ at 3 different temperatures (T$_1$=RT, T$_2$=LN$_2$ and T$_3$=+50$^\circ$C) with a single dose ($D = 2xD_3 = 5x10^{16}$ cm$^{-2}$). The samples implanted at RT were then thermally annealed in Ar atmosphere at 3 different temperatures: +50$^\circ$C, +120$^\circ$C and +250$^\circ$C. All implanted samples were structurally analysed using vibrational spectroscopies, like Raman and infra-red (IR) spectroscopy, to define the optimum implantation conditions. IR transmittance measurements were performed with a Fourier Transform spectrophotometer Bruker (model IFS 113 V) in the region of 550–2200 cm$^{-1}$. Raman spectra are collected in ambient air and at different temperatures (T$_1$=RT and T$_2$=LN$_2$(liquid nitrogen)) with a Renishaw spectrometer. An excitation laser with a wavelength of 532 nm, focused to a spot size of 1.5 micrometers diameter and an x100 objective lens are used. To avoid sample damage or laser induced heating, the incident power is kept at 5 mW.

3. Results and discussion

3.1. Infra-red (IR) spectroscopy results on a-Si$_{1-x}$C$_x$:H/c-Si samples implanted with Ga$^+$ broad-beam implantation at different temperatures

The ion-implanted samples with Ga$^+$ broad-beam implantation at different temperatures (T$_1$=RT, T$_2$=LN$_2$(liquid nitrogen), and T$_3$= +50$^\circ$C), were studied by infra-red (IR) spectroscopy in the range 300 – 4500 cm$^{-1}$. Results are shown in figure 1.
The observed bands for the case of the lower carbon content samples (figure 1a) are as follows:

- C-C, 460 cm\(^{-1}\), at all samples
- Si-C, 780 cm\(^{-1}\), stretching mode, pronounced at X1Ref, the band smears under implantation at all temperatures
- Si-O, stretching mode, at 1043 cm\(^{-1}\) at all samples
- C-C, at about 1358-1569 cm\(^{-1}\), at sp\(^3\) C-configuration at 1374 cm\(^{-1}\) (X1Ref) and 1358 cm\(^{-1}\) at T2 and T1, at T3 disappears; sp\(^2\) C-configuration at 1550 cm\(^{-1}\) (T1), 1569 cm\(^{-1}\) (T2 and T3), but at X1Ref it is absent
- C-H and C-H\(_2\), at about 1739 cm\(^{-1}\) at sample X1Ref, under implantation this band smears.

This analysis clearly shows that at all temperatures of ion implantation considerable additional disorder is introduced, as Si-C bond (780 cm\(^{-1}\)) is largely broken, while all C-H bonds (C-H, C-H\(_2\) and C-H\(_n\)) are also broken accompanied by the loss of the hydrogen from the films as a result of the ion beam bombardment. The results for the films with the higher carbon content (X2) also show the same trend (figure 1b).

The obtained IR spectra were also studied for evidence of possible Si-Ga bond vibrations. Due to the considerable noise in the registered spectra in the range 350 - 400 cm\(^{-1}\), where the main Si-Ga vibration modes appear, there is available reliable data only for the RT implanted samples with two different Ga\(^+\) ion doses: D1=5x10\(^{16}\) cm\(^{-2}\) and D2=2.5x10\(^{16}\) cm\(^{-2}\) (figure 2).

The following bands for present Si-Ga bonds were observed:

- at 358 cm\(^{-1}\) – present for both samples implanted with D1 and D2 (X1T1D1 and X1T1D2)
- at 375 cm\(^{-1}\) – present for both samples implanted with D1 and D2 (X1T1D1 and X1T1D2)
- at 398 cm\(^{-1}\) – present only in the case of D1 (X1T1D1); for D2 (X1T1D2) this band smears.

