The Effect of Tin Impurities in the Annealing of Vacancy-Oxygen Related Defects in Czochralski Si.

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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 induces tensile strains in the Si lattice. On the other hand, oxygen is located interstitially in the Si lattice being also electrically inactive. Although both impurities do not introduce electrical levels in the gap, however during processing or/and irradiation give rise to electrically active complexes which affect the properties and behaviour of Si material. Furthermore, 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_{Sn} = *1.41* Å, r_{Si} = *1.17* Å) Sn acts as a trap for vacancies and small impurity atoms as for example carbon. In any case, the simultaneous presence of carbon and tin in the Si lattice is expected to affect the balance of vacancies and self-interstitial defects available due to irradiation and thermal treatments and therefore affect the formation of oxygen-related defects.

The immediate products of irradiation are vacancies and self-interstitials. Oxygen is the main trap for vacancies leading to the formation of VO defect ($V+O_i \rightarrow VO$) the so-called A-center [1, 2] which introduces a level at Ec-0.17 eV in the gap [3]. Carbon is the main trap for self-interstitials leading to the formation of the C_iO_i and the C_iC_s defects [4] in Si, through the Watkins exchange mechanism ($C_s + Si_I \rightarrow C_i$). In Cz-Si the C_iO_i center is the dominant carbon-related defect giving rise to a level at Ev+0.36 eV in the gap [4, 5]. Both VO and C_iO_i defects are optically active. An IR band at 830 cm^{-1} has been assigned to the VO defect [2]. At least six bands, with the strongest one at 860 cm^{-1}, have been assigned to the C_iO_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 VO_n complexes [2, 6]. VO defect is stable to ~ 300 ^oC and then becomes mobile to produce VO_2 defect ($VO+O_i \rightarrow VO_2$). An IR band at 885 cm^{-1} has been assigned to the VO_2 defect [5, 6]. VO_2 defect is stable to ~ 400^oC and then it is captured by a mobile oxygen atom leading to the formation of VO_3 defect ($VO_2+O_i \rightarrow VO_3$). Three IR bands at 904, 968 and 1000 cm^{-1} have been assigned to the VO_3 defect [5, 6]. VO_3 defect is stable to ~ 500 ^oC and then by capturing an oxygen atom forms VO_4 defect ($VO_3+O_i \rightarrow VO_4$) which is stable to ~ 550 ^oC. Two bands at 985 and 1009 cm^{-1} have been assigned to the VO_4 defect [7]. At higher temperatures, where oxygen atoms are very mobile in the Si lattice, VO_5 and VO_6 defects are formed either from the addition of an oxygen atom via the reactions $VO_4+O_i \rightarrow VO_5$, $VO_5+O_i \rightarrow VO_6$ correspondingly, or with the participation of oxygen dimmers by following the reactions $VO_3+O_{2i} \rightarrow VO_5$, $VO_4+O_{2i} \rightarrow VO_6$ [8, 9]. Other reactions are also possible as for example $V_2O_3+O_i \rightarrow V_2O_4$, $V_2O_3 + 2O_i \rightarrow V_2O_5$, $V_3O_2 + O_i \rightarrow V_3O_3$, etc leading generally to the formation of V_nO_m defects [7]. A number of bands have been generally correlated with the VO_5/ VO_6 defects [8, 9] or/and with V_nO_m structures [7]. Any particular assignment of bands to the VO_5 or the VO_6 defect has not been made so far. Furthermore the thermal stability of the VO_5 and VO_6 defects has not been investigated. The main objective of this work was to study the effect of Sn doping in the behaviour of vacancy-oxygen related defects in Si.

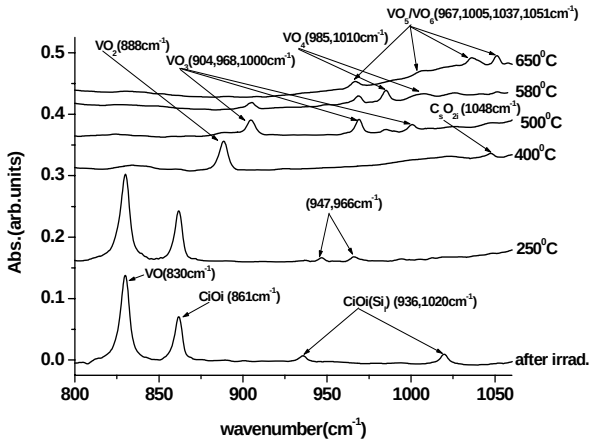

Figure 1 Fragments of the IR spectra at characteristic temperatures for the Sn-doped Si samples.

