FORMATION AND ELIMINATION OF RADIATION DEFECTS RESPONSIBLE FOR CHARGE CARRIER REMOVAL IN BORON DOPED SILICON

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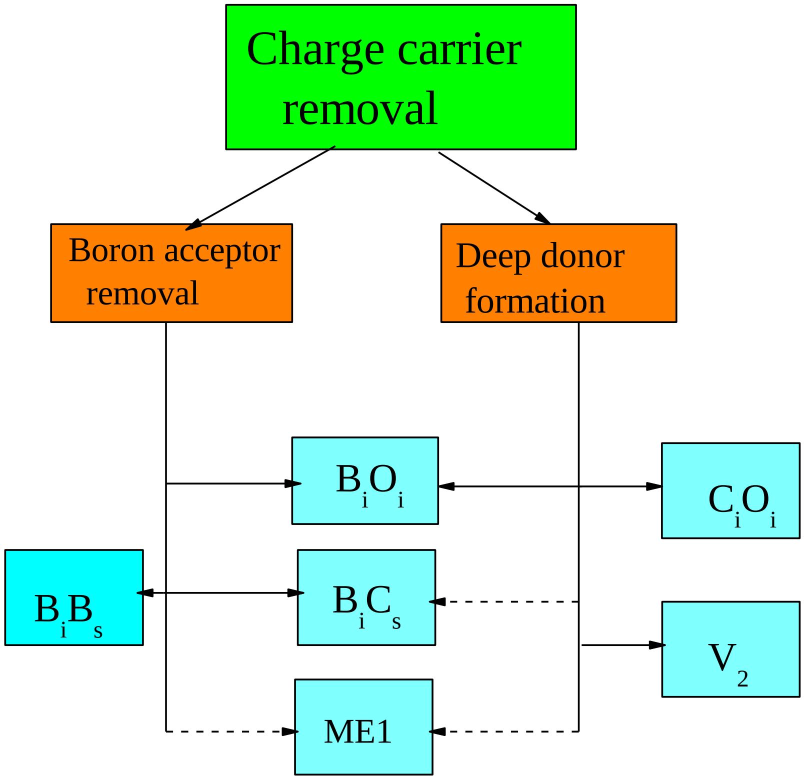
Introduction



At room temperatures

$\Delta p=2[B_iO_i]+2[B_iB_s]+f_1[C_iO_i]+f_2[B_iC_s]$

At liquid nitrogen temperatures

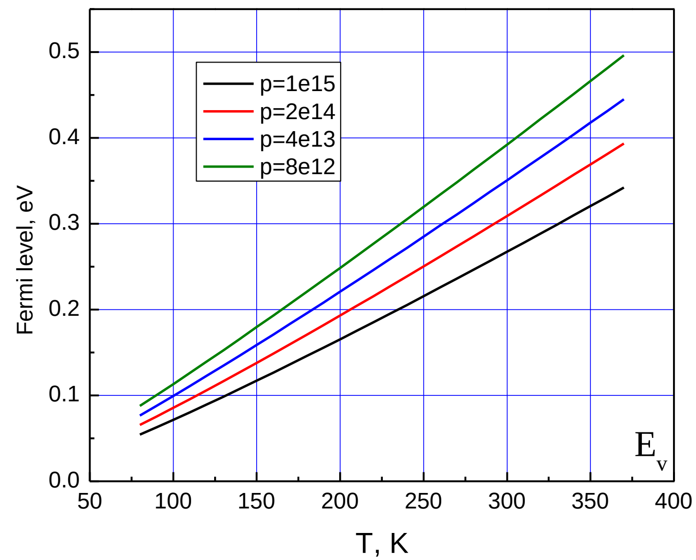
$\Delta p=2[B_iO_i]+2[B_iB_s]+[C_iO_i]+[B_iC_s]+f_3[V_2]$

Hole occupancy factor

$$f_i=\frac{1}{1+\exp\left(\frac{E_F-E_i}{kT}\right)}$$

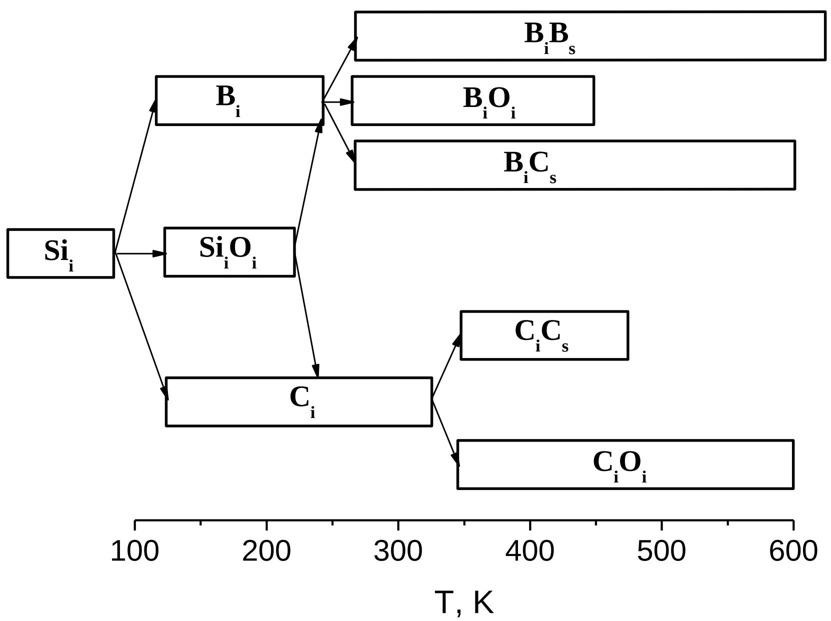
Fermi level: $E_F\text{-}E_v=kT\cdot ln(N_v/p)$

Energy level: $E_i\text{-}E_v=\Delta H_i\text{-}T\Delta S_i$



Temperature dependence of Fermi level in materials with different boron doping

Properties of interstitial defects in boron doped silicon (according to KABDC model)*



Hierarchy of the self-interstitial defect reactions in silicon. The temperature scale shows the stability of each product under quiescent conditions.

