X-ray photoelectron study of high-energy He\textsuperscript{+} implanted a-SiC:H thin films

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Abstract. The implantation with high-energy He\textsuperscript{+} ion beam results in modification of the optical band-gap and absorption coefficient of a-Si\textsubscript{1-x}C\textsubscript{x}:H films. X-ray photoelectron spectroscopy was used to characterize a-Si\textsubscript{1-x}C\textsubscript{x}:H thin films deposited by r.f. magnetron sputtering and implanted with high-energy He\textsuperscript{+} ions. The non-implanted films show the expected variety of chemical bonds: silicon-silicon and silicon-carbon bonds, carbon being three- and fourfold coordinated. The X-ray and Raman spectra show that high-energy He\textsuperscript{+} ion implantation leads to the introduction of additional disorder in the films. The X-ray photoelectron spectra of the implanted films show that, in addition to the already mentioned changes, the high-energy He\textsuperscript{+} ion bombardment results in an increase of the threefold coordinated as compared to the fourfold coordinated carbon bonds, i.e. increased graphitization of the carbon content in the films. These structural modifications, due to the high-energy He\textsuperscript{+} ion implantation, are the reasons for the observed changes in the optical properties of the films.

1. Introduction

Hydrogenated amorphous silicon-carbide (a-Si\textsubscript{1-x}C\textsubscript{x}:H) alloy films have been studied for many years as structural materials for high-temperature electronics and for various optoelectronic elements and devices operating in aggressive environment (acid vapors, radiation, open space, etc.) [1,2]. It is particularly attractive for various optoelectronic applications due to its comparatively wide band gap which may be tailored in the range 1.8-3.0 eV [2].

The studied material can be prepared in thin film form on various substrates by chemical vapour deposition [3], or by radio-frequency (RF) reactive magnetron sputtering method [4]. The mechanical, optical and electrical properties of the material can be varied controllably by changing the relative composition ratio of the constituent elements (x).

In addition, control of the material properties can also be achieved using ion implantation [5,6]. Recently, using the emerging technology of ion micro-beam implantation [7], promising results have been obtained for possible applications of these materials in high-density optical data storage [8,9].
This approach has been further developed by implementing ion doping with focused ion beam (FIB) systems that use Ga⁺ or other chemically active species as implants [10-13]. Another approach was also used applying focused high-energy (MeV range) ion implantation with H⁺ and He⁺ ion beams for the formation of optical contrast of suitable size to be used for optical data storage in a-Si₁₋ₓCₓH films [14]. In order to study the underlying high-energy ion beam induced structural modification of the implanted material, additionally some broad-beam high-energy H⁺ and He⁺ ion implantation has been performed. The implanted films have been studied using optical transmission, reflection and photo-deflection spectroscopy (PDS) in the ultraviolet (UV) and visible range of the spectrum [15,16].

In the present paper X-ray photoelectron spectroscopy (XPS) was used to characterize a-Si₁₋ₓCₓH thin films deposited by r.f. magnetron sputtering and implanted with high-energy He⁺ ions. Additionally, some optical transmission measurements in the infra-red (IR) and Raman spectroscopy have been used to characterize the ion beam induced structural modification of the implanted material.

2. Experimental

Thin (d ~ 1 μm) a-Si₁₋ₓCₓ:H films (x=0.18) were deposited onto polished silicon substrates by RF (13.56 Hz) reactive magnetron sputtering. A composite target, composed of mono-crystalline (100) silicon wafer with chips of pure graphite placed on it, was sputtered in an Ar-20%H₂ gas mixture. Typical deposition conditions are RF power 150 W (power density 1.91 W/cm²), total gas pressure 1P, substrate temperature 275 °C, and graphite-to-silicon target ratio 0.025. The film thickness was determined by Talystep to be 1 μm. Rutherford backscattering spectrometry was used to determine the carbon content, x, of the films.