The Si material used in this work was Czochralski crystals doped with tin (Sn). The Sn concentration was $[Sn]_o=3x10^{17}$ cm^{-3}. The oxygen and carbon concentrations were $[O_i]_o=9.6 \times 10^{17}$ cm^{-3} and $[C_s]_o=4.7x10^{17}$ cm^{-3}, respectively. The samples were irradiated with 2 MeV electrons at 95 ^oC using the Dynamitron accelerator at Takasaki-JAERI (Japan). The irradiation dose was $1x10^{18}$ cm^{-2}. The evolution of the radiation induced defects were studied by 20 min isochronal anneals in steps of 10 ^oC up to 750 ^oC. After each annealing step, the IR spectra were recorded at room temperature by means of a FTIR spectrometer with a resolution of 1cm^{-1}. Fig. 1

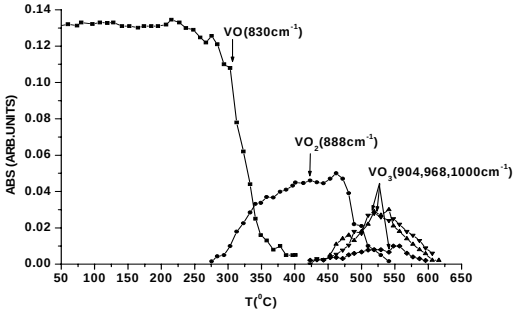

Figure 2 The thermal evolution of VO, VO_2, and VO_3 defects in the Sn-doped Si samples.

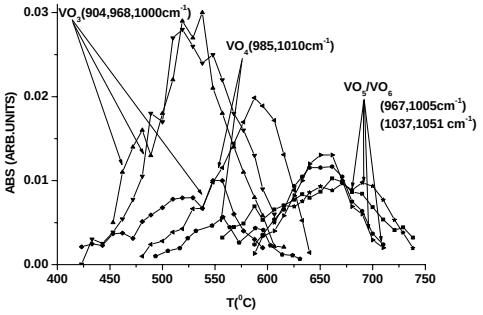

Figure 3 The thermal evolution of VO_3, VO_4, and VO_5/VO_6 defects in the Sn-doped Si

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 cm^{-1}), VO_2 (888 cm^{-1}), VO_3 (904, 968, 1000 cm^{-1}), VO_4 (985, 1009 cm^{-1}) are present in the spectra together with the less known bands at 967, 1005, 1037 and 1051 cm^{-1} which appear above 550 ^oC. Figs 2 and 3 show the thermal evolution of all the bands in the samples. Noticeably, at room temperature the two bands at 1037 and 1051 cm^{-1} have been seen previously and attributed to either V_nO_m structures [7] and/or to VO_5/ VO_6 [8, 5] defects. The two other bands at 967 and 1005 cm^{-1} have also been detected previously [7] in neutron irradiated Si and correlated with V_nO_m defects. On the other hand, measurements at cryogenic temperatures of electron-irradiated Si have detected additional bands at 992, 1024, and 1108 cm^{-1} which were correlated [8] with the VO_5/ VO_6 defects. In the present detailed work we have observed that the bands at 1037 and 1051 cm^{-1} appear together in the spectra upon annealing of the VO_4 defects and disappear also together just above 700 ^oC. Another pair of bands at 967 and 1005 cm^{-1} also appear together in the spectra upon disappearing of the VO_4 defect and decay out also together about 740 ^oC. Judging from their thermal stability we tentatively correlated the first pair of bands at 1037, 1051 cm^{-1} with the VO_5 defect and the other pair at 967 and 1005 cm^{-1} to the VO_6 defect. In this attribution we have taken into account that all the bands emerge in the spectra upon annealing of the VO_4 defect and therefore it is more reasonable to correlate them with VO_4 defects, instead of the more general attribution to V_nO_m structures. From the general behaviour of the thermal stability of the VO_n ($1 \leq n \leq 4$), where the larger the number n of the oxygen atoms the higher the annealing temperature of the structure, we attribute the first pair of bands (1037, 1051 cm^{-1}) to the VO_5 defect annealing out at ~710 ^oC and the second pair of bands at (967, 1005 cm^{-1}) to the VO_6 defect which anneals out at a higher temperature (~750 ^oC). It is worth noting that the above four weak bands of VO_5 and VO_6 defects appear in the IR spectra of neutron irradiated Cz-Si received at room temperature [7], as well as in the spectra of electron irradiated Si received at He liquid temperatures [8]. Understandingly, in neutron irradiation the concentration of defects is comparably larger than that of electron irradiation, allowing their detection at room temperature 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.

In summary, we have studied the evolution of VO_n defects in Si material containing carbon and tin by FTIR. Noticeably, signals from VO_n structures with $n>4$ are present in the IR spectra of Sn-doped Si and two pairs of bands at (1037, 1058 cm^{-1}) and (967, 1005 cm^{-1}) were correlated with the VO_5 and VO_6 defects, respectively. The effect of Sn presence in the Si lattice was considered and it was found that Sn plays an important role in the enhanced formation of VO_5/ VO_6 defects.

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