Defect	E_T, eV	Charge State	Stability	REDR	
$(Si)_iO_i$	-	-	230 K	-	?
B_i	E(0.13) E(0.45)	0/+ -/0	240 K	+	
B_iB_s	H(0.30)	-	>400 ^oC	-	?
B_iO_i	E(0.26)	-	150-200 ^oC	-	?
B_iC_s	H(0.29)	-	400^oC	-	
C_i	E(0.12) H(0.27)	-/0 0/+	50 ^oC	+	?
C_iC_s	ME(0.17) ME(0.10) MH(0.09) MH(0.05)	-/0 -/0 0/+ 0/+	225 ^oC	+	
C_iO_i	H(0.36)	0/+	400 ^oC	-	

Table I. Interstitial Defect States in Silicon

*Kimerling, L. C., Asom, M. T., Benton, J. L., Drevinsky, P. J., & Caefer, C. E. (1989). Interstitial defect reactions in silicon. In *Materials Science Forum* (Vol. 38, pp. 141-150). Trans Tech Publications.

Description of defect reaction kinetics

Watkins replacement reactions: $B_s + Si_i \xleftrightarrow[k_2]{k_1} B_i + Si_s$; $C_s + Si_i \xleftrightarrow[k_4]{k_3} C_i + Si_s$

Interstitial boron reactions: $B_i + B_s \xleftrightarrow[k_6]{k_5} B_iB_s$; $B_i + O_i \xleftrightarrow[k_8]{k_7} B_iO_i$; $B_i + C_s \xleftrightarrow[k_{10}]{k_9} B_iC_s$

Interstitial carbon reactions: $C_i + C_s \xleftrightarrow[k_{12}]{k_{11}} C_iC_s$; $C_i + O_i \xleftrightarrow[k_{14}]{k_{13}} C_iO_i$

$$\frac{d[B_s]}{dt} = -k_1[Si_i][B_s] - k_5[B_i][B_s]$$

$$\frac{d[C_s]}{dt} = -k_3[Si_i][C_s] - k_9[B_i][C_s] - k_{11}[C_i][C_s]$$

$$\frac{d[O_i]}{dt} = -k_7[B_i][O_i] - k_{13}[C_i][O_i]$$

$$\frac{d[B_i]}{dt} = k_1[Si_i][B_s] - k_5[B_i][B_s] - k_7[B_i][O_i] - k_9[B_i][C_s]; \quad \frac{d[B_iO_i]}{dt} = k_7[B_i][O_i];$$

$$\frac{d[C_i]}{dt} = k_3[Si_i][C_s] - k_{11}[C_i][C_s] - k_{13}[C_i][O_i]; \quad \frac{d[C_iO_i]}{dt} = k_{13}[C_i][O_i]$$

And the rate of self-interstitial production:

$$\frac{d[Si_i]}{dt} = \sigma N\left[\frac{d}{dt}\Phi(t)\right] - k_1[Si_i][B_s] - k_3[Si_i][C_s]$$

Initial conditions are $[O_i]$, $[C_s]$ and $[B_s]$ at t=0 and 0=$[B_i]$= $[C_i]$= $[Si_i]$=…

Reaction constants are defined as

$$k_i = 4\pi R_i D_i$$

R_i is the capture radius of *i-th* atom, and D_i is its diffusion coefficient defined as

$$D_i = D_{0i} \exp\left(-{H_i^*}/{kT} \right)$$

The capture radius depends on charge states of mobile atom and trapping center. If they are neutral then R_i is suggested to be about 0.2-0.5 nm. If they have opposite charges then the radius can much larger. For example, if we suggest that the self-interstitial atoms in p-Si are doubly positively charged then we have to expect that they will be more effectively captured by negatively charged boron atoms than by neutral carbon atoms.

At high irradiation fluences already formed radiation-induced complexes may act as new traps for primary radiation defects (Si_i and V) and more complicated complexes begin to form. Such processes are well known from IR-absorption experiments for carbon related defects (see for example, *Davies, G. (1989). Carbon-related processes in crystalline silicon. In Materials Science Forum (Vol. 38, pp. 151-158) Trans Tech Publications* and references therein).

So to model dose dependencies of defect formation one has to know initial impurity concentrations and reaction coefficients. However there are some difficulties to realize this approach for detectors made of p-Si. To discuss some improvements of the KABDC model is the aim of this talk.

The further consideration is based on our results obtained with the use DLTS and C-V measurements.

Samples and irradiations

Silicon n^+-p diodes with different doping of p-region were used for investigations:

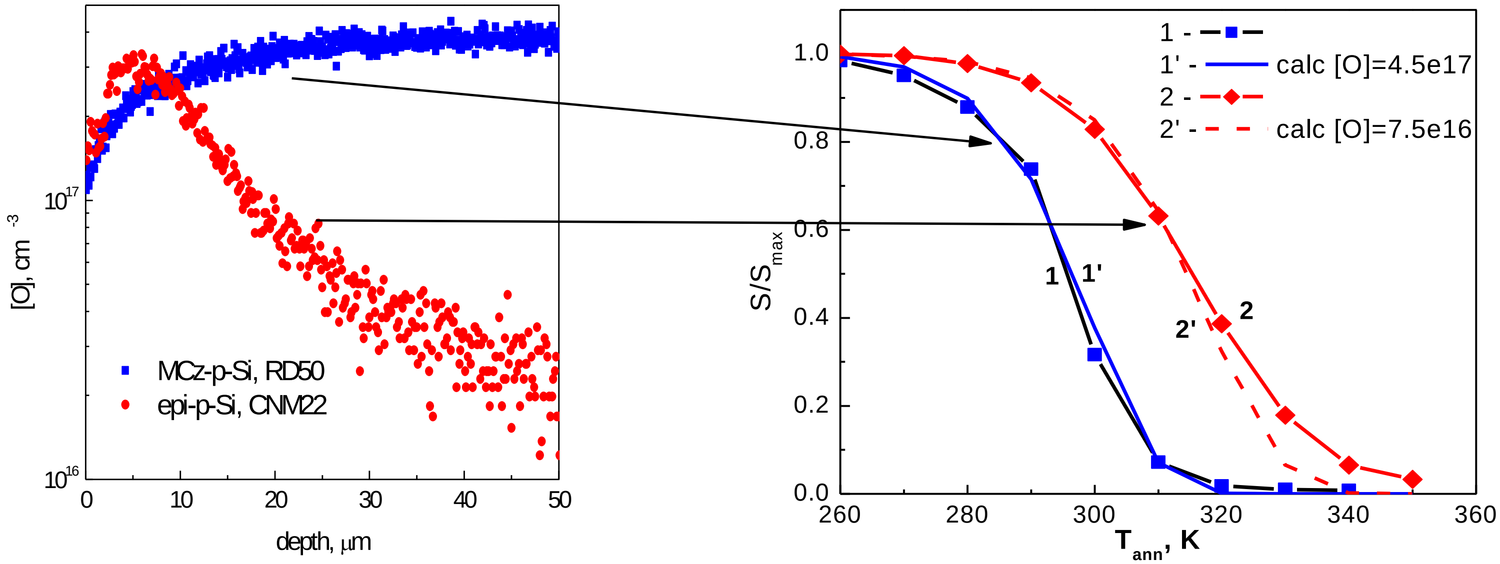
- Epitaxial, $p=1.15\times10^{15}$ cm^{-3} (10 Ω·cm);
- Epitaxial, $p=2\times10^{14}$ cm^{-3} (50 Ω·cm)
- Epitaxial, $p=4\times10^{13}$ cm^{-3} (250 Ω·cm)
- Czochralski-grown, $p=1.05\times10^{15}$ cm^{-3} (10 Ω·cm)

Diodes were irradiated with high energy electrons (E= 3.5 and 5.5 MeV) or alpha-particles (E≅5.15 MeV with penetration range into silicon of about 25 μm).
Irradiation temperatures were usually 273-300 K (RT).

The electrically active defects induced by irradiation with alpha-particles and electrons were investigated by means of the Deep Level Transient Spectroscopy (DLTS) technique in the 79-270 K temperature range (and several measurements have been made in the range 30-270 K).
C-V measurements were performed with reverse bias in the range 0–150 V. The measurement frequency was 1 MHz. The distribution of charge carriers (holes) in the diode base was calculated from C-V characteristics using finite-difference technique (see for example *Blood, P., & Orton, J. W. (1992). The Electrical Characterization of Semiconductors: Majority Carriers and Electron States*, *Academic. New York, 13).*

How to get information on background impurities in Si diodes

Oxygen concentration can be assessed from annealing study of interstitial carbon.



SIMS data for oxygen distribution in Si diodes

Annealing kinetics of C_i in the same Si diodes

Calculations of Ci annealing have been performed with parameters presented in: *Makarenko, L. F., Moll, M., Korshunov, F. P., & Lastovski, S. B. (2007). Reactions of interstitial carbon with impurities in silicon particle detectors. Journal of applied physics, 101(11), 113537*

Isochronal annealing of interstitial carbon in diodes under study

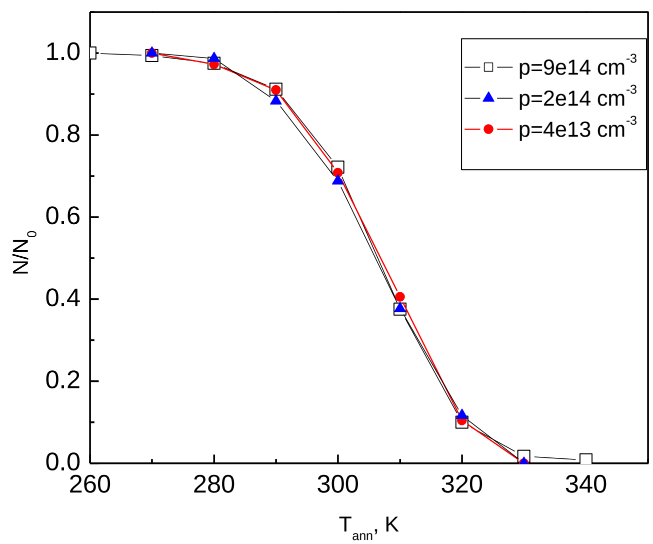


Fig.1. Isochronal annealing of C_i in epi-Si diodes with different boron doping.

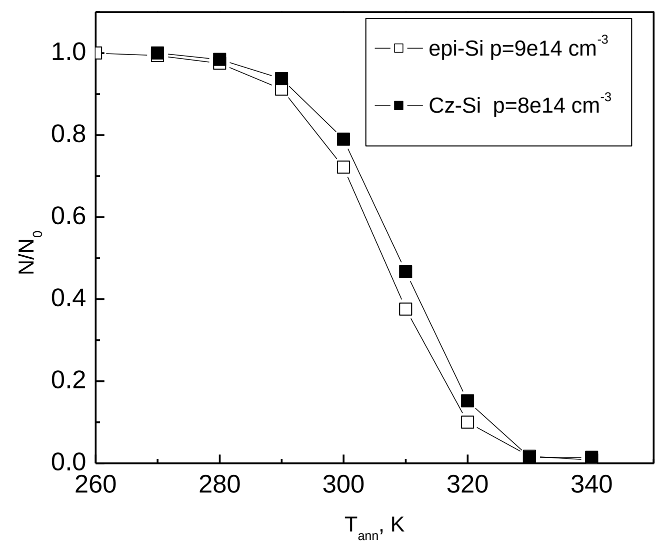


Fig.2. Isochronal annealing of C_i in epi- and Cz-Si diodes manufactured with similar technological conditions.