Only in these spectra the bands corresponding to vibrations of Si-Ga bonds can be initialized; in the other spectra due to the high level of noise signals such bands smear.
3.2. Infra-red(IR) spectroscopy results on a-SiC:H/c-Si samples implanted with RT Ga⁺ broad-beam implantation and after treatments with post-implantation thermal annealing

The observed bands for the case of the lower carbon content samples (figure 3 a) are as follows:
- C-C, 456 cm⁻¹ at all samples without shift after annealing;
- Si-C, stretching mode, 786 cm⁻¹ at all samples after annealing at 802 cm⁻¹ (X1T1D2AsImpl), 802 cm⁻¹ (X1T1D1AsImpl) and 820 cm⁻¹ (X1T1D1Ann250°C);
- Si-O, 1053 cm⁻¹, stretching mode, without shift after annealing;
- C-C, 1373 cm⁻¹ sp³ and 1538 cm⁻¹ sp² C-configuration (X1T1D2AsImpl); after annealing the bands smear (X1T1D2Ann250°C); 1363 cm⁻¹ at sp³ and 1520 cm⁻¹ sp² C-configuration (X1T1D1AsImpl); after annealing the bands smear (X1T1D1Ann250°C);
- C-H and C-H₂ stretching mode, broad band at ~1750 cm⁻¹ (X1T1D2AsImpl), it shifts with low intensity at ~1658 cm⁻¹ after annealing (X1T1D2Ann250°C); less pronounced at 1628 cm⁻¹ (X1T1D1AsImpl) and 1658 cm⁻¹ (X1T1D1Ann250°C);
- C-Hn, 2875 cm⁻¹ sp² and 2924 cm⁻¹ sp³ C-configuration (X1T1D2AsImpl), after annealing with low intensity of the band at 2860 cm⁻¹ sp² and 2920 cm⁻¹ sp³ C-configuration (X1T1D2Ann250°C); 2845 cm⁻¹ sp² and 2920 cm⁻¹ sp³ C-configuration (X1T1D1AsImpl), after annealing at 2870 cm⁻¹ at sp² and 2920 cm⁻¹ at sp³ C-configuration (X1T1D1Ann250°C).

This analysis shows that the C-C bond at 456 cm⁻¹ and Si-O bonds at 1053 cm⁻¹ do not show changes after annealing at +250°C; however, the C-C bonds for both sp³ and sp² C-configuration (i.e. the diamond-like and graphitic carbon bonds) are modified due to the influence of the presence of Ga nano-clusters, i.e. Ga colloid formation and growth.

Similarly modified are also the main bonds present in the a-SiC:H films – the Si-C and C-H bonds - due to the change in the back-bone configuration of the a-SiC:H host lattice.

The results for higher carbon content films (figure 3 b) also show the same trends as above.

3.3. Raman spectroscopy results on a-SiC:H/c-Si samples implanted with Ga⁺ broad-beam implantation at different implantation temperatures

Wide bandgap a-Si₁₋ₓCₓ:H (x₁=0.18; x₂=0.35) thin film (d=200nm) samples deposited on c-Si substrates, as prepared by rf magnetron sputtering and ion-implanted with Ga⁺ broad-beam implantation at different temperatures (T1 and T2), were studied by Raman spectroscopy in the range 100 – 3500 cm⁻¹. The Ga⁺ ion doses were in the range D = 10¹⁵ – 10¹⁷ ions.cm⁻² (D1=1x10¹⁵ cm⁻², D2=5x10¹⁵ cm⁻², D3=2.5x10¹⁶ cm⁻² and D4=1.25x10¹⁷ cm⁻² (last dose only at RT). The Raman spectra were measured at different points on the sample (m₁, m₂, etc.).

The as-deposited samples show greater sp² - type carbon (graphitic type carbon-configuration) in the a-Si₁₋ₓCₓ:H films with the higher carbon content (x₂=0.35) as demonstrated in figure 4, where a clear band at ~1500 cm⁻¹ appears for the case of X₂ (x₂=0.35) (figure 4 b), which could be assigned to graphitic carbon, and which is not present in the case of X₁ (x₁=0.18) (figure 4 a).
Figure 4. Raman spectra of as-deposited a-Si_{1-x}C_{x}:H (X1=0.18 (a), X2=0.35 (b)) films.

In the case of the lower carbon content (x1=0.18) (figure 5 a), the RT Ga⁺ ion implantation results in graphitization of the sp³ type carbon and the appearance of a graphitic (sp²) type carbon related band at 1500 cm⁻¹ even at relatively lower ion doses (D3) (figure 5 b), but is especially expressed for the highest dose (figure 5 c). However, at lower implantation temperatures (T2), this graphitic (sp²) type carbon related band at 1500 cm⁻¹ is smeared as a result of the ion bombardment (figure 5 d).

