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Nuclear Instruments and Methods in Physics Research B 186 (2002) 121–125

NIM B
Beam Interactions
with Materials & Atoms

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Defect engineering in Czochralski silicon by electron irradiation at different temperatures

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Abstract

Infrared absorption studies of defect formation in Czochralski silicon irradiated with fast electrons in a wide range of temperatures (80–900 K) have been performed. The samples with different contents of oxygen (¹⁶O, ¹⁸O) and carbon (¹²C, ¹³C) isotopes were investigated. The main defect reactions are found to depend strongly on irradiation temperature and dose, as well as on impurity content and pre-history of the samples. Some new radiation-induced defects are revealed after irradiation at elevated temperatures as well as after a two-step (hot + room-temperature (RT)) irradiation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Silicon; Electron irradiation; Defects; Oxygen; Carbon

1. Introduction

Defects formed in CZ silicon during electron-irradiation and subsequent annealings have been the subject of extensive investigations [1–14]. Vacancies (V) and interstitials (I) produced in the crystal during irradiation act as vehicles for various diffusion mechanisms and interact with impurities to form complex defects. The experimental results

reported usually refer to irradiation at room-temperature (RT) or lower temperatures. During the following annealing procedures, new defect centers can arise where typically oxygen and carbon-related defects are the most frequently appearing. Several factors can have an influence on the final result of an electron irradiation treatment. Among them the most important are the energy and fluence of electrons, the temperature during irradiation and the amount of impurities.

In this report we used 2.5 MeV electrons in which case simple point defects should dominate over more complex and extended defects. We focus on defect formation in different temperature

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ranges. We also limit our presentation to the main impurities in CZ silicon, oxygen and carbon, in order to show examples of how defect engineering can be performed. The experimental technique used is infrared (IR) absorption and the defects are identified by absorption bands related to local vibrational modes (LVMs).

2. Experimental

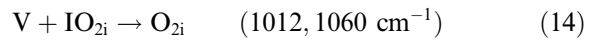
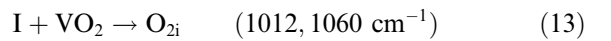
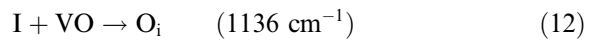
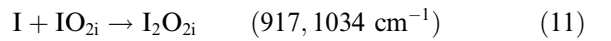
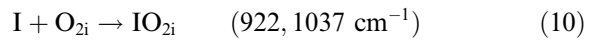
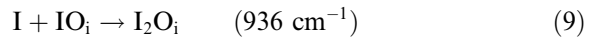
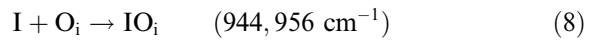
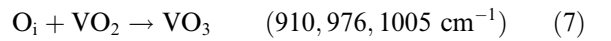
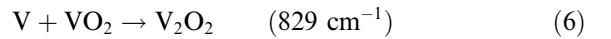
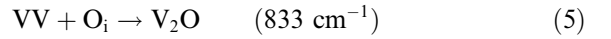
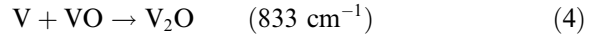
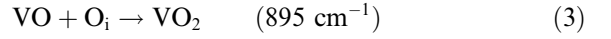
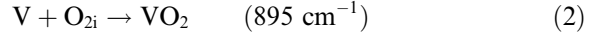
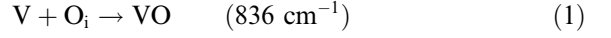
The samples used in this investigation were as-grown CZ-Si, doped with P to resistivities of about $60 \, \Omega \, \text{cm}$. The concentrations of interstitial oxygen ($[O_i]$) and substitutional carbon ($[C_s]$) were monitored by measuring the well-known absorption bands at 1107 [15] and $605 \, \text{cm}^{-1}$ [10], respectively. The $[O_i]$ in all the samples was about $1 \times 10^{18} \, \text{cm}^{-3}$. The $[C_s]$ in carbon-lean material was below the detection limit ($5 \times 10^{15} \, \text{cm}^{-3}$), while in carbon-rich Si it was about 5×10^{16} or $3 \times 10^{17} \, \text{cm}^{-3}$. We also included a few samples enriched with the isotopes ^{18}O and ^{13}C . The samples were polished to an optical surface on two sides and the dimensions were $10 \times 5 \times 3 \, \text{mm}^3$. The irradiation was performed in a temperature regulated holder in air at temperatures in the range 20–600 °C to different doses from 1×10^{16} to $5 \times 10^{18} \, \text{cm}^{-2}$, using 2.5 MeV electrons. The beam current was in the range 5–12 $\mu\text{A} \, \text{cm}^{-2}$. A few samples were irradiated at about 80 K in a liquid nitrogen cryostat. IR absorption analysis was carried out using a Bruker IFS 113v Fourier transform IR (FTIR) spectrometer. A spectral resolution of $0.5\text{--}1.0 \, \text{cm}^{-1}$ was used and the samples were measured at 10 K and at RT.

