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The effect of thermal treatments on the annealing behaviour of oxygen-vacancy complexes in irradiated carbon-doped silicon

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Abstract. Cz-grown, carbon-doped silicon samples were irradiated by fast neutrons. We investigated the annealing behaviour of oxygen-related defects, by infrared spectroscopy. We studied the reaction channels leading to the formation of various V_mO_n defects and in particular the VO_n defects formed by the accumulation of oxygen atoms and vacancies in the initially produced by the irradiation VO defects, as the annealing temperature ramps upwards. We mainly focused on bands appearing in the spectra above 450 °C. A band at 1005 cm^{-1} is found to be the convolution of two bands at 1004 and 1009 cm^{-1}. The latter band has the same thermal stability with the 983 cm^{-1} of the VO_4 defect and therefore is also attributed to this defect. The former band has the same thermal stability with three other bands at 965, 1034 and 1048 cm^{-1}. These four bands may be attributed to VO_n (n=5,6) defects, although other V_mO_n complexes are also potential candidates. Furthermore, we found that pre-treatments of the samples at 1000 °C, with or without the application of high hydrostatic pressure lead to an increase in the concentration of the VO_2, VO_3 and generally VO_n defects in comparison with that of the untreated samples.

Introduction

The more we know about defect characteristics and their behaviour in general the better we understand and connect their microscopic features with macroscopic device properties. The behaviour of the various V_mO_n defects in silicon has been extensively investigated in the literature. These defects appear in silicon as a result of thermal treatments or/and as a result of radiation damage and subsequent thermal anneals. Although the V_mO_n defects have been studied [1-7] both experimentally and theoretically and most of them are well-known, there are still some points related to them which are not understood. More specifically, there are large V_mO_n clusters for which the corresponding infrared bands in the spectra have not been positively identified so far, although on the other hand, there are signals in the spectra which remain unassigned. This work is a contribution towards the completion of the picture concerning the identification of certain infrared bands and more specifically their connection with large V_mO_n clusters. It is also known that thermal pre-treatments with or without the application of high hydrostatic pressure performed prior to irradiation affect [8,9] the formation and the annealing behaviour of oxygen-vacancy-related defects in silicon. In this work, we also study the annealing behaviour of the V_mO_n defects in initially pre-treated samples and from the observed differences in comparison with the initially untreated samples we try to cast new light on the mechanisms governed the accumulation of oxygen atoms and vacancies in the initial VO defect core formed by the irradiation. Notice that at annealing temperatures higher than 450 °C there exist more than one reaction channels that could operate to form a V_mO_n complex, depending on the initial oxygen content, the dopant impurity, the kind of irradiation and any particular thermal pre-treatments of the Si material.

Experimental details

Cz-grown ($[O_i]_o$= 7.2x10^{17} cm^{-3}), carbon-doped ($[C_s]_o$= 1.72x10^{17} cm^{-3}) pre-polished Si samples of 2 mm thickness, purchased from MEMC, were used. One sample was treated at 1000 °C at atmosphere pressure (1 bar), for 5h and another one at 1000 °C, under high hydrostatic pressure (11 kbars), for 5h. Afterwards, one as-grown sample and the above two treated samples were subjected to 5 MeV fast neutron irradiation at a fluence of 10^{17} n/cm^2. The temperature of irradiation was just below 50 °C. Then, 20 min isochronal anneals, of 10 °C steps were carried out in open furnaces in the temperature range of 50-750 °C. After each annealing step the infrared spectra of the defects introduced in the samples were recorded with a Jasco-700 IR spectrometer of dispersive kind, operating at room temperature.

