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# IR studies of oxygen-related and carbon-related defects in Sn-doped silicon

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The ability of tin (Sn) to capture vacancies in silicon material attracts considerable interest in relation with electronic applications where radiation hardness is necessary. In this sense the full knowledge of the behavior of radiation-induced defects in Sn-doped Si is particularly important. The present report gives a systematic study of the evolution of the vacancy-oxygen ( $\text{VO}_n$ ,  $1 \leq n \leq 6$ ) defects and the carbon-oxygen ( $\text{C}_i\text{O}_i$ ) defect in electron-irradiated Sn-doped Cz-Si containing carbon. The radiation-induced defects and their reactions were investigated by Infrared Spectroscopy (IR) in the course of 20 min isochronal an-

neals from room temperature up to  $\sim 750$  °C. Interestingly, in Sn-doped Cz-Si samples we were able to monitor and study IR bands correlated with  $\text{VO}_5/\text{VO}_6$  defects. In particular, we tentatively attributed two bands at 1037, 1051  $\text{cm}^{-1}$  to the  $\text{VO}_5$  defect, and two other bands at 967, 1005  $\text{cm}^{-1}$  to the  $\text{VO}_6$  defect. Concerning carbon-related defects, our results show that the disappearance of the 862  $\text{cm}^{-1}$  band of the  $\text{C}_i\text{O}_i$  defect is accompanied in the spectra by the emergence of a band at 1048  $\text{cm}^{-1}$  previously correlated with a  $\text{C}_5\text{O}_{2i}$  structure.

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**1 Introduction** Carbon and oxygen are the main unintentionally added impurities in Si during growth. Carbon is an isovalent impurity in Si at substitutional sites, being electrically inactive. Due to its smaller covalent radius than that of Si ( $r_C = 0.77$  Å,  $r_{Si} = 1.17$  Å) carbon presence induces tensile strains in the Si lattice. On the other hand, oxygen is located interstitially in the Si lattice being also electrically inactive. Both impurities do not introduce levels in the gap. However, during the various processing stages of the Si material, for instance during irradiation, they participate in the production of electrically active complexes which affect the properties and behavior of Si.

The immediate products of irradiation are vacancies and self-interstitials. Oxygen is the main trap for vacancies leading to the formation of VO defect ( $\text{V} + \text{O}_i \rightarrow \text{VO}$ ) the so-called A-center [1, 2] which introduces a level at  $E_c - 0.17$  eV in the gap [3]. Carbon is the main trap for self-interstitials leading to the formation of the  $\text{C}_i\text{O}_i$  and the

$\text{C}_i\text{C}_s$  defects [4] in Si, through the Watkins exchange mechanism ( $\text{C}_s + \text{Si}_i \rightarrow \text{C}_i$ ). In Cz-Si the  $\text{C}_i\text{O}_i$  center is the dominant carbon-related defect giving rise to a level at  $E_v + 0.36$  eV in the gap [4, 5]. Both VO and  $\text{C}_i\text{O}_i$  defects are optically active. An IR band at 830  $\text{cm}^{-1}$  has been assigned to the VO defect [2]. At least six bands, with the strongest one at 860  $\text{cm}^{-1}$ , have been assigned to the  $\text{C}_i\text{O}_i$  defect [4].

The main reaction channel that VO defect participates upon annealing is that of the addition of oxygen atoms, leading to the formation of  $\text{VO}_n$  complexes [2, 6]. VO defect is stable to  $\sim 300$  °C and then becomes mobile to produce  $\text{VO}_2$  defect ( $\text{VO} + \text{O}_i \rightarrow \text{VO}_2$ ). An IR band at 885  $\text{cm}^{-1}$  has been assigned to the  $\text{VO}_2$  defect [6, 7].  $\text{VO}_2$  defect is stable to  $\sim 400$  °C and then it is captured by a mobile oxygen atom leading to the formation of  $\text{VO}_3$  defect ( $\text{VO}_2 + \text{O}_i \rightarrow \text{VO}_3$ ). Three IR bands at 904, 968 and 1000  $\text{cm}^{-1}$  have been assigned to the  $\text{VO}_3$  defect [6, 7].  $\text{VO}_3$  de-

