

Influence of Hot Implantation on Residual Radiation Damage in Silicon Carbide

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Remarkable thermomechanical and electrical properties of silicon carbide (SiC) make this material very attractive for high-temperature, high-power, and high-frequency applications. Because of very low values of diffusion coefficient of most impurities in SiC, ion implantation is the best method to selectively introduce dopants over well-defined depths in SiC. Aluminium is commonly used for creating *p*-type regions in SiC. However, post-implantation radiation damage, which strongly deteriorates required electric properties of the implanted layers, is difficult to anneal even at high temperatures because of remaining residual damage. Therefore implantation at elevated target temperatures (hot implantation) is nowadays an accepted method to decrease the level of the residual radiation damage by avoiding ion beam-induced amorphization. The main objective of this study is to compare the results of the Rutherford backscattering spectroscopy with channeling and micro-Raman spectroscopy investigations of room temperature and 500 °C Al⁺ ion implantation-induced damage in 6H-SiC and its removal by high temperature (up to 1600 °C) thermal annealing.

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1. Introduction

Silicon carbide, because of its excellent thermo-mechanical and electrical properties has attracted a great attention of many researchers [1–3]. SiC is a very promising material for high-temperature, high-frequency and high-power electronic devices. However, manufacturers of such devices encounter many technical problems which originate in specific physical properties of SiC [4, 5]. Those properties are, among others, the following: very low dopant diffusion coefficients, high susceptibility to amorphization during ion-irradiation and relatively high sublimation temperature.

High fluence Al⁺ ion implantation is the most promising procedure to fabricate low resistivity *p*-type regions in SiC [3, 6]. However, radiation damage consisting of vacancies, interstitials and extended defects is the undesired effect of ion implantation, which at high ion fluences can even lead to amorphization of subsurface SiC layers of a few hundred nanometers thickness. This work is focused on crystalline quality improvement of the Al⁺ ion implanted 6H-SiC by performing ion implantation into targets at elevated temperatures (hot implantation) to hinder amorphization process. As a result, after post-

-implantation annealing at 1500–1600 °C the quality of the hot-implanted layers is expected to be higher than following implantations at room temperature (RT), and in some cases the lattice recovery is almost complete.

One of the well-established methods of radiation damage investigation in semiconductors is the Rutherford backscattering spectrometry with channeling (RBS/C). Although very useful, the technique is destructive, time-consuming and needs expensive equipment to accelerate protons or alpha particles in the MeV energy range. The Raman scattering is a fast, relatively cheap and non-destructive method for the investigation of phonons in solids. More specifically, the technique can be used for investigation of residual damage in ion-implanted materials. The present work is aimed at comparison of the information obtained from RBS/C and micro-Raman investigations of Al⁺ ion-implanted and annealed SiC.

2. Experiment

Single crystals of silicon carbide (6H polytype) were grown in the Institute of Electronics Materials Technology (ITME) in Warsaw. Polished 6H-SiC platelets were implanted with the UNIMAS 79 ion implanter (Maria Curie-Skłodowska University) using Al⁺ ion beam at the angle 10° from [0001] 6H-SiC to avoid channeling. We used an arc discharge ion source of our construction to produce Al⁺ ions [7–9]. The ion beam current

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density at the target was kept below $1.0 \mu\text{A}/\text{cm}^2$. Implantation process was simulated with the SRIM 2008 computer code [10]. To obtain a quasi-rectangular shape of Al concentration depth profiles, sequential implantations were performed starting from the highest ion energy (220 keV) to the lowest (90 keV). For hot implantation at target temperature of 500°C a specially designed hot stage with a Boraelectric (Tectra) HTR 1002 heater was used. Total ion fluence was $9 \times 10^{14} \text{ cm}^{-2}$ (Table I). After the implantation process 6H-SiC samples were annealed at 1300, 1500 or 1600°C for 10 min in Ar atmosphere at a pressure of 100 Pa.

TABLE I
Sequential implantation parameters.

Ion energy [keV]	Fluence [ion/cm^2]
220	5.15×10^{14}
165	1.02×10^{14}
130	1.64×10^{14}
90	1.16×10^{14}

The analysis of implanted 6H-SiC layers was performed by the RBS/C at the Rossendorf Institute [11]. We used a 1.7 MeV He^+ ion beam of 1 mm diameter. Energy spectra of ions backscattered from the [0001] oriented 6H-SiC samples were measured at an angle of 170° at RT.

The Raman scattering investigations of implanted samples were performed at RT with a Renishaw inVia micro-Raman spectrometer in backscattering geometry. The excitation light was provided by the 514.5 nm wavelength argon ion laser beam of a $1 \mu\text{m}$ focus diameter. All the spectra were taken at the incident beam power of 10 mW and using the same slits width of the Raman microscope. Both the excitation and collection of the scattered light were performed using a confocal system with a $100\times$ Raman microscope objective. Time of data acquisition of each spectrum was 10 s with 6 accumulations.