In the case of the higher carbon content (x2=0.35) (figure 6 a), the RT Ga⁺ ion implantation results in increased graphitization and better expressed graphitic (sp²) type carbon related band at ~1500 cm⁻¹ even at relatively lower ion doses (D3) (figure 6 b), but it is especially expressed for the highest dose D4 (figure 6 c). However, at lower implantation temperatures (T2), this graphitic (sp²) type carbon related band at 1500 cm⁻¹ is smeared as a result of the ion bombardment, due to the increased defects introduction and further breaking of the graphitic carbon bonds (figure 6 d).

4. Conclusion
Ga⁺ broad-beam ion implantation in a-SiC:H samples was carried out at different substrate temperatures (T1=RT, T2=LN2(liquid nitrogen), and T3=+50°C) and some of the RT implanted samples were further annealed at higher temperatures in vacuum. The expected benefit for the optical data storage method, which relies on reduced optical transmission detected by SNOM, was that lower implantation temperature would result in an increased amount of defects leading to further absorption increase, and hence further decrease in transmission. This effect was indeed observed but was overridden by an effect of increased ion beam induced sputtering yield, which greatly reduced the film thickness and hence increased the transmission. Likewise, the expected increase in the optical reflectivity (due to Ga clusters coalescing into bigger Ga colloids which
have higher reflectivity and hence should decrease the transmission) as a result of higher implantation temperature or high temperature post-implantation annealing was indeed observed but was overridden by an ion beam induced decrease of defect concentration (due to self annealing) that leads to an absorption decrease and hence further transmission increase. Therefore, it could be concluded that the best conditions for optical data storage for archival storage applications would be using Ga⁺ ion implantation in a-SiC:H films with an optimal dose of D=5x10¹⁶ cm⁻² at RT. The fact that the optimum implantation temperature for storage applications has been found to be that of room temperature is fortuitous since it means that the required ion-implantation process is simplified and reduced in cost.

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References
[1] Powell J A and Matus L 1989 *Amorphous and Crystalline Silicon Carbide*, ed G L Harris and C Y W Yang (Berlin: Springer)
[2] Ziegler J F 1988 *Ion Implantation* (New York: Academic Press)
[3] Ruttensperger B, Kröz G, Müller G, Derst G and Kalbitzer S 1991 *J Non-Cryst Solids* 137-138 635
[4] Tsvetkova T 1996 *Beam Processing of Advanced Materials*, ed J Singh, S Copley and J Mazumder (Metals Park: ASM International) p 207
[5] Tsvetkova T, Takahashi S, Zayats A, Dawson P, Turner R, Bischoff L, Angelov O and Dimova-Malinovska D 2005 *Vacuum* 79 94
[6] Tsvetkova T, Takahashi S, Zayats A, Dawson P, Turner R, Bischoff L, Angelov O and Dimova-Malinovska D 2005 *Vacuum* 79 100
[7] Takahashi S, Dawson P, Zayats A, Bischoff L, Angelov O, Dimova-Malinovska D, Tsvetkova T and Townsend P D 2007 *J Phys D: Appl Phys* 40 7492
[8] Bischoff L, Teichert J, Kitova S and Tsvetkova T 2003 *Vacuum* 69 73
[9] Tsvetkova T, Angelov O, Sendova-Vassileva M, Dimova-Malinovska D, Bischoff L, Adriaenssens G J, Grudzinski W and Zuk J 2003 *Vacuum* 70 467
[10] Townsend P D, Chandler P J and Zhang L 1994 rev. 2006 *Optical effects of ion implantation* (Cambridge: Cambridge University Press)
[11] Hole D E, Townsend P D, Barton J D, Nistor L C and Van Landuyt J 1995 *J. Non-Cryst. Sol.* 180 266
[12] Richards D and Zayats A V 2004 *Nano-Optics and Near-Field Microscopy* *Phil. Trans. R. Soc. London* 362 699
[13] Takahashi S, Dickson W, Pollard R and Zayats A V 2004 *Ultramicroscopy* 100 443
[14] Tsvetkova T, Wright C D, Hosseini P, Bischoff L and Zuk J 2012 *Acta Physica Polonica* in press