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fect is stable to  $\sim 500$  °C and then by capturing an oxygen atom forms  $\text{VO}_4$  defect ( $\text{VO}_3 + \text{O}_i \rightarrow \text{VO}_4$ ) which is stable to  $\sim 550$  °C. Two bands at  $985$  and  $1009$   $\text{cm}^{-1}$  have been assigned to the  $\text{VO}_4$  defect [8]. At higher temperatures, where oxygen atoms are very mobile in the Si lattice,  $\text{VO}_5$  and  $\text{VO}_6$  defects are formed either from the addition of an oxygen atom via the reactions  $\text{VO}_4 + \text{O}_i \rightarrow \text{VO}_5$ ,  $\text{VO}_5 + \text{O}_i \rightarrow \text{VO}_6$  correspondingly, or with the participation of oxygen dimers by following the reactions  $\text{VO}_3 + \text{O}_{2i} \rightarrow \text{VO}_5$ ,  $\text{VO}_4 + \text{O}_{2i} \rightarrow \text{VO}_6$  [9, 10]. Other reactions are also possible as for example  $\text{V}_2\text{O}_3 \rightarrow \text{O}_i \rightarrow \text{V}_2\text{O}_4$ ,  $\text{V}_2\text{O}_3 + 2\text{O}_i \rightarrow \text{V}_2\text{O}_5$ ,  $\text{V}_3\text{O}_2 + \text{O}_i \rightarrow \text{V}_3\text{O}_3$ , etc leading generally to the formation of  $\text{V}_n\text{O}_m$  defects [8]. A number of bands have been generally correlated with the  $\text{VO}_5/\text{VO}_6$  defects [9, 10] or/and with  $\text{V}_n\text{O}_m$  structures [8]. Any particular assignment of bands to the  $\text{VO}_5$  or the  $\text{VO}_6$  defect has not been made so far. Furthermore the thermal stability of the  $\text{VO}_5$  and  $\text{VO}_6$  defects has not been investigated.

The formation of the  $\text{C}_i\text{O}_i$  defects occurs when a mobile  $\text{C}_i$  atom is trapped by an  $\text{O}_i$  atom ( $\text{C}_i + \text{O}_i \rightarrow \text{C}_i\text{O}_i$ ). It has been reported that the  $\text{C}_i\text{O}_i$  defect, which is stable up to  $300$  °C, is then destroyed either by dissociation or by reaction with another defect [4, 11].

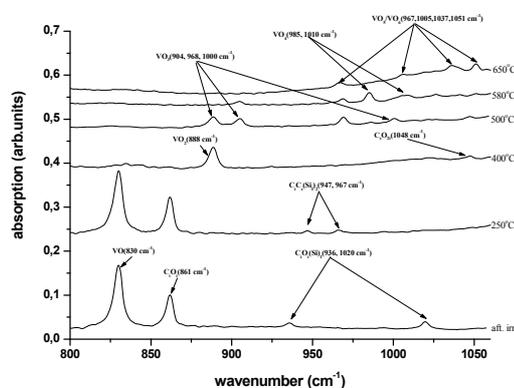
Doping of Si with isovalent impurities improves the performance of devices for certain applications. Due to its larger covalent radius than that of Si ( $r_{\text{Sn}} = 1.41$  Å,  $r_{\text{Si}} = 1.17$  Å) Sn acts as a trap for vacancies and small impurity atoms as for example carbon. Noticeably, the formation of SnV [12] and  $\text{SnC}_i$  [13] defects has been reported in the literature. On the other hand, C reacts promptly with self-interstitials. Thus, after the irradiation the simultaneous presence of carbon and tin in the Si lattice affects the number of vacancies and self-interstitials available to participate in the various reactions and in particular those involving C and O impurities. Therefore, the formation of oxygen-related and carbon-related defects is expected to be affected.