Experimental results and discussion

For device processing in the electronic industry it is necessary to perform heat treatments at high temperatures and the 1000 °C is a commonly used temperature for diffusion processes in Si material. Treatments at this temperature however, introduce [10,11] oxygen precipitates and other structural defects the appearance of which is enhanced [12] by the application of high hydrostatic pressure. It is therefore of interest to know the effect of thermal treatments at 1000 °C on the behaviour of the radiation-induced defects in Si. The reason of using C-doped samples was to increase the concentration of the VO centers produced by the irradiation. Actually, carbon is a selective trap of Si_i’s [13], and therefore the annihilation of vacancies by Si_i’s in the course of the radiation process ($V+Si_i \rightarrow \emptyset$) is expected to be reduced. As a result more vacancies would be available for pairing with O_i ($V+O_i \rightarrow VO$) and therefore the concentration of the VO centers and that of the subsequent formed VO_n centers during anneals is expected to be higher. This facilitates the study of weak signals in the spectra. Carbon-related radiation-induced centers have been studied elsewhere [14] and they will not concern the present work.

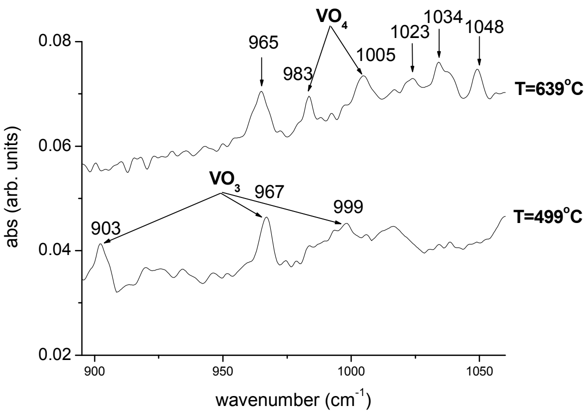

Fig. 1 Section of absorbance spectra of neutron-irradiated Si at two characteristic temperatures.

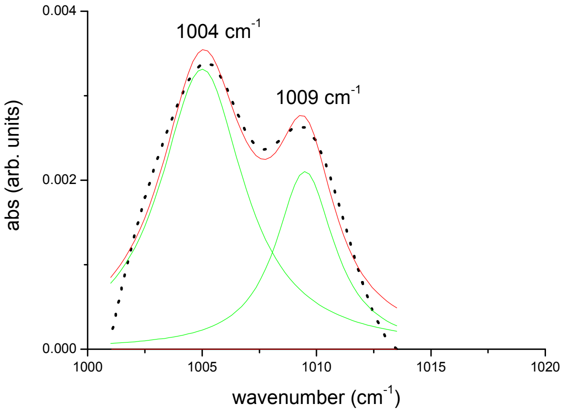

Fig. 2 Lorentzian profiles of the 1005 cm^{-1} band.