3. Results and discussion

3.1. RBS/C investigations

The results of the RBS/C measurements are displayed in Figs. 1–3. 6H-SiC samples were subjected to Al^+ ion implantation at RT, followed by high temperature annealing at 1300, 1500 or 1600°C . Substantial dechanneling of the analyzing ions without any damage peaks is observed in the RBS/C spectra when compared to aligned spectrum taken on unimplanted (virgin) 6H-SiC (Fig. 1). After annealing at 1300°C the level of residual radiation damage in samples implanted at RT is much higher than in hot-implanted (500°C) 6H-SiC. The annealing at 1500°C of the hot-implanted samples results in a remarkable reconstruction of crystalline order, whereas 6H-SiC implanted at RT does not show such properties

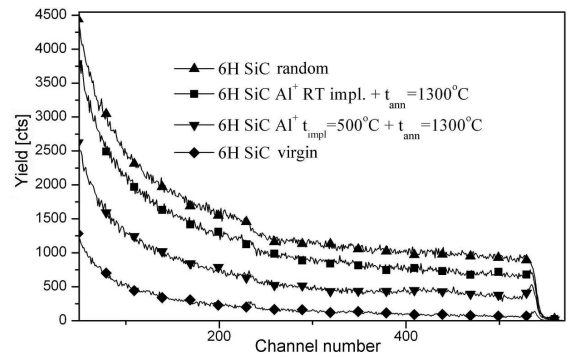


Fig. 1. RBS/C spectra of Al^+ implanted and 1300°C annealed 6H-SiC samples. Additionally, aligned and random spectra of a virgin sample are shown.

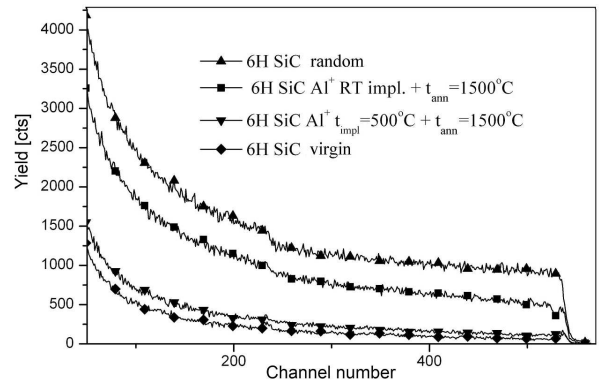


Fig. 2. RBS/C spectra of Al^+ implanted and 1500°C annealed 6H-SiC samples. Additionally, aligned and random spectra of unimplanted 6H-SiC are shown.

(Fig. 2). When annealing at 1600°C was applied, the hot-implanted samples recovered nearly to the perfect crystalline quality of virgin 6H-SiC (Fig. 3). It is also shown in the same figure that the yield corresponding to the non-annealed, RT implanted sample reaches the random

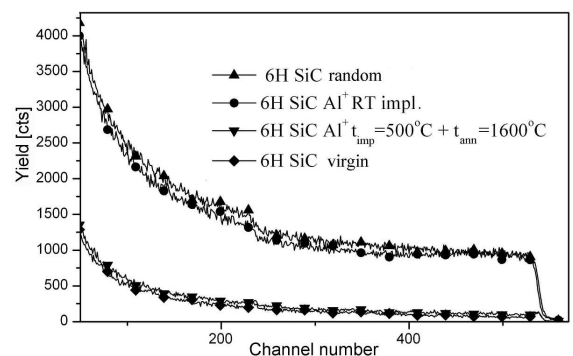


Fig. 3. RBS/C spectra of Al^+ implanted and 1600°C annealed 6H-SiC samples. Additionally, aligned and random spectra of unimplanted 6H-SiC are shown.

level. This is an evidence of complete amorphization of a subsurface silicon carbide layer of a few hundred nanometer thickness.

3.2. Micro-Raman spectroscopy

Unpolarized Raman scattering spectra measured on the unimplanted 6H-SiC, Al⁺ implanted at RT and 500 °C, and annealed at 1600 °C 6H-SiC samples are shown in Fig. 4. The first-order narrow Raman lines and much broader, two-phonon Raman modes were observed and assigned to acoustic and optic phonons of different symmetries, propagating in single-crystalline 6H-SiC. Their wave-number positions are explained by the effect of folding of the Brillouin zone that makes phonon modes away from the Γ point present in the Raman spectra [12]. For example, the doublet structure E_2 at 767 and 790 cm⁻¹ corresponds to the folded transverse optic (TO) modes in 6H-SiC. Al⁺ ion implantation into 6H-SiC at RT results in a serious decrease of the first-order Raman lines intensity in comparison to the virgin sample and vanishing of the two-phonon lines in the region 1500–1800 cm⁻¹ (Fig. 4). Broad bands emerge in the Raman spectrum. These features correspond to vibrational modes of homonuclear bonds Si-Si and C-C, as well as to vibrations typical for amorphous SiC_x compounds. Similar bands were observed previously in the Raman spectroscopic investigations of 155 keV Na⁺ implanted 6H-SiC [13] and 4 MeV Au⁺ implanted 6H-SiC [14] and are a fingerprint of complete amorphization of implanted layers.