Given in addition the variety of reactions that carbon interstitials participate and their sensitivity in the annealing behaviour under various conditions [4, 14–16] it would be interesting to investigate the interaction between radiation-induced defects and their behaviour upon thermal anneals in Si material containing carbon and tin. The main objective of this work was to study the effect of Sn doping in the behaviour of oxygen-related and carbon-related defects in Si and in particular those of  $\text{VO}_n$  and  $\text{C}_i\text{O}_i$  defects.

**2 Experimental details** The Si material used in this work was Czochralski crystals doped with tin (Sn). The Sn concentration was  $[\text{Sn}]_0 = 3 \times 10^{17} \text{ cm}^{-3}$ . The oxygen and carbon concentrations were  $[\text{O}_i]_0 = 9.6 \times 10^{17} \text{ cm}^{-3}$  and  $[\text{C}_i]_0 = 4.7 \times 10^{17} \text{ cm}^{-3}$ , respectively. The samples were irradiated with 2 MeV electrons at  $95$  °C using the Dynamitron accelerator at Takasaki-JAERI (Japan). The irradiation dose was  $1 \times 10^{18} \text{ cm}^{-2}$ . The evolution of the radiation induced defects were studied by 20 min isochronal anneals in steps of  $10$  °C up to  $750$  °C. After each annealing step, the

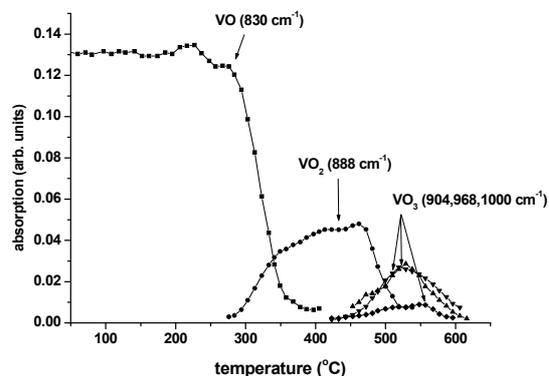
IR spectra were recorded at room temperature by means of a FTIR spectrometer with a resolution of  $1 \text{ cm}^{-1}$ . The two phonon intrinsic absorption was always subtracted by using a float-zone sample of equal thickness.

**3 Experimental results and discussion** Figure 1 presents sections of the IR spectra of the Sn-doped samples immediately after irradiation and at various selective temperatures in a course of the isochronal anneals. A number of defects were observed. Actually, the well-known defects VO ( $830 \text{ cm}^{-1}$ ),  $\text{VO}_2$  ( $888 \text{ cm}^{-1}$ ),  $\text{VO}_3$  ( $904, 968, 1000 \text{ cm}^{-1}$ ),  $\text{VO}_4$  ( $985, 1009 \text{ cm}^{-1}$ ) are present in the spectra together with the less known bands at  $967, 1005, 1037$  and  $1051 \text{ cm}^{-1}$  which appear above  $550$  °C. Figures 2 and 3 show the

