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SUPERDIFFUSION OF CARBON BY VACANCIES IRRADIATED  
WITH SOFT X-RAYS IN Cz SILICONA. J. Janavičius<sup>1</sup>, A. Mekys<sup>2</sup>, R. Purlys<sup>2</sup>, Ž. Norgėla<sup>1</sup>,  
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The soft X-ray photons absorbed in the inner  $K$ ,  $L$ ,  $M$  shells of Si atoms produce photoelectrons and Auger electrons, thus generating vacancies, interstitials and metastable oxygen complexes. The samples of Czochralski silicon crystals covered with 0.1  $\mu\text{m}$  thickness layer of carbon have been irradiated by X-rays using different voltages of Cu anode of the Russian diffractometer DRON-3M. The influence of X-rays on the formation of point defects and vacancy complexes, and their dynamics in Cz-Si crystals have been studied by infrared absorption. We have measured and calculated dynamics of concentration of carbon and interstitial oxygen using FTIR spectroscopy at room temperature after irradiation by soft X-rays. Using transmittance measurements and nonlinear diffusion theory we have calculated densities increasing for substitutional carbon and interstitial oxygen by reactions and very fast diffusion. The superdiffusion coefficients of carbon in silicon at room temperature generated by X-rays are about hundred thousand times greater than diffusion coefficients obtained for thermodiffusion.

**Keywords:** Auger effect, point defects, silicon, superdiffusion, vacancies.

## 1. INTRODUCTION

Czochralski crystals are the most thoroughly studied after irradiation with electrons, neutrons and other particles. Nevertheless, a number of problems about irradiation with X-rays still remain to be solved. The soft X-ray photons absorbed in the surface region of silicon generate photoelectrons and Auger electrons. The Auger effect makes electrons moving from outer to the photoionized inner shells of atoms emitting photons or Auger electrons. It can produce vacancies and interstitials in the lattice of crystals by sudden changes of atomic potentials [1]. Irradiation by

soft X-rays can produce the very fast diffusing vacancies [2], [3] and their complexes in the crystal silicon at room temperature. For example, some properties of the charged vacancies and vacancies–oxygen complexes  $VO$  in crystalline silicon [1]–[4] can be investigated by measuring electrical conductivity [3], Hall mobility and lattice relaxations [4]. Superdiffusion of vacancies [2] irradiated by soft X-rays at room temperature and phosphorus and boron [5] have been investigated. Here we provide the analysis of superdiffusion of carbon from layer growth by vacuum evaporation on the surface [100] of silicon irradiated by soft X-rays. Fourier transform infrared (FTIR) spectroscopy has been used like powerful and sensitive technique to analyse the introduction of impurities into Czochralski silicon by point defects generated by irradiation with fast electrons [6], neutrons [7] as well as soft X-rays [5].

## 2. EXPERIMENTAL PART

The aim of the present research is to investigate the changes of infrared absorption in Czochralski silicon (Cz-Si) samples covered with thin layers of carbon. The layers, whose thickness is 0.1  $\mu\text{m}$ , have been obtained with VPU-4 (Russian device). Before and after irradiation with soft X-rays, we have applied FTIR measurements. The film of carbon grown on the Si crystalline substrate accepts the atomic arrangement similar to a crystallographic structure of crystal silicon (Cz-Si).

Infrared measurements for investigation of generated point defects have been performed with a Vertex 70 Fourier interferometer manufactured by Bruckner. The detector system has been cooled to liquid nitrogen temperature, a spectral range has been chosen from 500 to 2000  $\text{cm}^{-1}$  with a 1  $\text{cm}^{-1}$  step and a signal average of 128 scans. The sample has been mounted in a special optical two-mirror system placed between the detector and interferometer output. All measurements have been taken at room temperature in a closed chamber with dried air.

The silicon wafers of thickness ( $d_1 = 0.166$  cm,  $d_2 = 0.134$  cm,  $d_3 = 0.150$  cm) and diameter  $r = 0.5$  cm have been irradiated for 1 h by X-rays with the diffractometer DRON-3M (Russian device) using Cu anode voltages of 10 kV, 20 kV, 30 kV and tube current of 20 mA. We have measured infrared absorption spectra and compared results for non-irradiated samples.