$[O] \cong 1.5 \times 10^{17}\ cm^{-3}$

Electrically active defects formed after irradiation of Si diodes

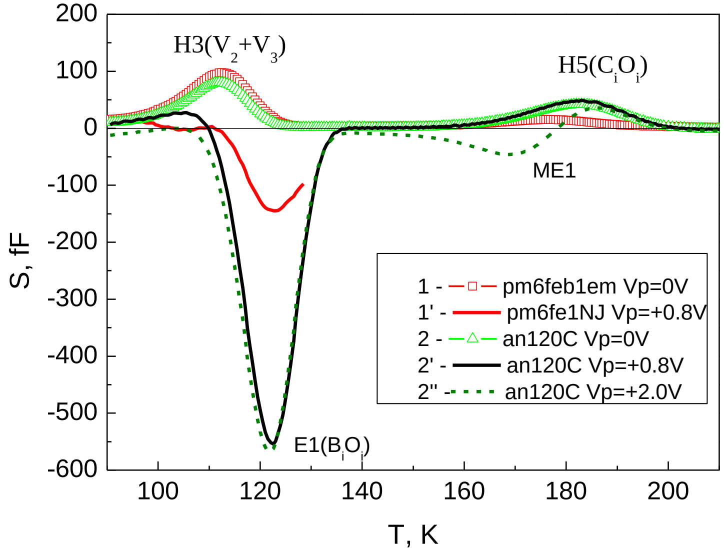


Fig.3. DLTS and MCTS spectra for 10 Ω epi-Si diodes irradiated with alpha particles (E≅5 MeV) and annealed at 400 K.

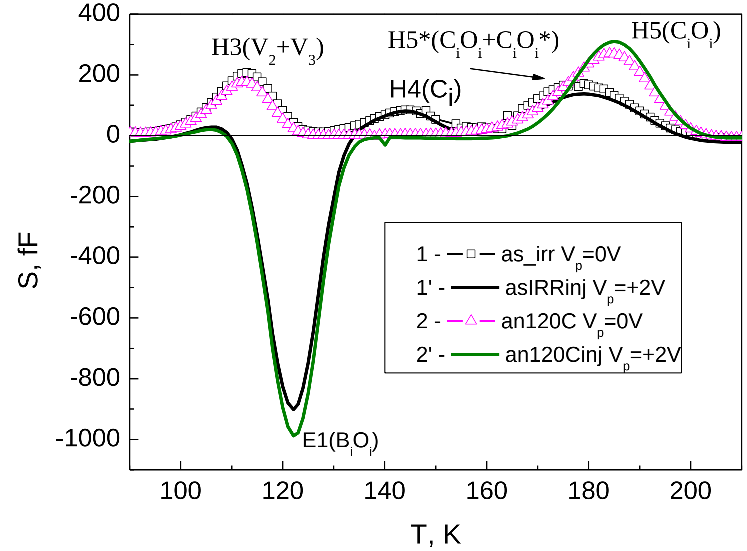


Fig.4. DLTS and MCTS spectra for 10 Ω epi-Si diodes irradiated with high energy electrons (E=5.5 MeV) and annealed at 400 K.

Immediately after alpha-irradiation some self-interstitials remain in immobile form ($Si_i^* \equiv I^*$).

Immediately after electron irradiation we can observe interstitial carbon atoms which are mobile at near room temperatures.

The reaction coefficients for Si_i trapping by C_s and B_s (k_1 and k_3) depend on irradiation particles.

Electrically active defects formed after irradiation of Si diodes

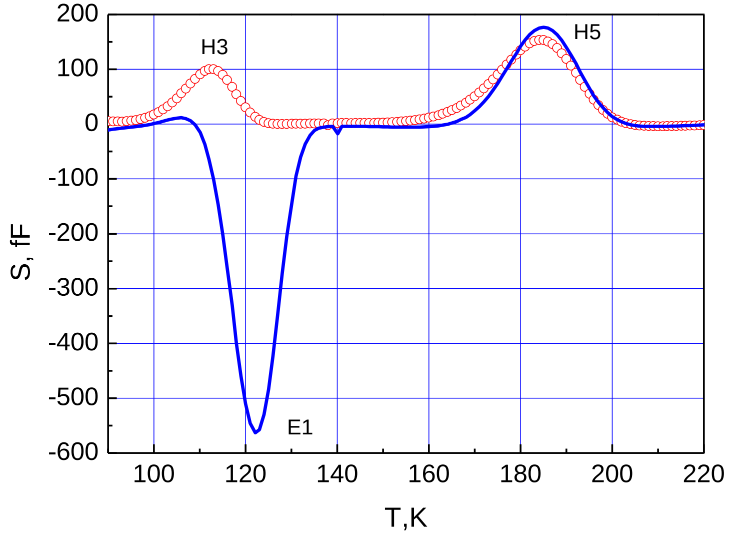


Fig.5. DLTS and MCTS spectra for 10 Ω epi-Si diodes irradiated with electrons (E≅3.5 MeV).