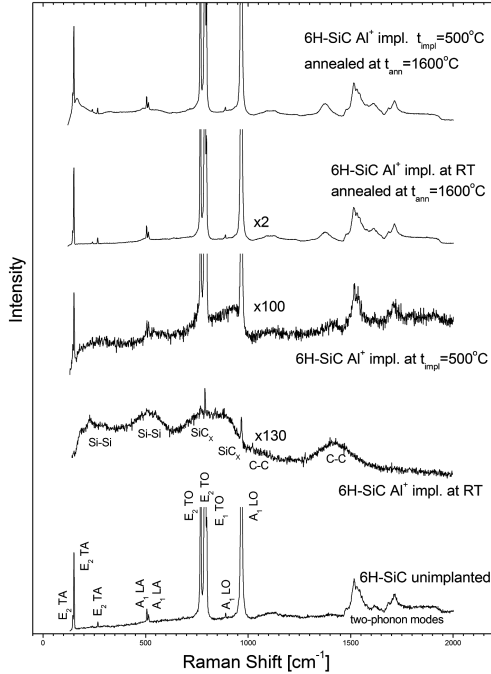


Fig. 4. Raman spectra of Al⁺ implanted (at RT and 500 °C) and 1600 °C annealed 6H-SiC samples.

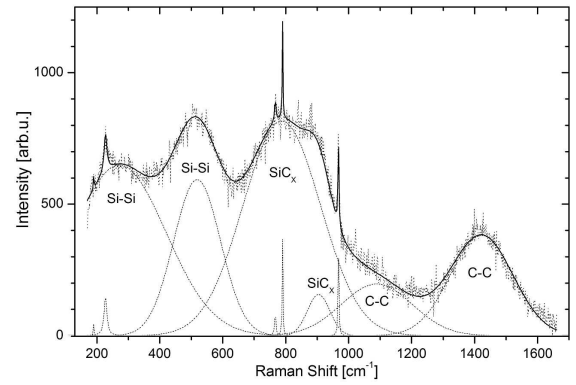


Fig. 5. Curve fit (solid line) of a full-range Raman spectrum for RT Al⁺ implanted 6H-SiC with shown deconvoluted lines and bands (dotted line).

TABLE II

Parameters of fitted Raman lines and bands.

Assignment	Lineshape type	Position [cm ⁻¹]	Height [arb.u.]	FWHM [cm ⁻¹]
cryst. Si (TA)	Lorentz	190.1	56.0	2.2
	Lorentz	227.5	147.6	11.0
Si-Si vibr.	Gauss	271.7	648.7	349.0
Si-Si vibr.	Gauss	518.5	593.3	175.6
E_2 (TO)	Lorentz	766.7	82.9	5.8
Si-C vibr.	Gauss	787.4	816.4	290.5
E_2 (TO)	Lorentz	789.9	388.1	2.6
Si-C vibr.	Gauss	904.5	156.8	84.4
A_1 (LO)	Lorentz	967.3	383.2	2.9
C-C vibr.	Gauss	1089.2	196.6	265.2
C-C vibr.	Gauss	1422.3	381.5	233.9

The Raman spectrum for RT-implanted 6H-SiC was fitted with a combination of Gaussian (broad bands) and Lorentzian (phonon lines) functions. Figure 5 shows the result of the best-fit calculations with components deconvoluted from the spectrum. The line-shape parameters and assignments are presented in Table II. Comparison between the above Raman spectrum and the one corresponding to 6H-SiC sample implanted at 500 °C (Fig. 4) clearly indicates differences between both spectra. The positions of the Raman bands from the region of the Si-Si and SiC_x modes in the 500 °C implanted sample are shifted to higher wave numbers. Additionally, the Raman lines typical for crystalline material (including two-phonon features) are observed. The ratio of integrated intensities of phonon lines and amorphous bands increases, indicating a mixture of crystalline and disordered (but not amorphous) phases in the implanted subsurface layer. The subsequent annealing for 10 min at 1600 °C in argon atmosphere removes the Si-Si, C-C and SiC_x features from the Raman spectra and restores nar-

row phonon lines. This observation shows a good crystalline order recovery in the implanted 6H-SiC layers with a higher Raman scattering intensity obtained on the 500 °C implanted sample. In addition, a new feature at about 170 cm^{-1} of unknown origin is observed in the spectrum collected from the same sample, not present in unimplanted 6H-SiC. Also, a band at about 1400 cm^{-1} , attributed to the C–C bonds becomes quite strong in the Raman spectra following high temperature annealing, when compared to the virgin 6H-SiC material. Origin of the increasing C–C band intensity can be explained by diffusion of carbon into the surface during annealing process at such high temperature. Interestingly, this band is much weaker for the 6H-SiC samples implanted under the same conditions but subjected to the 1500 °C annealing.