High energy ion implantation of He⁺ was performed at energies 0.2, 0.5 and 1.0 MeV at room temperature and ion beam intensity 2-5 μA.cm⁻². Various ion doses were implanted in the range 1x10¹⁶ – 1x10¹⁷ cm⁻². Water cooling system for the sample holder was used to maintain room temperature during the implantation process.

The XPS studies were carried out on an ESCALAB MK II (VG Scientific) electron spectrometer with base pressure in the preparation and analysis chambers of 2×10⁻⁸ Pa and 1×10⁻⁸ Pa, respectively. The photoelectrons were excited using X-ray source Mg Kα (hv=1256.6 eV). The surface sensitivity was estimated as ~ 10 monolayers. A strip of gold, deposited on the surface of the sample, was used as a binding energy (BE) reference. The BE of Au 4f7/2 was assumed to be 83.8 eV. This allowed a determination of the binding energies of the C 1s, O 1s, Si 2p and Si 2s peaks with an accuracy of ±0.1 eV. The depth profiling was carried out by sputter etching at 90° using a defocused Ar⁺ ion beam of 3 keV energy and a current density of 16 μA.cm⁻².

The Raman spectra were taken at room temperature using a SPEX 1403 double beam spectrometer. The instrument was equipped with a photomultiplier, working in a photon counting mode and a spectral resolution of 4 cm⁻¹. The 488nm excitation line of an Ar⁺ laser was used for the measurements.

3. Results and discussion

Figure 1a shows the XPS Si2p spectra of unimplanted a-Si₁₋ₓCₓ:H thin film. Si2p peak recorded from the surface is centred at 101.7 eV. After 30 min sputtering it is positioned at 100.7 eV and in depth of the sample after 60 min and 120 min the peak shifts back to 101.0 eV and 101.5 eV. Cubic silicon carbide crystal SiC characterised by the fourfold coordinated carbon bonds [17] shows similar values of binding energy (100.3 eV). Some small amount of bonds of the type Si-O̶, met in non-stoichiometric silicon oxide [18], are characterized by Si2p position at 103.2 eV which is confirmed by O1s peak (not shown) at 533.8 eV [19]. There is some contribution of Si-Si bonds characteristic of elemental silicon Si 2p 3/2 - 99.85 eV [20]. C1s peaks of the same sample are shown on Figure 1b. After sputtering in depth of the layer C1s peak is positioned at 283.4 eV characteristic of n-type beta-SiC [21] in which carbon is fourfold coordinated. In Figure 1c VB spectra of unimplanted a-Si₁₋ₓCₓ:H thin film are shown. In depth of the sample there is a broad peak at around 10 eV which is probably due to dangling bonds in SiC. The non-implanted films show the expected variety of chemical bonds: silicon-silicon and silicon-carbon bonds, carbon being three- and fourfold coordinated.
Figure 1. X-ray photoelectron spectra of (a) Si2p and (b) C1s electrons, and (c) Valence band (VB) of an unimplanted a-Si_{1-x}C_{x}:H sample.

Figure 2a shows Si2p spectra of a-Si_{1-x}C_{x}:H thin film implanted with 200 keV He⁺ ions. The Si2p peak is broadened and shifted to higher energies compared to the peak recorded from the unimplanted a-Si_{1-x}C_{x}:H thin film. Figure 2b shows C1s peaks of the same sample. The peak is broadened and shifted to higher energies compared to the peak recorded from unimplanted sample. Figure 2c shows the VB spectra. A broad peak at around 7 eV is probably due to dangling bonds.

Figure 2. X-ray photoelectron spectra of (a) Si2p and (b) C1s electrons, and (c) Valence band (VB) of He⁺ unimplanted a-Si_{1-x}C_{x}:H sample at ion beam energy of E = 200 keV and a dose D = 1×10^{17} cm⁻².