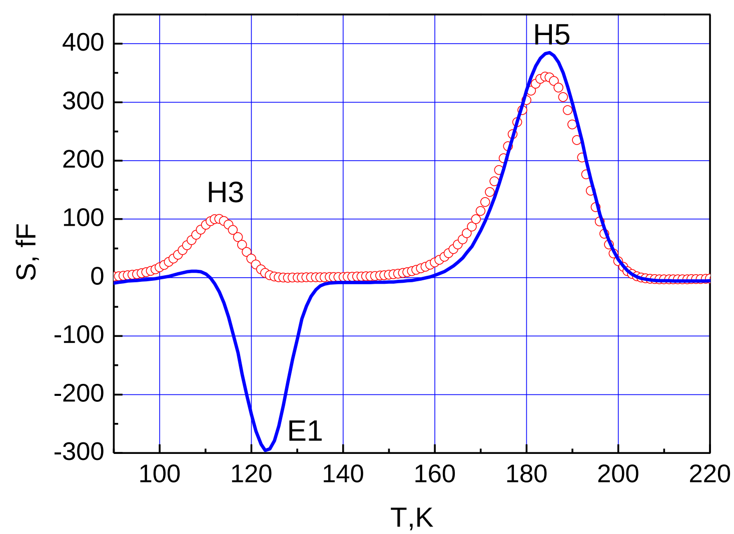


Fig.6. DLTS and MCTS spectra for 50 Ω epi-Si diodes irradiated with high energy electrons (E=3.5 MeV).

These spectra can be used to assess carbon concentration if capture radii of self-interstitials by carbon and boron are known. However the ratio between these two radii is controversial. According KABDC model this ratio (η) is equal to 7. But G. Davies (Davies, G. (1989). Carbon-related processes in crystalline silicon. In *Materials Science Forum* (Vol. 38, pp. 151-158). Trans Tech Publications) reported essentially higher value for it (η=50).

$[C] \cong 1\text{-}2\times10^{15}\ cm^{-3}$ in epi-Si diodes

Electrically active defects formed after irradiation of Si diodes

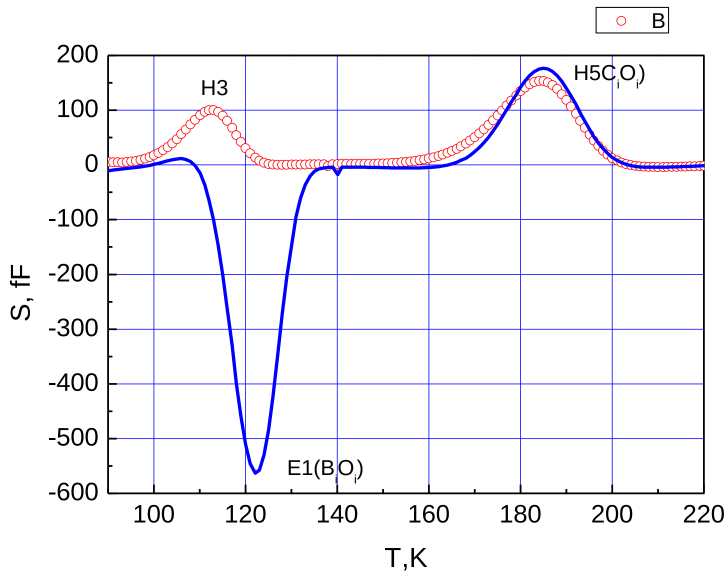


Fig.7. DLTS and MCTS spectra for 10 Ω epi-Si diodes irradiated with high energy electrons (E≅5.5 MeV).

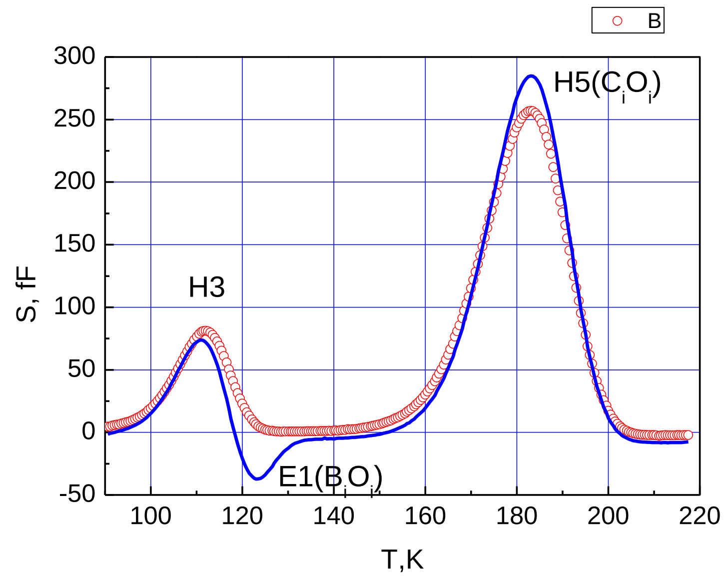


Fig.8. DLTS and MCTS spectra for 10 Ω Cz-Si diodes irradiated with high energy electrons (E=5.5 MeV).

Charge carrier removal in Si diodes irradiated with electrons

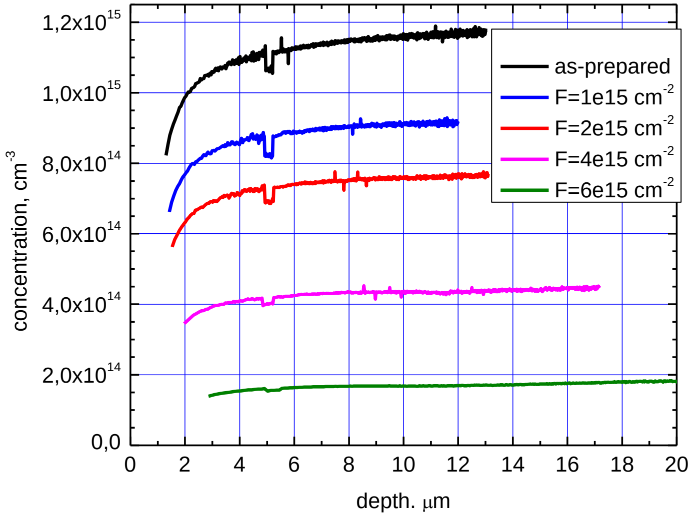


Fig.9. Charge carrier distribution (T=300 K) in 10 Ω epi-Si diodes irradiated with high energy electrons (E≅5.5 MeV).