## 3. RESULTS AND DISCUSSION

In Cz-Si crystals [6], we usually have concentration about  $10^{18} \text{cm}^{-3}$  of interstitial  $O_i$  oxygen and substitutional  $C_s$  carbon exceeding  $10^{17} \text{cm}^{-3}$ . Carbon atoms in the silicon can produce silicon carbide ( $SiC$ ) and  $C_iO_i$  complexes by reactions  $C_i + O_i \rightarrow C_iO_i$  after irradiation when substitution carbon is transmitted in the interstitial positions. However, in our case we have the Watkins replacement mechanism [6]  $C_s + I \rightarrow C_i$  when the mobile self-interstitial  $I$  silicon atoms take part in  $Si$  atom replacement from lattice into interstitial positions by the Auger effect. Also we have diffusion of irradiated vacancies and reactions [8]  $V + C_i \leftrightarrow C_s$  which are increasing concentration of substitutional carbon  $C_s$ . At the interface with the great concentration of mobile silicon interstitials, produced by the Auger effect, and sub-

stitutional carbon atoms form  $SiC$  precipitations by reactions [8]  $I + C_s \rightarrow SiC$ .

We have measured peaks of IR absorption bands  $1107\text{ cm}^{-1}$  and  $605\text{ cm}^{-1}$  for interstitial oxygen  $O_i$  and substitution carbon  $C_s$  at four different anode voltages of the diffractometer DRON-3M. Taking into account the transmittances presented in Fig. 1 for  $C_s$  at band  $605\text{ cm}^{-1}$ , and applying the standard formula [9]

$$\frac{I_i}{I_0} = \exp[-\alpha_i d], \quad \alpha_i = \alpha_f + \alpha_{iC}, \quad (1)$$

for irradiated samples ( $i=1,2,3$ ) using Cu anode voltages of 10 kV, 20 kV, 30 kV and a tube current of 20 mA, we have obtained absorption coefficients  $\alpha_i$

$$\alpha_1 = 8.97\text{ cm}^{-1}, \quad \alpha_2 = 8.51\text{ cm}^{-1}, \quad \alpha_3 = 8.32\text{ cm}^{-1}. \quad (2)$$

For non-irradiated sample, we have obtained

$$\alpha = 7.93\text{ cm}^{-1}. \quad (3)$$

The absorption coefficients after irradiation are increased in percent

$$\varepsilon_{1C}=13.1\%, \quad \varepsilon_{2C}=7.3\%, \quad \varepsilon_{3C}=4.96\%. \quad (4)$$

Excluding the phonon absorption coefficient [9]  $\alpha_f = 7\text{ cm}^{-1}$  from (2) of TO+TA lattice phonons for band at  $611\text{ cm}^{-1}$ , we have obtained the absorption coefficients for substitutional carbon  $C_s$  in irradiated  $\alpha_{iC}$  and non-irradiated samples  $\alpha_C$

$$\alpha_{1C} = 1.97\text{ cm}^{-1}, \quad \alpha_{2C} = 1.51\text{ cm}^{-1}, \quad \alpha_{3C} = 1.32\text{ cm}^{-1}, \quad \alpha_C = 0.93\text{ cm}^{-1} \quad (5)$$

Multiplying these coefficients by the calibration factor [7]  $\sigma_C = 1.0 \times 10^{17}\text{ cm}^{-2}$ , we have obtained the concentrations of  $C_s$  carbon in the irradiated and non-irradiated samples

$$\begin{aligned} N_{1C} &= 1.97 \cdot 10^{17}\text{ cm}^{-3}, \\ N_{2C} &= 1.51 \cdot 10^{17}\text{ cm}^{-3}, \\ N_{3C} &= 1.32 \cdot 10^{17}\text{ cm}^{-3}, \\ N_C &= 0.93 \cdot 10^{17}\text{ cm}^{-3}. \end{aligned} \quad (6)$$

Here, the obtained results at room temperature are important. For example, fully substitutional incorporation in silicon from a layer of molecular beam epitaxy is possible only by heating [9] at  $450^\circ\text{C}$ .