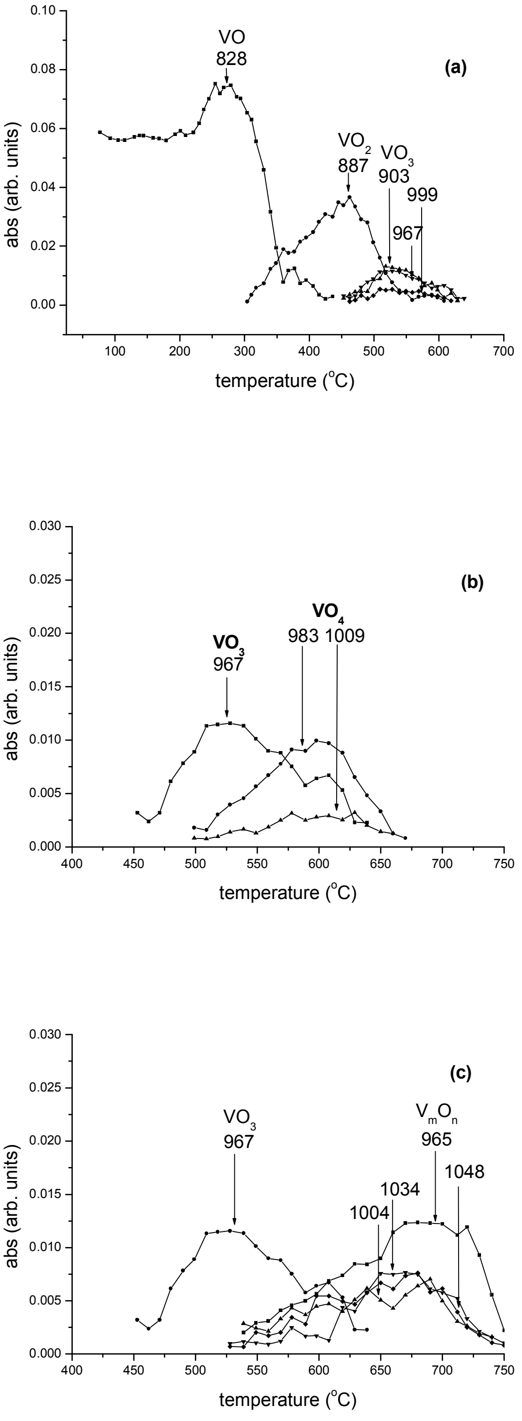

Fig. 3 The thermal evolution curves of the a) VO, VO_2 and VO_3 defects, b) VO_3 and VO_4 defects and c) the various V_mO_n related bands in as-grown, neutron-irradiated Si.

In the untreated material the VO defects (828 cm^{-1}) start to disappear around 300 °C to form VO_2 defects (887 cm^{-1}). VO_2 defects disappear at around 450 °C to form VO_3 defects (903, 967 and 999 cm^{-1}). Up to this temperature the VO and the VO_2 defects migrate in the lattice and by capturing O_i atoms form the VO_2 and the VO_3 defects, correspondingly. However, above 450 °C O_i atoms begin to migrate and the formation of larger VO_n ($n \geq 4$) complexes occurs. But the picture is not so clear [7]. Actually, a band at 983 cm^{-1} arising in the spectra at slightly higher temperatures than the appearance of the three bands of the VO_3 defect has been attributed [3] to a VO_3 defect modified by one more oxygen atom, although other studies have attributed [2] two bands at 983 and 1004 cm^{-1} to the VO_4 defect. Fig. 1 shows IR spectra at two characteristics temperatures, 499 and 639 °C, where the VO_3 and VO_4 bands together with bands of more complex V_mO_n defects appear, correspondingly. In our studies a complex band at ~1005 cm^{-1} is found, by making Lorentzian profiles (Fig. 2), to be the convolution of two bands at 1004 cm^{-1} and 1009 cm^{-1}. Fig. 3 presents the thermal evolution of various oxygen-vacancy bands in the untreated Si material after the neutron irradiation. The pair of bands at 983 and 1009 cm^{-1} has the same thermal stability (Fig. 3b) and is attributed to the VO_4 defect. On the other hand, the 1004 cm^{-1} band persists in the spectra after the disappearance of the 983 and 1009 cm^{-1} bands, and has the same thermal stability and evolution (Fig.3c) with three other bands at 965, 1034 and 1048 cm^{-1}. At 450 °C, the abundance of oxygen atoms allows the simultaneous formation of the VO_5 and the VO_6 defects through the realization of the additional reactions $VO_3+2O_i \rightarrow VO_5$, $VO_4+O_i \rightarrow VO_5$ and $VO_4+2O_i \rightarrow VO_6$. However, around 440 °C centers as the V_3O and the V_2O_2, and around 475 °C centers as the V_3O_2 become thermally unstable [15,16]. Thus reactions as the $V_2O_3+O_i \rightarrow V_2O_4$, $V_2O_3+2O_i \rightarrow V_2O_5$, $V_3O_2+O_i \rightarrow V_3O_3$, etc. are possible.