4. Conclusion

We have presented the results of RBS/C and micro-Raman spectroscopy investigations of RT and 500 °C Al^+ ion implantation-induced damage in 6H-SiC and its removal by high temperature (up to 1600 °C) thermal annealing. The RBS/C spectra allow us to estimate the degree of radiation damage in the subsurface layers of implanted 6H-SiC by comparison with the aligned and random backscattered He^+ ion yields for the unimplanted 6H-SiC. Following the 1300–1600 °C annealing, a level of residual radiation damage in the samples implanted at RT is higher than at the 500 °C implantation. Almost complete recrystallization was confirmed in the RBS/C spectrum of hot-implanted and annealed at 1600 °C samples.

Micro-Raman scattering measurements of RT Al^+ implanted 6H-SiC showed the appearance of broad bands attributed to Si–Si, C–C and SiC_x vibrational modes characteristic for amorphous silicon carbide. Practically no evidence of crystalline material was present in the subsurface implanted layer. Complete deconvolution of the Raman spectrum allowed us to extract parameters of the bands and the Raman lines and propose their assignment. Micro-Raman probing also indicated that the hot-implantation of 6H-SiC samples causes generally less damage with weaker bands characteristic for disordered but not amorphous silicon carbide. Annealing at 1600 °C confirms recrystallization of implanted 6H-SiC subsurface layers. The above information on damage formation and annealing as obtained by micro-Raman characterization is in a good agreement and equivalent to that from the RBS/C measurements. However, the Raman spectroscopy gives additional details on chemical reordering and formation of homonuclear bonds in damaged layers.

Acknowledgments

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References

- [1] H.H. Zhang, C.H. Zhang, B.S. Li, L.H. Han, Y. Zhang, *Nucl. Instrum. Methods Phys. Res. B* **268**, 2318 (2010).
- [2] K. Kawahara, G. Alfieri, T. Kimoto, *J. Appl. Phys.* **106**, 013719 (2009).
- [3] A. Poggi, F. Moscatelli, S. Solmi, A. Armigliato, L. Belsito, R. Nipoti, *J. Appl. Phys.* **107**, 044506 (2010).
- [4] M. Gurfinkel, S. Potbhare, H.D. Xiong, J.S. Suehle, Y. Shapira, A.J. Lelis, D. Habersat, N. Goldsman, *J. Appl. Phys.* **105**, 084511 (2009).
- [5] I. Pintilie, C.M. Teodorescu, F. Moscatelli, R. Nipoti, A. Poggi, S. Solmi, L.S. Løvlie, B.G. Svensson, *J. Appl. Phys.* **108**, 024503 (2010).
- [6] V. Heera, D. Panknin, W. Skorupa, *Appl. Surf. Sci.* **184**, 307 (2001).
- [7] M. Turek, S. Prucnal, A. Drozdziel, K. Pyszniak, *Rev. Sci. Instrum.* **80**, 043304 (2009).
- [8] M. Turek, A. Drozdziel, K. Pyszniak, S. Prucnal, J. Żuk, *Przegląd Elektrotechniczny* **86**, 193 (2010).
- [9] M. Turek, S. Prucnal, A. Drozdziel, K. Pyszniak, *Nucl. Instrum. Methods Phys. Res. B* **269**, 700 (2011).
- [10] J.F. Ziegler, J.P. Biersack, M.D. Ziegler, *The Stopping and Range of Ions in Matter*, Lulu Press Co., Morrisville, NC, USA 2009.
- [11] J. Romanek, D. Grambole, F. Herrmann, M. Voelkskov, M. Posselt, W. Skorupa, J. Żuk, *Nucl. Instrum. Methods Phys. Res. B* **251**, 148 (2006).
- [12] D.W. Feldman, J.H. Parker Jr., W.J. Choyke, L. Patrick, *Phys. Rev.* **170**, 698 (1968).
- [13] W. Bolse, J. Conrad, T. Roedle, T. Weber, *Surf. Coat. Technol.* **74-75**, 927 (1995).
- [14] S. Sorieul, J.-M. Costantini, L. Gosmain, L. Thome, J.-J. Grob, *J. Phys., Condens. Matter* **18**, 5235 (2006).