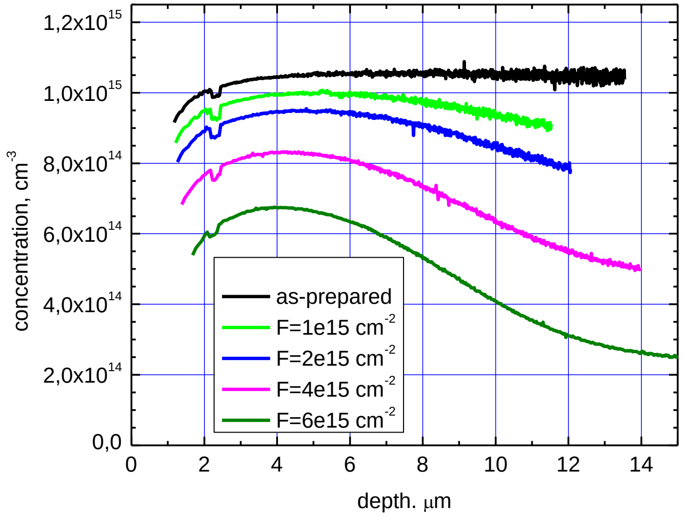


Fig.10. Charge carrier distribution (T=300 K) in 10 Ω Cz-Si diodes irradiated with high energy electrons (E=5.5 MeV).

A beneficial effect of higher carbon concentration is seen when compared epi- and Cz-Si diodes. And an inhomogeneous distribution of radiation defects is observed for Cz-Si diodes.

Occupancy of C_iO_i complex at room temperature

At room temperature

$$\Delta p=2[B_iO_i]+ f_{p1}[C_iO_i]$$

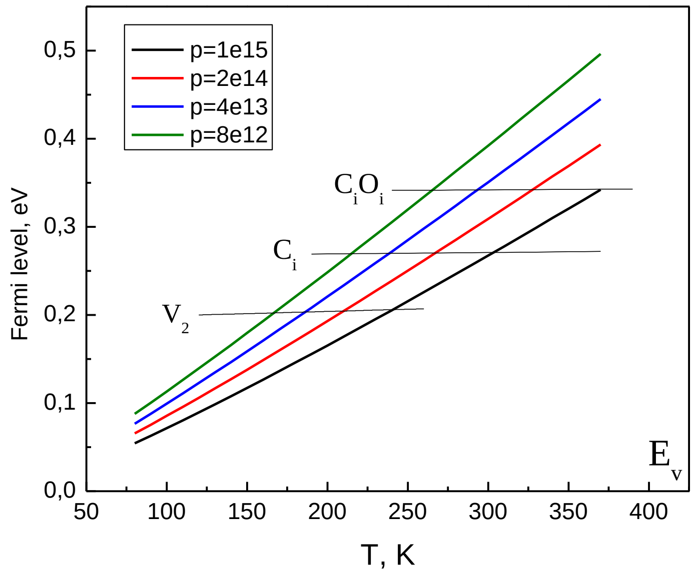


Fig.11. Calculated temperature dependence of Fermi level in materials with different boron doping.

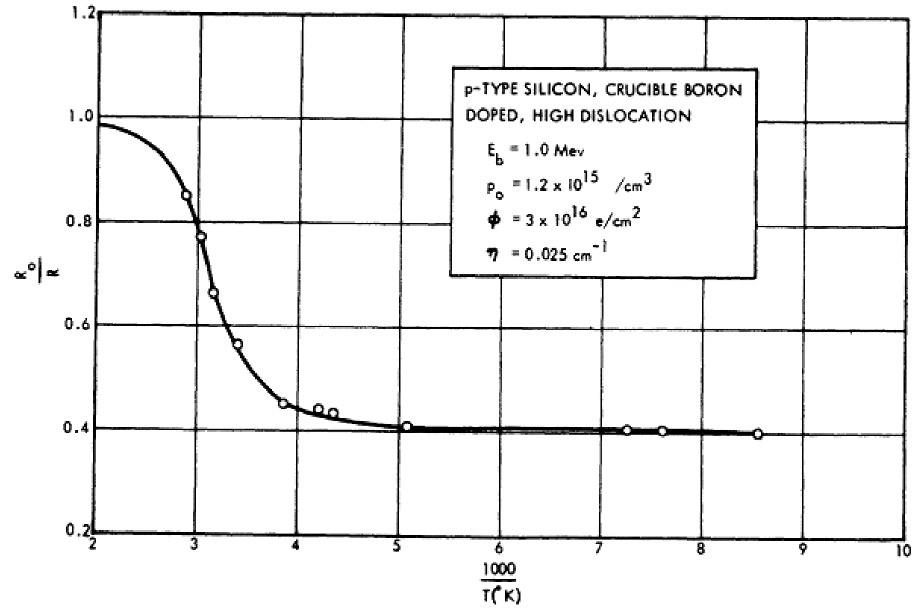


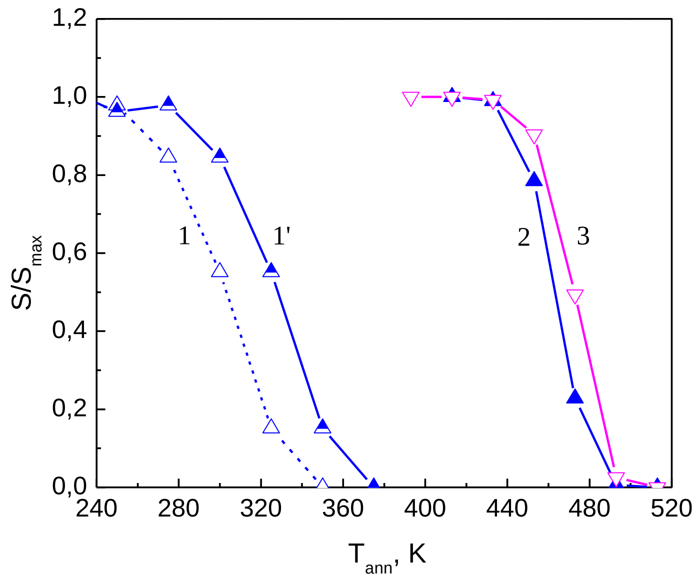
Figure 1. Hall Coefficient of Electron Irradiated Boron Doped Crucible Grown p-Type Silicon

Fig.12. From
Carter, J. R. (1966). Defect-Impurity Relationships in Electron-Damaged Silicon. *IEEE Transactions on Nuclear Science*, *13*(6), 24-32.