Figure 3a shows Si2p spectra of a-Si_{1-x}C_{x}:H thin film implanted with 500 keV He⁺ ions. Figure 3b shows C1s peaks of the same sample. The peak is broadened and shifted to higher energies around 284.0 eV due to threefold coordinated Si-C bonds characteristic of highly oriented pyrolytic graphite [22]. Figure 3c shows the VB spectra. A broad peak at around 7 eV probably due to dangling bonds appears only in depth of the sample.
Figure 3. X-ray photoelectron spectra of (a) Si2p and (b) C1s electrons, and (c) Valence band (VB) of He⁺ unimplanted a-Si₁₋ₓCₓ:H sample at ion beam energy of E = 500 keV and a dose D = 1×10¹⁷ cm⁻².

Figure 4a shows Si2p spectra of a-Si₁₋ₓCₓ:H thin film implanted with 1 MeV He⁺ ions. Figure 4b shows C1s peaks of the same sample. On the surface there is a peak centered at 284.9 eV which is similar to the peak position characteristic of highly oriented pyrolytic graphite [22] and in depth at 283.3 eV characteristic of n-type beta-SiC [21] in which carbon is fourfold coordinated. Figure 4c shows the VB spectra. A broad peak at around 7 eV probably due to dangling bonds is clearly visible from the surface of the sample.

Figure 4. X-ray photoelectron spectra of (a) Si2p and (b) C1s electrons, and (c) Valence band (VB) of He⁺ unimplanted a-Si₁₋ₓCₓ:H sample at ion beam energy of E = 1 MeV and a dose D = 1×10¹⁷ cm⁻².

The XPS spectra show that high energy He⁺ ion implantation leads to introduction of additional disorder in the films. The XPS spectra of the implanted films show that in addition to the already mentioned changes the high-energy He⁺ ion bombardment results in an increase of the threefold coordinated as compared to the fourfold coordinated carbon bonds, i.e. increased graphitization of the carbon content of the films. The structural modifications due to the high-energy He⁺ ion implantation, as revealed by the XPS measurement, essentially confirm the optical modification effects [15].
As can be seen from the Full Width at Half Maximum (FWHM) of Si and C peaks, the damage level for both sublattices C and Si differs after implantation with 200 keV. According to the shape of peaks, the sublattice of C shows a maximum damage level located at a depth of 120 nm sputtering beneath the surface. The damage in the sample implanted with 500 keV is still visible in both sublattices. However, the C1s peak is flatter and has a larger width, as compared to the case for 200 keV implantation, which makes the evaluation of the aligned spectrum rather difficult. After implantation with 1 MeV, the peaks of Si2p and C1s are narrow and positioned at energies characteristic of SiC. This could possibly be explained by some kind of annealing during implantation.

The results of the Raman measurements (Figures 5 and 6) could also be considered as justification of the above reasoning. As it is seen, the Full Width at Half Maximum (FWHM) of the Si-Si TO-like peak at about 470 cm\(^{-1}\) increases with the dose and energy (figure 5 a and figure 6 a), which is better expressed at the lowest dose and energy. With the further dose and energy increase this change is more subtle. The changes in FWHM imply that there is an effect of increased disorder with the dose in the Raman spectra for one and the same energy – an additional amorphisation of the films takes place during the implantation. In the higher energy region of the Raman spectra (figure 5 b and figure 6 b), the wide band corresponding to the C-C bonds is present. For the unimplanted material, the sp\(^3\) (diamond-like) carbon bonding is predominant. After the ion implantation its partial transformation into sp\(^2\) (graphitic) bonding is observed, particularly well expressed for the highest implantation energy and dose (figure 6 b).

![Figure 5. Raman spectra of unimplanted and He\(^+\) implanted a-Si\(_{0.82}\)C\(_{0.18}\):H films at ion beam energy E = 0.5 MeV and different doses in the range 1x10\(^{16}\) – 1x10\(^{17}\) cm\(^{-2}\), in the regions 350÷1250 cm\(^{-1}\) (a) and 1250÷1750 cm\(^{-1}\) (b).](image1)