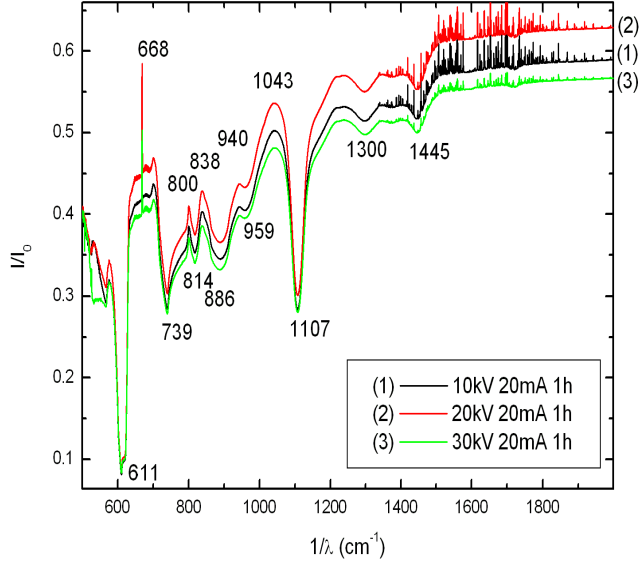


Fig. 1. FTIR absorption spectra after 1 h irradiation with X-rays of Cz Si samples covered with carbon using Cu anode voltages of 10 kV, 20 kV, 30 kV and tube current of 20 mA.

Applying formula [10]

$$\Delta N_{iC} d = 0.5492 N_S x_{0i}, \quad x_{0i} = 1.616 \sqrt{D_{Si} t}, \quad \Delta N_{iC} = N_i - N_C, \quad i = 1, 2, 3 \quad (7)$$

for density increase  $\Delta N_{iC}$  of carbon atoms in CZ silicon samples of  $d$  thickness of orientation  $\langle 100 \rangle$  by superdiffusion [5], [11] we can find its penetration depths  $x_{0i}$  for diffusion time  $t$  and coefficient  $D_{Si}$ . Here  $N_S$  is the concentration of diffusing carbon atoms on the irradiated surface of silicon taking part in the kick-out reaction [7], [8]



when substitution carbon  $C_S$  interacts with high mobility interstitials  $I$  of silicon produced by irradiation with X-rays.

Taking into consideration that on the irradiated surface many chemical bonds of silicon are broken by the Auger effect [3] and ionization, we can suppose that the maximum concentration of carbon at the surface of silicon is equal to the concentration of carbon [12]  $N_S = 4.5 \cdot 10^{17} \text{ cm}^{-3}$  at the melting temperature ( $T = 1414 \text{ }^\circ\text{C}$ ). Now, using (6), (7) we can calculate carbon penetration depths  $x_{0i}$  and superdiffusion coefficients  $D_{Si}$  for different voltages of anode

$$x_{0i} = \frac{\Delta N_{iC} d}{0.5492 N_S}, \quad D_{Si} = \frac{x_{0i}^2}{1.616^2 t} \quad (9)$$

after 1 h irradiation at room temperature. Using (6), (7) and (9), we have calculated and presented the carbon penetration depths  $x_{oi}$  and superdiffusion coefficients  $D_{Si}$  in Table 1. As a source of X-rays, we have used the diffractometer DRON-3M with Cu anode at voltages of 10, 20, 30 kV; consequently,  $i = 1,2,3$  for the tube current of 20 mA.

Table 1

$x_{oi}, D_{Si}$  Dependence on  $\Delta N_i$

$\Delta N_{iC} \text{ cm}^{-3}$	$1.04 \cdot 10^{17}$	$0.58 \cdot 10^{17}$	$0.39 \cdot 10^{17}$
$x_{oi} \text{ mm}$	0.421	0.235	0.158
$D_{Si} \text{ cm}^2 / s$	$1.88 \cdot 10^{-7}$	$5.86 \cdot 10^{-8}$	$2.65 \cdot 10^{-8}$

We can compare the presented results in Table 1 for superdiffusion coefficients  $D_{Si}$  with the diffusion coefficients calculated from experimental profiles presented in [13], where diffusion has been realized from a silicon layer  $0.1 \mu\text{m}$  with carbon spikes at temperature  $T_1 = 730^0 \text{ C}$  for a heating time of 20 h and at  $T_2 = 830^0 \text{ C}$  for 3 h. Using experimentally found penetration depths  $x_{o1} = 1 \mu\text{m}$  and  $x_{o2} = 1.2 \mu\text{m}$  from (2.9), we have calculated diffusion coefficients  $D_1 = 5.32 \cdot 10^{-14} \text{ cm}^2 / s$  and  $D_2 = 5.4 \cdot 10^{-13} \text{ cm}^2 / s$ . The superdiffusion coefficients of carbon in silicon at room temperature generated by X-rays are about a hundred thousand times greater than diffusion coefficients obtained for thermodiffusion.