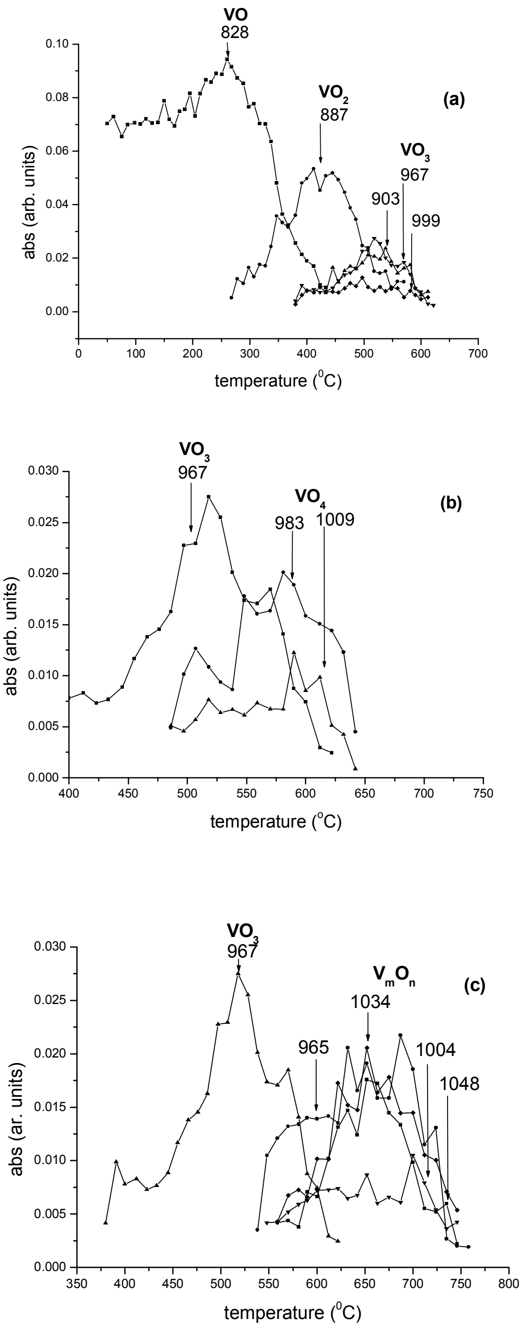

Fig. 4 The thermal evolution curves of the a) VO, VO_2 and VO_3 defects, b) VO_3 and VO_4 defects and c) the various V_mO_n related bands in pre-heat treated at 1000 °C, neutron-irradiated Si.