Energy levels are plotted according to DLTS results by Hallen et al. (Hallén, A., Keskitalo, N., Masszi, F., & Nagl, V. (1996). Lifetime in proton irradiated silicon. *Journal of Applied Physics*, *79*(8), 3906-3914) and Lastovskii et al. (Lastovskii, S. B., Gusakov, V. E., Markevich, V. P., Peaker, A. R., Yakushevich, H. S., Korshunov, F. P., & Murin, L. I. (2017). Radiation-induced interstitial carbon atom in silicon: Effect of charge state on annealing characteristics. *physica status solidi (a)*, *214*(7)).

There is some inconsistency between old Hall data and C-V and DLTS data when one evaluate the f_{p1} factor.

Effect of forward current enhanced annealing on charge carrier removal



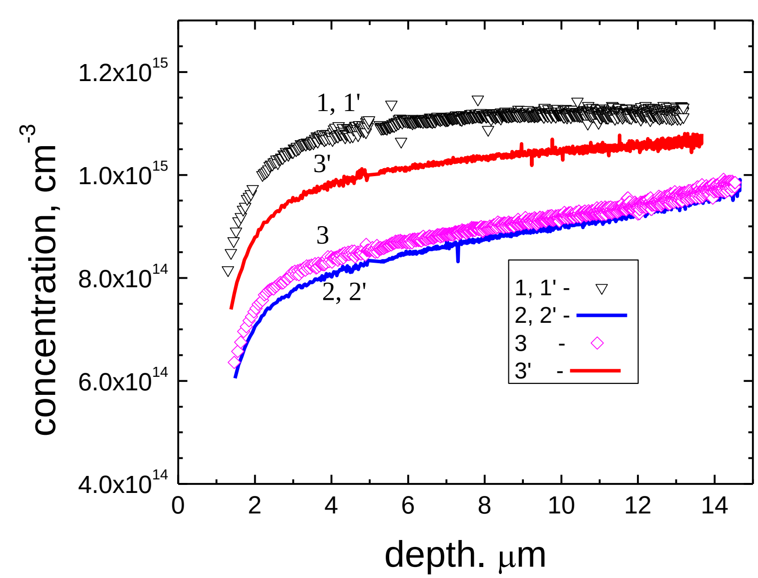
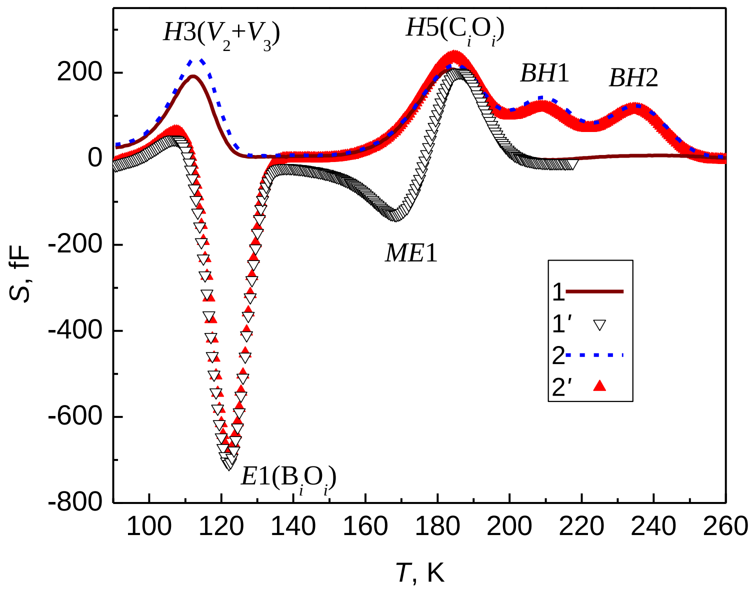


Fig.13. Isochronal FCE (1, 1′) and thermal (2, 3) annealing behavior of B_iO_i. Curve 1 is plotted using the temperature inside of the measuring cell (cryostat). Curve 1' is the same curve but with the corrected diode temperature. Curves 2 and 3 represent thermal annealing behavior of B_iO_i in different materials: 2 – p=8x10^{14} cm^{-2} and 3 – p=5x10^{13} cm^{-2}..

Fig.14. Changes of charge carrier (hole) (profile) distribution in two identical diodes after complete disappearance of E1-trap (B_iO_i):
1, 1' – as-prepared;
2, 2' – after α-irradiation for 450 minutes and stabilizing annealing;
3 – after conventional thermal annealing at 200 °C during 60 minutes;
3′ – after FCE annealing at 320 K during 150 min with forward current density J_f =32 A/cm^2.

The FCE annealing helps to mitigate the effect of radiation on charge carrier removal.