Oxygen and oxygen precipitates play an important role in the formation of defects by the influence of irradiation in CZ silicon. Carbon, silicon and oxygen are interacting on an atomic level. The great binding energies, about -2.34 eV between carbon and interstitial silicon atoms in  $C_iS_i$  and less than -1.60 eV for  $C_iO_i$  [14], are increasing probability of silicon carbide precipitations or grain formation at the surface of crystal silicon. The precipitations of silicon carbide associated [10] with silicon reaction with carbon, like prevailing impurities at the surface, generate a volume shrinkage and produce  $SiC$  grains presented in Fig. 2.



Fig. 2 . Length of this picture is 0.8 mm. Diameter of precipitations of carbon on silicon in the irradiated right side is about  $1 \mu\text{m}$  . Left side is not irradiated.

We used influence of irradiation with soft X-rays for formation of the micro crystals instead the initial carbon layer on the silicon's surface.

Created by irradiation at the crystal surface, negative vacancies that are very fast excited with diffusion coefficient [3]  $D^- = 4.4 \cdot 10^{-5} \text{ cm}^2 / \text{s}$  can penetrate in CZ crystal at 0.06 cm distance by 1 h. The same quantity of oxygen atoms interacting with vacancies will diffuse from atmosphere in irradiated crystal. Absorbed at the surface of crystal interstitial atoms,  $O_i$  atoms react with irradiated vacancies  $V + O_i \Rightarrow VO$  (presented according to [15] like absorption of vibration modes at 800  $\text{cm}^{-1}$  and 838  $\text{cm}^{-1}$  in Fig. 1.) producing mobile complexes  $VO$ , which transmit oxygen atoms from the atmosphere in the volume of crystal. It is important to remark that vacancies produced by the Auger effect generated by soft X-rays can exist [16] after irradiation for more than 1.5 h at room temperature. Interstitial  $O_i$  can interact with many other defects and impurities. In our case, interstitial oxygen  $O_i$  can be produced by the reaction  $I + VO \Rightarrow O_i$  of irradiated self-interstitial  $I$  in the silicon [7] with  $VO$  complexes. Vacancies and interstitials produced [8] by the Auger effect transmit the diffusing carbon atoms from the irradiated layer in the volume of silicon and are partially used for production of  $VO$  and  $O_i$ . Calculating absorption coefficients from transmittances presented in Fig. 1 for the peak at 1107  $\text{cm}^{-1}$  for interstitial oxygen  $O_i$  and phonons 2TO+TA with absorption coefficient  $\alpha_f = 0.85 \text{ cm}^{-1}$  [6] at 1118  $\text{cm}^{-1}$ , we have obtained

$$\alpha_{10} = 3.20 \text{ cm}^{-1}, \alpha_{20} = 3.13 \text{ cm}^{-1}, \alpha_{30} = 3.03 \text{ cm}^{-1}. \quad (10)$$

From these coefficients and calibration factor [7]  $\sigma_o = 3.14 \times 10^{17} \text{ cm}^{-2}$ , we have obtained interstitial oxygen  $O_i$  concentrations of irradiated samples for different anode voltages of 10, 20, 30 kV, consequently,

$$N_{10} = 1.1 \times 10^{18} \text{ cm}^{-3}, N_{20} = 9.82 \times 10^{17} \text{ cm}^{-3}, N_{30} = 9.51 \times 10^{17} \text{ cm}^{-3}, \quad (11)$$

and for the non-irradiated sample

$$\alpha_o = 1.30 \text{ cm}^{-1} \quad N_o = 4.1 \times 10^{17} \text{ cm}^{-3}, \quad (12)$$

which is significantly less. We have measured the concentrations of interstitial oxygen  $O_i$  and substitutional carbon  $C_S$  using [17] well-known absorption bands at 1107  $\text{cm}^{-1}$  and 605  $\text{cm}^{-1}$  respectively. In Fig. 1, it is interesting to note that complexes  $VO_2$  presented at band 886  $\text{cm}^{-1}$ , where there is no significant difference [17] from 889  $\text{cm}^{-1}$ , can be explained by irradiation influence on crystal lattice [4]. These mobile complexes play an important role in superdiffusion of the impurities [5] or in this case of carbon atoms at room temperature. These complexes can be produced by interstitial oxygen reactions with vacancies generated by the Auger effect [8]. The Auger effect can be implemented using photons with energies [17] greater than  $K$  electron energy edge at 1.839 keV of silicon atoms.