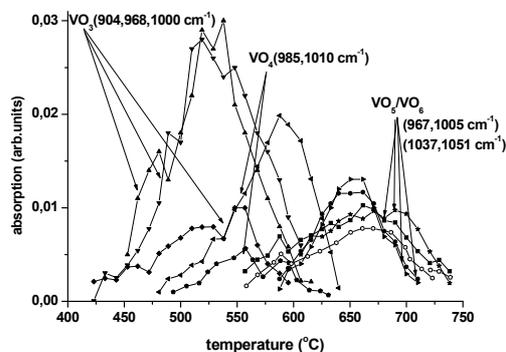


**Figure 1** Fragments of the IR spectra at characteristic temperatures for the Sn-doped Si samples.

thermal evolution of all the bands in the samples. Noticeably, at room temperature the two bands at  $1037$  and  $1051 \text{ cm}^{-1}$  have been seen previously and attributed to either  $\text{V}_n\text{O}_m$  structures [8] and/or to  $\text{VO}_5/\text{VO}_6$  [9, 6] defects. The two other bands at  $967$  and  $1005 \text{ cm}^{-1}$  have also been detected previously [8] in neutron irradiated Si and correlated with  $\text{V}_n\text{O}_m$  defects. On the other hand, measurements at cryogenic temperatures of electron-irradiated Si have detected additional bands at  $992, 1024,$  and  $1108 \text{ cm}^{-1}$  which were correlated [9] with the  $\text{VO}_5/\text{VO}_6$  defects. In the present detailed work we have observed that the bands at  $1037$  and  $1051 \text{ cm}^{-1}$  appear together in the spectra upon annealing of the  $\text{VO}_4$  defects and disappear also together just above  $700$  °C. Another pair of bands at  $967$  and  $1005 \text{ cm}^{-1}$  also appear together in the spectra upon disappearing of the  $\text{VO}_4$  defect and decay out also together about  $740$  °C. Judging from their thermal stability we tentatively correlated the first pair of bands at  $1037, 1051 \text{ cm}^{-1}$  with the  $\text{VO}_5$  defect and the other pair at  $967$  and  $1005 \text{ cm}^{-1}$  to the  $\text{VO}_6$  defect. In this attribution we have taken into account that all the bands emerge in the spectra upon annealing of the  $\text{VO}_4$  defect and therefore it is more reasonable to correlate them with  $\text{VO}_4$  defects, instead of the more general attribution to  $\text{V}_n\text{O}_m$  structures. From the general behavior of the thermal stability of the  $\text{VO}_n$  ( $1 \leq n \leq 4$ ), where the larger the number



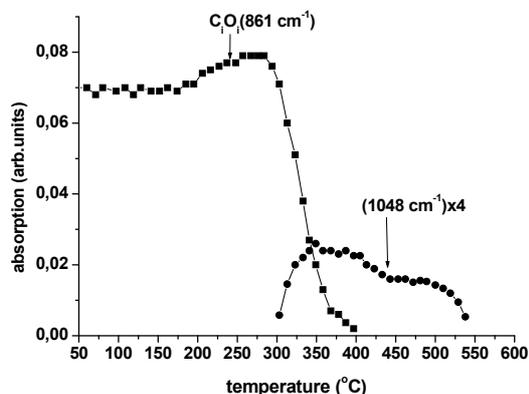
**Figure 2** The thermal evolution of VO, VO<sub>2</sub>, and VO<sub>3</sub> defects in the Sn-doped Si samples.



**Figure 3** The thermal evolution of VO<sub>3</sub>, VO<sub>4</sub>, and VO<sub>5</sub>/VO<sub>6</sub> defects in the Sn-doped Si samples.

n of the oxygen atoms the higher the annealing temperature of the structure, we attribute the first pair of bands (1037, 1051 cm<sup>-1</sup>) to the VO<sub>5</sub> defect annealing out at ~710 °C and the second pair of bands at (967, 1005 cm<sup>-1</sup>) to the VO<sub>6</sub> defect which anneals out at a higher temperature (~750 °C). It is worth noting that the above four weak bands of VO<sub>5</sub> and VO<sub>6</sub> defects appear in the IR spectra of neutron irradiated Cz-Si received at room temperature [8], as well as in the spectra of electron irradiated Si received at He liquid temperatures [9]. Understandingly, in neutron irradiation the concentration of defects is comparably larger than that of electron irradiation, allowing their detection at room temperatures measurements in the former case which may not be detected in the latter case. Also measurements at cryogenic temperatures allow for weak signals to be seen in the IR spectra, although may pass undetected in room temperature measurements. We note that the two bands at 947 and 966 cm<sup>-1</sup>, arising in the spectra in the course of isochronal anneals at T = 250 °C, are most probably related to the C<sub>i</sub>C<sub>s</sub>(Si<sub>i</sub>)<sub>2</sub> defect [17]. Figure 4 shows the evolution of the C<sub>i</sub>O<sub>i</sub> defect in the Sn-doped Si samples. Interestingly, the