3. Results and discussion

3.1. Electron irradiation of carbon-lean CZ silicon

The main impurity in this material is oxygen ($\sim 10^{18} \, \text{cm}^{-3}$) and there are always some amounts ($10^{14}\text{--}10^{15} \, \text{cm}^{-3}$) of the oxygen dimer [16,17]. The important reactions to be considered should therefore involve oxygen, the oxygen dimer, vacancies

and self-interstitials. The set of reactions that should be discussed is therefore the following:



The LVMs are observed at 10 K, the wavenumbers for the reaction product are within brackets.

3.1.1. Irradiation temperatures below 300 K

Several IR absorption studies [3,5] have been performed in this range. Reactions (1) and (8) were found to be the dominant ones in CZ-Si irradiated in the temperature range 80–150 K and the bands at 944 and $956 \, \text{cm}^{-1}$ were assigned to different configurations of a bistable IO_i complex. This defect anneals out already at about 200–250 K with a partial transformation into another center which gives rise to a band at $936 \, \text{cm}^{-1}$ and is stable up to 350 K. When the irradiation dose was high, the band at $936 \, \text{cm}^{-1}$ was observed after low-temperature irradiation as well. We have recently [14] assigned this band to I_2O_i complex which is formed via reaction (9).

It should be noted that the 936 cm^{-1} band has never been observed in CZ-Si crystals irradiated with electrons at RT. At RT the IO_i complexes are not stable and their quasi-equilibrium concentration during electron irradiation is expected to be low. Hence, reaction (9) could not be efficient in this case. However, in the case of ion or neutron irradiation, due to a very high local density of primary defects produced at the collision event, reactions (8) and (9) could occur on the same time scale. This may account for the observation of the 936 cm^{-1} band in CZ-Si irradiated with fast neutrons at RT [9].

3.1.2. The temperature range 300–600 K

Most studies of irradiation-induced defects in CZ-Si are performed in this range. It is well known that the VO center and the divacancy are the most important defects in undoped or moderately doped materials. Isochronal and isothermal annealing studies have been used to study the reactions involved when a defect disappears. For the VO center, which anneals out at about 600 K, it is found [8] that typically besides dissociation, three processes are involved according to reactions (3), (4) and (12). The I in (12) is released from another defect during annealing and in (3) VO is mobile and trapped at an interstitial oxygen atom.

For the divacancy, which anneals out already around 550 K, similar reactions can be expected, a diffusion process where the divacancy is trapped according to (5) and a dissociation process. Disappearance of divacancies has been found recently [13] to correlate with a growth of the absorption band at 833 cm^{-1} that has allowed assigning it to V_2O complex.

3.1.3. Irradiation in the temperature range 600–750 K

At higher temperatures when the most common defects are unstable new reactions can be expected. It is well known from annealing experiments [1,7,8] that reaction (3) is important and that VO_2 is a very stable defect typically transferred to VO_3 at temperatures where diffusion of interstitial oxygen occurs. Irradiation at 620 and 670 K has revealed [11,12] that another defect identified as the oxygen dimer with vibrational absorption bands at 1012

and 1060 cm^{-1} is formed in concentrations comparable to VO_2 . The concentration of VO is found to be very low. Apparently, reaction (3) is still important and reaction (12) is strongly suppressed. The consequence of this will be that the equilibrium concentration of I during irradiation will be higher and reaction (13) may proceed efficiently. Due to high concentration of VO_2 , the vacancies may also interact with this defect (reaction (6)) that should result in formation of V_2O_2 . The appearance of the band at 829 cm^{-1} is typically observed after irradiation at around 620 K. This band is suggested to be related to the V_2O_2 defect. It is worth mentioning that the 829 cm^{-1} band has been observed previously [2,4] in irradiated CZ-Si upon annealing at 580–700 K and is known as the S_1 satellite of the A-center.

3.1.4. Irradiation above 750 K

Increasing the temperature to above 750 K seems not to give any new oxygen-related defects. The loss of O_i is decreasing as well as the concentration of VO_2 and O_{2i} [12,13]. Another observation is that there are no signs of oxygen precipitation. One interesting result is found from photoluminescence measurements [18] on samples irradiated above 800 K where luminescence bands called D1 and D2 appear. Apparently, the relatively high quasi-equilibrium concentration (estimated to 10^{13} cm^{-3}) of V and I during irradiation is causing dislocations to grow.