## 4. CONCLUSIONS

The applied anode potential of 10 kV is more effective for the production of vacancies than 20 kV in a Si crystal. The generated vacancies initiate superdiffusion of carbon in the crystal silicon from a deposited layer on silicon crystal at room temperature. We have obtained weaker effects at Cu anode voltages of 20 kV, 30 kV because Auger transitions for light atoms are intensive [18] only for the excitation energies in the 5-10 keV interval. The results (7) for  $\Delta N_{iC}$  presented in Table 1 are average carbon density values in the volume of samples with different thickness  $d_1 = 0.166$  cm,  $d_2 = 0.134$  cm,  $d_3 = 0.150$  cm. Real average values of introduced carbon densities

$$\begin{aligned} \Delta \bar{N}_{iC} &= \Delta N_{iC} \frac{d_i}{x_{0i}}, \\ \Delta \bar{N}_{1C} &= 4.10 \cdot 10^{17} \text{ cm}^{-3}, \quad \Delta \bar{N}_{2C} = 3.31 \cdot 10^{17} \text{ cm}^{-3}, \quad \Delta \bar{N}_{3C} = 3.70 \cdot 10^{17} \text{ cm}^{-3} \end{aligned} \quad (13)$$

have been calculated taking into account the penetrations depths  $x_{0i}$ . In the penetration region, carbon density has increased by about 3–4 times in the silicon samples after one hour of irradiation. It is interesting that carbon density  $\Delta \bar{N}_{1C} = 4.10 \cdot 10^{17} \text{ cm}^{-3}$  introduced by irradiation with soft X-rays is near the carbon density  $N_S = 4.5 \cdot 10^{17} \text{ cm}^{-3}$  in silicon at the melting temperature. Carbon introduction in a silicon lattice by irradiation with X-rays takes part by forming SiC bonds [9] and SiC precipitations (peaks at  $722 \text{ cm}^{-1}$  and  $814$  (or  $817$ )  $\text{cm}^{-1}$  presented in Fig. 1) in the interface region.

Additionally, on the left side of a polished Si sample with the thickness of carbon layer of  $0.1 \text{ }\mu\text{m}$  we have displayed a steel setting-rule, where the sample has been irradiated by X-rays diffractometer with Cu anode at the voltage of 10 kV and current of 20 mA. The result is presented in Fig. 2. We have photographed precipitations by microscope. The measured average diameter of precipitations, presented on the right side of Fig. 2, is about  $1 \text{ }\mu\text{m}$ . The superdiffusion of carbon like impurities in crystal silicon by the Auger effect can be implemented [5], [11] at room temperature only from SiC precipitates. By optimising irradiation, we can use the proposed method for new silicon carbide technologies in electronics.

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## SUPERDIFŪZIJA AR VAKANCĒM IESTAROTA AR MĪKSTAJIEM RENTGENSTARIEM Cz SILĪCIJĀ.

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### K o p s a v i l k u m s

Rezumējums: Rentgena staru fotoni, absorbēti Si atoma iekšējos slāņos, izstaro fotoelektronus un Ožē elektronus, ģenerējot vakances, starpmezglu silīcija atomus, vakanču un skābekļa kompleksus. Čohraļska silīcija kristāli, kas pārklāti ar oglekli 0.1 μm biezuma kārtā, tika apstaroti ar rentgena stariem, izmantojot krievu difraktometru DRON-3M. Oglekļa un skābekļa difūzija un koncentrāciju izmaiņa silīcijā tika izmērīta izmantojot infrasarkano staru FTIR spektroskopiju. Rentgena staru ģenerētās ļoti ātrās oglekļa difūzijas vai superdifūzijas koeficients istabas temperatūrā silīcijā ir simtiem tūkstošu reižu lielāks nekā termodifūzijas gadījumā.

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