Properties of ME1 center



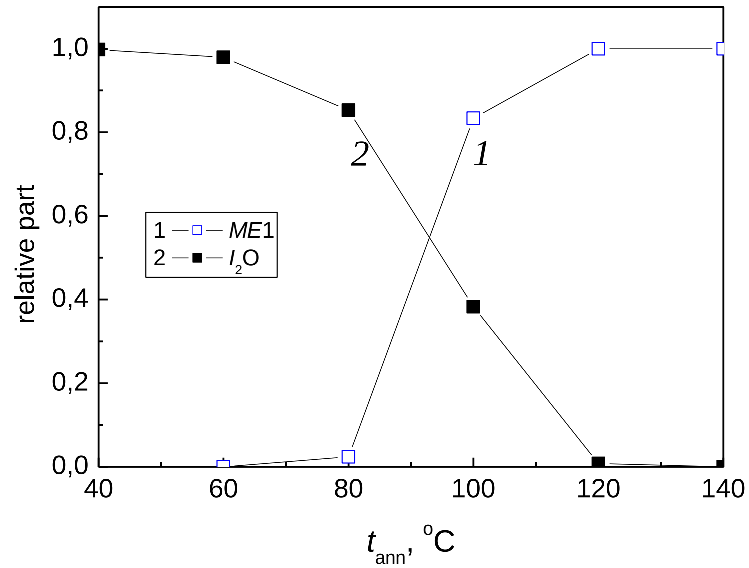


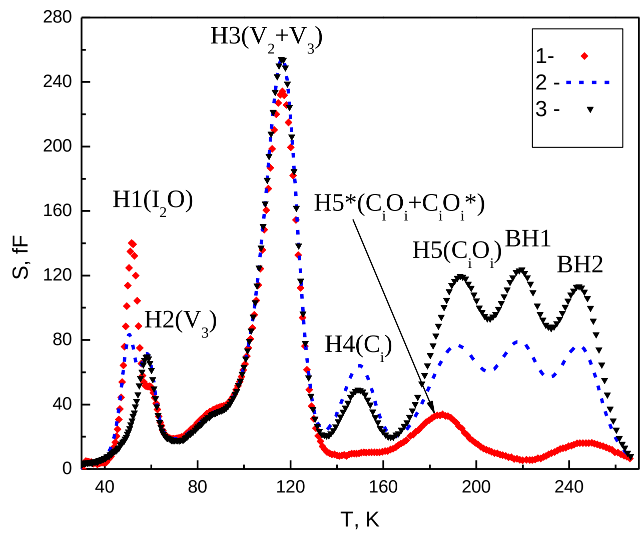
Fig.2. Conventional DLTS (lines) and MC-DLTS (symbols) spectra for the same diode as in Fig.1 registered immediately after annealing at 80 °C during 20 minutes (1, 1′) and after forward current injection with density J_f=1.6 A/cm^2 (2, 2′). Measurements settings were: emission rate window e_w = 19 s^{-1} for all spectra, bias change –3 → 0 V, and filling pulse duration t_p=10 ms for spectra 1, 2; bias change –3→+2.0 V, and filling pulse duration t_p=10 ms for spectra 1′, 2′.

Fig.3. Formation of *ME1* trap at isochronal annealing (1). Curve 2 (calculated from experimental data of Ref. [9]) corresponds to the disappearance of I_2O center under same annealing conditions. Annealing duration was 20 minutes with temperature step 20 K.

For I_2O center see: Markevich, V. P., Peaker, A. R., Hamilton, B., Gusakov, V. E., Lastovskii, S. B., Murin, L. I., ... & Svensson, B. G. (2015). Structure, Electronic Properties and Annealing Behavior of Di-Interstitial-Oxygen Center in Silicon. *Solid State Phenomena*, *242*, 290.

It possible that some of observed annealing effects in p-type detectors are related to I_2O transformation to ME1 center

Forward current enhanced annealing of I_2O complex



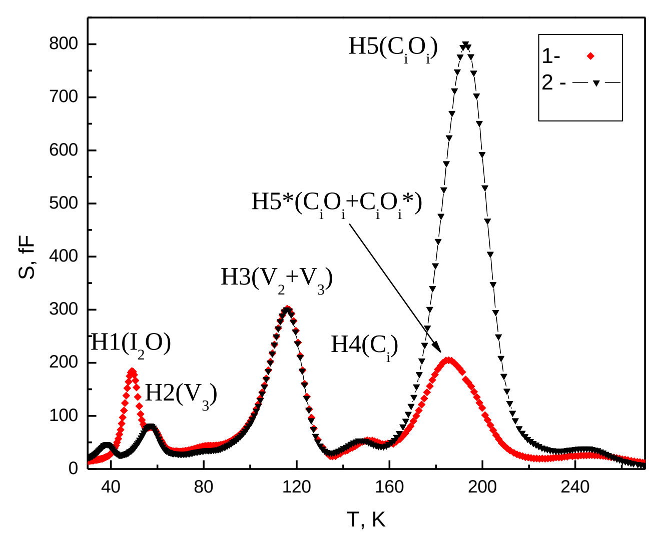


Fig.1. DLTS spectra registered for epi-Si diode after irradiation with alpha-particles (1) and after subsequent forward current injection during 2 minutes with density J_f=6.4 A/cm^2 (2), J_f=12.8 A/cm^2 (3). Measurements settings were: emission rate window e_w = 57 s^{-1} for all spectra, bias change –3 $\rightarrow$ 0 V, and filling pulse duration t_p=10 ms.

Fig.1. DLTS spectra registered for Cz-Si diode after irradiation with alpha-particles (1) and after subsequent forward current injection during 2 minutes with density J_f=12.8 A/cm^2 (3). Measurements settings were: emission rate window e_w = 57 s^{-1} for all spectra, bias change –3 $\rightarrow$ 0 V, and filling pulse duration t_p=10 ms.

So BH1/BH2 trap is a metastable configuration of ME1 center. Carbon impurity suppresses its formation. That is why we suggest this defect to be a boron containing complex. This complex can be important at higher irradiation fluences.

Summary

The model suggested by Kimerling et al. is a good starting point to understand interstitial defect kinetics in boron doped silicon.

However this model should be improved for p-type detectors.

A new model should

1) explain behavior of self-interstitials in alpha-irradiated silicon;

2) take into account defects complexes related to Si di-interstitials;

3) take into account electron injection effect on the formation and elimination of boron containing centers.

Acknowledgements

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