3.1.5. Irradiation treatment in two steps

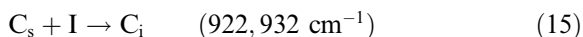
The possibility to produce high concentrations of oxygen dimers in carbon-lean crystals as described above with reaction (13) makes it possible to study interactions between the dimer and V and I by an additional irradiation at 300 K. In this case, along with reaction (1), reactions (2) (10) and (11) should be possible to observe before reaction (12) is dominating. The appearance of new LVM band pairs at $(922, 1032\text{ cm}^{-1})$ and $(917, 1034\text{ cm}^{-1})$ has been observed in such crystals [19]. The new defects, according to their generation kinetics, are suggested to be IO_{2i} and I_2O_{2i} , respectively. Studies of isotopically doped material show that these LVMs are all related to oxygen.

The new defects appear to be electrically active and anneal out below 550 K.

3.2. Electron irradiation of carbon-rich silicon

3.2.1. Irradiation temperatures below 300 K

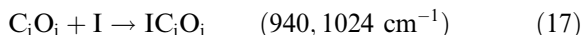
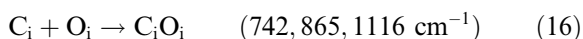
The most important reason for the difference between carbon-lean and carbon-rich materials during irradiation is a very efficient reaction called the Watkins replacement mechanism



Due to the efficiency of this reaction other reactions like (12) are suppressed and an increased concentration of VO and divacancies could be observed [4]. An additional reaction can be expected at higher doses when C_i traps an I and gives rise to LVMs at 959 and 966 cm^{-1} [20].

3.2.2. The temperature range 300–600 K

The effects of carbon in irradiated and annealed silicon have been widely studied [10]. Several oxygen–carbon-related defects as well as carbon–carbon defects have been identified. Examples of reactions in this range are

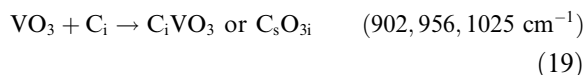
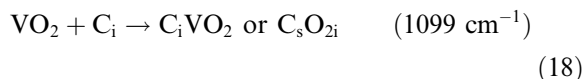


Reaction (16) gives rise to the well-known C3 center, which can trap an I according to (17) with a formation of the so-called C4 center. Our studies of materials enriched with ^{18}O isotope have shown that the LVMs at 742 (C3) and 1024 cm^{-1} (C4) are oxygen-related.

3.2.3. Irradiation in the temperature range 600–800 K

In this temperature range, VO_2 and VO_3 were found to be the dominant defects [12]. There were no signs of the oxygen dimer, which strongly appears in the carbon-lean samples. This defect was suggested to form according to reaction (13). VO_2 is present in rather high concentration so our conclusion is that the I is completely involved in another reaction, the Watkins replacement mechanism (15). It is reasonable to expect that generated mobile C_i atoms may interact with VO_2 and

VO_3 defects, i.e. the following reactions likely occur



A strong increase in the strength of the band at 1099 cm^{-1} has been observed with a maximum irradiation temperature at about 720 K. This band is suggested to originate from a symmetrical C_sO_{2i} defect where two oxygen atoms give rise to the same LVM. A family of new bands (902, 956 and 1025 cm^{-1}) has been revealed as well (Fig. 1), with the formation kinetics similar to that of VO_3 [12]. All three bands were found to be oxygen-related LVMs. The isotopic shifts as well as the temperature shift from RT to 10 K of the bands show a strong similarity with the three bands assigned to VO_3 . Our suggestion is therefore that we have a VO_3C defect formed via reaction (19). Such a defect could not be detected in carbon-rich Si irradiated at RT temperature and then annealed (see Fig. 1), probably due to a lack of free I and C_i atoms at the VO_3 formation temperatures.

3.2.4. Irradiation above 800 K

There is an extensive loss of both oxygen and carbon in the carbon-rich material and broad absorption bands probably related to precipitates are

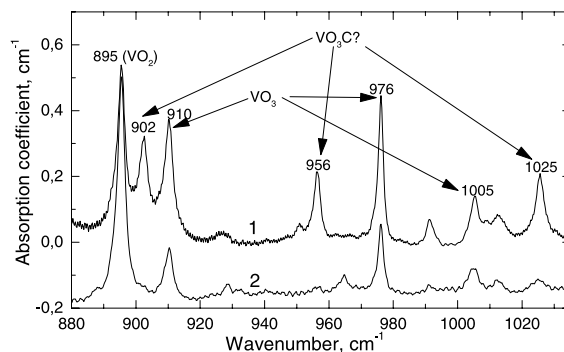


Fig. 1. Section of absorption spectrum measured at 10 K for carbon-rich CZ-Si ($[\text{C}_s] = 3 \times 10^{17} \text{ cm}^{-3}$) irradiated with electrons ($1 \times 10^{18} \text{ cm}^{-2}$) at (1) 770 K and (2) 300 K and then isochronally (30 min) annealed in 50 K steps up to 770 K.