disappearance of the C<sub>i</sub>O<sub>i</sub> band is accompanied in the spectra by the emergence of another band at 1048 cm<sup>-1</sup>. This band is very weak and has not been reported in early works, see for example Ref. [4]. Recently, this band has been detected [18] and correlated with a C<sub>s</sub>O<sub>2i</sub> structure. Possible formation reaction may be C<sub>i</sub>O<sub>i</sub> + VO → C<sub>s</sub>O<sub>2i</sub>. Both the VO and C<sub>i</sub>O<sub>i</sub> defects anneal out at around the same temperature ~300 °C. It deserves noting at this point that two bands at 1052 and 1099 cm<sup>-1</sup> have been reported in Si material containing carbon either non-irradiated [19] or irradiated at elevated temperatures in the range 400-600 °C [20]. In these studies [19, 20] the measurements were carried out at cryogenic temperatures. The bands were correlated with the C<sub>s</sub>O<sub>2i</sub> defect. The suggested formation reaction was VO<sub>2</sub> + C<sub>i</sub> → C<sub>s</sub>O<sub>2i</sub> [20]. In our studies, the 1099 cm<sup>-1</sup> was not detected. However, its weak signal could have been masked in our RT measurements by the very strong signal of O<sub>i</sub> in this region.



**Figure 4** The thermal evolution of C<sub>i</sub>O<sub>i</sub> and C<sub>s</sub>O<sub>2i</sub> in the Sn-doped Si samples.

Based on the above results a possible explanation of the role of the tin impurity on the evolution of the oxygen-related radiation-induced defects VO<sub>n</sub> (1 ≤ n ≤ 6) and in particular on the formation of the VO<sub>5</sub>/VO<sub>6</sub> defects could be envisaged. It has been reported that the diffusion constant of oxygen is considerably enhanced in Si doped with tin [21]. This is possibly due to the elastic strains introduced in the lattice, as a result of the larger covalent radius of Sn than that of the Si atoms. This may lead to a decrease of the potential barrier for the diffusion of the interstitial oxygen atom. Consequently, the trapping rates of oxygen in the reactions VO<sub>4</sub> + O<sub>i</sub> → VO<sub>5</sub>, VO<sub>5</sub> + O<sub>i</sub> → VO<sub>6</sub>, become larger leading to an enhanced formation of the VO<sub>5</sub> and VO<sub>6</sub> defects. Similarly, the reactions VO<sub>3</sub> + O<sub>2i</sub> → VO<sub>5</sub> and VO<sub>4</sub> + O<sub>2i</sub> → VO<sub>6</sub>, which involve dimers are affected. Dimers are much faster diffusion species than single oxygen atoms. The formation of dimers and also their diffusivity is also expected to be enhanced. Thus, larger concentrations of VO<sub>5</sub> and VO<sub>6</sub> defects are produced, making them detectable in the IR spectra. On the other hand, the role of tin on the evolution of carbon-related defects and in par-

ticular on the formation of the  $C_sO_{2i}$  defect cannot be definite extracted from these measurements. The carbon content of the samples was quite high and the detection of the  $1048\text{ cm}^{-1}$  band of the defect may be related simply with this. Of course, Sn is an efficient trap of vacancies, allowing for more self-interstitials to be trapped by substitutional carbon atoms in the course of irradiation. This is expected to lead to the formation of C-related defects in larger concentrations, something which is reflected in the spectra with the enhanced formation of the  $C_sO_{2i}$  defect.

**4 Conclusions** We have studied the evolution of  $VO_n$  and  $C_iO_i$  defects in Si material containing carbon and tin by FTIR. We found that signals from  $VO_n$  structures with  $n>4$  are present in the IR spectra and two pairs of bands at  $(1037, 1058\text{ cm}^{-1})$  and  $(967, 1005\text{ cm}^{-1})$  have been correlated with the  $VO_5$  and  $VO_6$  defects, respectively. Furthermore the decay out of the  $860\text{ cm}^{-1}$  band of  $C_iO_i$  defects was found to be accompanied in the spectra by the emergence of another band at  $1048\text{ cm}^{-1}$  attributed to a  $C_sO_{2i}$  structure. An explanation of the role of tin in the evolution of defects was offered.

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