![Figure 6. Raman spectra of unimplanted and He\(^+\) implanted a-Si\(_{0.82}\)C\(_{0.18}\):H films with ion dose D = 1x10\(^{17}\) cm\(^{-2}\) and different energies in the range 0.2 – 1.0 MeV, in the regions 350÷1250 cm\(^{-1}\) (a) and 1250÷1750 cm\(^{-1}\) (b).](image2)
4. Conclusion

The XPS and Raman spectra show that high energy He\(^+\) ion implantation leads to introduction of additional disorder in the films. The XPS spectra of the implanted films show that in addition to the already mentioned changes the high-energy He\(^+\) ion bombardment results in an increase of the threefold coordinated as compared to the fourfold coordinated carbon bonds, i.e. increased graphitization of the carbon content of the films. Additionally, also Si dangling bonds are revealed by the valence band study. The structural modifications due to the high-energy He\(^+\) ion implantation are the reasons for the observed changes in the optical properties of the films, which could potentially be of interest in relation to the recently developed high-energy ion micro-beam technologies.

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References

[1] Kanicki J 1991 *Amorphous and Micro-crystalline Semiconductor Devices* (Boston: Artech House)
[2] Powell J A, Matus L 1989 *Amorphous and Crystalline Silicon Carbide*, ed G L Harris and C Y W Yang, (Berlin: Springer)
[3] Heinrich J, Hemeltjen S and Marx G 2000 *Microchim. Acta* 133 209
[4] Bullot J and Schmidt M P 1987 *phys. stat. sol. (b)* 143 345
[5] Hirvonen J K 1984 *Ion Implantation and Ion Beam Processing of Materials* (Amsterdam: North Holland)
[6] Ziegler J F 1988 *Ion Implantation* (New York: Academic Press)
[7] Bohringer K, Jonsten K and Kalbitzer S 1988 *Nucl. Instrum. & Meth. B* 30 289
[8] Ruttensberger B, Krotz G, Muller G, Derst G and Kalbitzer S 1991 *J. Non-Cryst. Solids* 137-138 635
[9] Muller G 1993 *Nucl. Instrum. & Methods B* 80-81 957
[10] Tsvetkova T 1996 *Beam Processing of Advanced Materials*, ed J Singh, S Copley and J Mazumder (New York: Metals Park, ASM International) p 207
[11] Tsvetkova T, Tzenov N, Tzolov M, Dimova-Malinovska D, Adriaenssens G J and Pattyn H 2001 *Vacuum* 63 749
[12] Bischoff L, Teichert J, Kitova S and Tsvetkova T 2003 *Vacuum* 69 73
[13] Tsvetkova T, Angelov O, Sendova-Vassileva M, Dimova-Malinovska D, Bischoff L, Adriaenssens G J, Grudzinski W and Zuk J 2003 *Vacuum* 70 467
[14] Tsvetkova T, Takahashi S, Sellin P, Gomez-Morilla I, Angelov O, Dimova-Malinovska D and Zuk J 2010 *Acta Physica Polonica* in press
[15] Tsvetkova T, Sellin P, Carius R, Angelov O and Dimova-Malinovska D 2007 *Journal of Optoelectronics and Advanced Materials* 9 375
[16] Tsvetkova T, Sellin P, Carius R, Angelov O, Dimova-Malinovska D and Juk J 2009 *Nucl. Instrum. & Meth. B* 267 1583
[17] Tabata A, Fujii S, Suzuuki Y, Mizutani T and Ieda M 1990 *J. Phys. D* 23 316
[18] Aarnik W A M, Weishaupt A and van Silfout A 1990 *Appl. Surf. Sci.* 45 37
[19] Montero I, Galan L, de la Cal E, Albella J M and Pivin J C 1990 *Thin Solid Films* 193 325
[20] Magnusson K O, Wiklund S, Dudde R and Reihl B 1991 *Phys. Rev. B* 44 5657
[21] Mizokawa Y, Geib K M and Wilmsen C W 1986 *J. Vac. Sci. Technol. A* 4 1696
[22] Palchan I, Crespin M, Estrade-Szwarckopf H and Rousseau B 1989 *Chem.Phys.Lett.* 157 321