appearing [12]. This is opposite to what is observed in carbon-lean material where the loss of O_i is very low above 800 K. At these temperatures oxygen diffusion is important in both materials and may be enhanced strongly by irradiation. However, in the carbon-lean material the conditions for forming nuclei that can start a precipitation process seem not to be present. The explanation could be that possible nuclei like VO_2 and VO_3 can interact with I and form dimers and trimers which are not stable at these temperatures. Another possibility is that dimers and trimers capture I but again the new defects are not stable. In the case of carbon-rich material different C–O complexes are known to be stable above 800 K and can act as nuclei for precipitation processes.

4. Summary

The results of the present study have shown that electron irradiation at elevated temperatures (>600 K) appears to be a way to strongly increase the concentration of some defects, making it possible to perform detailed studies of their LVMs. In combination with using samples isotopically doped with oxygen (^{16}O , ^{18}O) and carbon (^{12}C , ^{13}C) a deeper understanding of the defect chemistry of silicon has been achieved. By preparing samples with a high concentration of oxygen dimers and then performing a second irradiation, LVMs for a new group of defects has been found and those are suggested to be a combination of dimers and self-interstitials. Carbon is found to have a very strong effect on the defect reactions due to its high efficiency in trapping self-interstitials.

Acknowledgements

We thank TFR, KVA, SI, and FOA in Sweden for financial support. We also acknowledge fi-

nancial support from the grant INTAS-Belarus 97-824.

References

- [1] J.W. Corbett, G.D. Watkins, R.S. McDonald, *Phys. Rev.* 135 (1964) A1381.
- [2] A.K. Ramdas, M.G. Rao, *Phys. Rev.* 142 (1966) 451.
- [3] R.E. Whan, F.L. Vook, *Phys. Rev.* 153 (1967) 814.
- [4] A.R. Bean, R.C. Newman, R.C. Smith, *J. Phys. Chem. Solids* 31 (1970) 739.
- [5] A. Brelot, J. Charlemagne, in: J.W. Corbett, G.D. Watkins (Eds.), *Radiation Effects in Semiconductors*, Gordon and Breach, London, 1971, p. 161.
- [6] Y.H. Lee, J.W. Corbett, *Phys. Rev. B* 13 (1976) 2653.
- [7] J.L. Lindström, B.G. Svensson, *Mater. Res. Soc. Symp. Proc.* 59 (1986) 45.
- [8] B.G. Svensson, J.L. Lindström, *Phys. Rev. B* 34 (1986) 8709.
- [9] H.J. Stein, *Appl. Phys. Lett.* 55 (1989) 870.
- [10] G. Davies, R.C. Newman, in: T.S. Moss (Ed.), *Handbook on Semiconductors*, Vol. 3b, Elsevier, Amsterdam, 1994, p. 1557.
- [11] J.L. Lindström, T. Hallberg, D. Åberg, B.G. Svensson, L.I. Murin, V.P. Markevich, *Mater. Sci. Forum* 258–263 (1997) 367.
- [12] J.L. Lindström, T. Hallberg, J. Hermansson, L.I. Murin, V.P. Markevich, M. Kleverman, B.G. Svensson, *Solid State Phenom.* 69–70 (1999) 297.
- [13] J.L. Lindström, L.I. Murin, V.P. Markevich, T. Hallberg, B.G. Svensson, *Physica B* 273–274 (1999) 291.
- [14] L.I. Murin, V.P. Markevich, T. Hallberg, J.L. Lindström, M. Kleverman, J. Hermansson, B.G. Svensson, in: C.L. Claeys (Ed.), *Proceedings of the 2nd ENDEASD Workshop*, Stockholm, 2000, p. 248.
- [15] A. Baghdadi et al., *J. Electrochem. Soc.* 136 (1989) 2015.
- [16] J.L. Lindström, T. Hallberg, *Phys. Rev. Lett.* 72 (1994) 2729.
- [17] L.I. Murin, T. Hallberg, V.P. Markevich, J.L. Lindström, *Phys. Rev. Lett.* 80 (1998) 93.
- [18] I.A. Buyanova, T. Hallberg, L.I. Murin, V.P. Markevich, B. Monemar, J.L. Lindström, *Physica B* 273–274 (1999) 528.
- [19] J.L. Lindström, T. Hallberg, J. Hermansson, M. Kleverman, L.I. Murin, B. Komarov, V.P. Markevich, B.G. Svensson, *Physica B*, in press.
- [20] S.P. Chappel, R.C. Newman, *Semicond. Sci. Technol.* 2 (1987) 691.