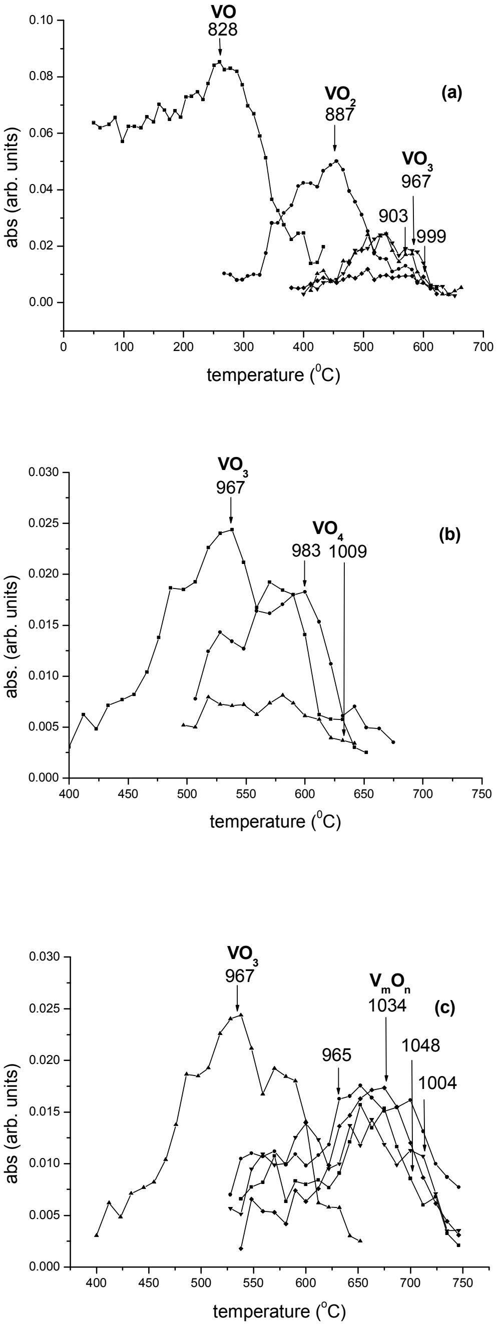

Fig. 5 The thermal evolution curves of the a) VO, VO_2 and VO_3 defects, b) VO_3 and VO_4 defects and c) the various V_mO_n related bands in pre-heat treated at 1000 °C, under hydrostatic pressure of 11 kbars, neutron-irradiated Si.

The pentavacancy (V_5) complex is also stable up to ~ 450 °C [17]. Thus the bands at 965, 1004, 1034 and 1048 cm^{-1} are possibly correlated with either the VO_5 and the VO_6 defects, or/and with large V_mO_n clusters produced by reactions where the V_3O, V_2O_2, V_3O_2 and the V_5 defects participate. It is worth noting that a weak band at 1023 cm^{-1} (Fig. 1) appearing in the spectra in the temperature range of 540-750 °C could also be tentatively attributed to a large V_mO_n complex.

In the samples pre-treated at 1000 °C at atmospheric pressure and at high hydrostatic pressure of ~ 11 kbars the same IR bands appear in the spectra as in the initially untreated sample. However, the amplitudes of the various V_mO_n related bands are different. Figs. 4 and 5 show the evolution with temperature of the amplitudes of the VO, VO_2, VO_3, VO_4 and of various V_mO_n defects for the initially thermally treated samples at 1000 °C without and with the application of external pressure, correspondingly. It is immediately seen that the amplitude of the VO_2 and the VO_3 defects (Figs. 4a and 5a) are higher in the pre-treated samples in comparison with those of the untreated sample (Fig. 3a). The VO_2 defects form at ~ 300 °C when mobile VO defects are captured by oxygen interstitial atoms ($VO+O_i \rightarrow VO_2$). Since the oxygen concentration of the material is much higher than that of the VO defect, the concentration of the VO_2 defects depends on the amount of the VO defects transforming to the VO_2 defects. However, at ~ 300 °C VO defects also interact with Si_i's ($VO+Si_i \rightarrow O_i$). Sources of Si_i's are large defect clusters [18] as well as the oxygen precipitate/Si matrix interface, formed due to the thermal pre-treatments [10,11]. The presence of carbon enhances the precipitation process [11,19]. Apparently, the concentration of the VO_2 defect depends on the balance between the above two reactions. In the case of carbon-doped material most of the Si_i's are expected to be trapped by carbon substitutional atoms. As a result, the contribution of the reaction $VO+Si_i \rightarrow O_i$ is diminished allowing for more VO defects to transform to VO_2 defects. Further on, the larger the concentration of the VO_2 defects, the larger the concentration of the VO_3 defects, assuming that the VO_3 defects form by the capture of the VO_2 defects by O_i atoms.

Summary

The status of the V_mO_n defects in carbon-doped, Cz-grown neutron-irradiated Si, was studied. A band at 1005 cm^{-1} was found to be the contribution of two bands at 1004 and 1009 cm^{-1}. The band at 1009 cm^{-1} has the same annealing behaviour as that of the 983 cm^{-1} band of the VO_4 defect and therefore is also attributed to the latter defect. The band at 1004 cm^{-1} has the same annealing behaviour as other bands at 965, 1034 and 1048 cm^{-1}. These four bands should be related to large defect clusters as for example the VO_5, VO_6, V_3O_3, V_3O_4, V_2O_5 etc. structures. Furthermore we found that the amplitudes of the VO_2 and VO_3 defects in pre-treated material at 1000 °C, with or without the application of high hydrostatic pressure are larger than that in the untreated material. The phenomenon was attributed to the presence of carbon which facilitates the transformation of the VO to the VO_2 defect indirectly by capturing Si_i's and therefore diminishing the destruction of the VO centers by them.

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