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Carbon-related complexes in neutron-irradiated silicon

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Abstract

In this work, we have studied point defects in carbon-doped Si material, irradiated by fast neutrons, via the observation of the Infrared absorption spectra. We mainly focus on carbon-related defects and their complexing with primary defects. We discuss the localized vibrational mode bands related to these defects, their annealing behavior and their interactions. Infrared spectra recorded at room temperature reveal the presence of a band at $544\,cm^{-1}$, appearing only in C-rich Si, and showing similar thermal stability to that of the di-carbon (C_iC_s) defect. In addition, its amplitude scales with the carbon content of the material. We attributed this band to the (C_iC_s) center. Two bands, at 987 and $993\,cm^{-1}$ were attributed to the $C_iC_s(Si_I)$ center. Furthermore, the origin of a C-related band at $943\,cm^{-1}$ is discussed.
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1. Introduction

When crystalline Si is subjected to energetic bombardment, primary defects are produced. These defects are vacancies (V) and self-interstitials (Si_I), which recombine with each other and to a large extent annihilate ($V+Si_I \rightarrow \varnothing$). However a small percentage of these defects escape recombination and migrating through the lattice interact either between themselves leading to the formation of larger vacancy and interstitial complexes or with impurities present in the crystal to form various complexes. The understanding of the formation processes and the detailed knowledge of the properties of these complexes are very important for the research in semiconductors.

Carbon, besides oxygen, is the most common impurity unintentionally added in the Si lattice, at substitutional sites (C_s), during crystal growth. C_s gives rise to an LVM band at $\sim 605\,cm^{-1}$. Upon irradiation, carbon interstitial atoms (C_i) form through the Watkins replacement mechanism. At room temperature, C_i atoms are enough mobile to migrate and to form defect complexes as the C_iO_i and the C_iC_s defects. The C_iO_i defect forms in Czochralski Si and gives rise [1] to LVM bands at 529, 550, 742, 865 and $1116\,cm^{-1}$. The most well-known of them is the $865\,cm^{-1}$ band. The C_iC_s defect formed in carbon-rich material is metastable and can exist in two configurations, A and B. Five LVM bands at 594.6, 596.9, 722.4, 872.6 and $953\,cm^{-1}$ are related to the A configuration and six

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LVM bands at 540.4, 543.3, 579.8, 640.6, 730.4 and 842.4 cm^{-1} are related to the B configuration of the defect [2]. The experimental values are in good agreement with theoretical calculations [3,4]. The intensities of the lines are quite low and they can be seen only at cryogenic temperatures. In this work, we detected an LVM band at 544 cm^{-1}, in spectra recorded at room temperature, which appears only in carbon-rich Si materials and has a similar thermal stability [1] with the di-carbon center.

Defects reactions modeling based on experimental data [5] led to the conclusion that with increasing radiation fluence the C_i, C_iO_i and C_iC_s defects can act as nucleation centers for the aggregation of self-interstitials, and families of centers of the forms $C_i(Si_I)_n$, $C_iO_i(Si_I)_n$ and $C_iC_s(Si_I)_n$ are expected to be produced. Two LVM bands at 959 and 966 cm^{-1} have been previously associated with the $C_i(Si_I)$ center [1] and another two LVM bands at 940 and 1024 cm^{-1} with the $C_iO_i(Si_I)$ center [1]. In this work, besides the above mentioned two pairs of bands, we detected a third pair at 987 and 993 cm^{-1}, which has been tentatively associated with the $C_iC_s(Si_I)$ defect. Furthermore, the defect structure of another band at 943 cm^{-1} appearing in the spectra immediately after the neutron irradiation of C-rich silicon is discussed.

2. Experimental details

We used the following prepolished Si samples, of 2 mm thickness, with various initial oxygen and carbon concentrations: $M_1([O_i] = 6.97 \times 10^{17}\,cm^{-3}$, $[C_s] = 5.85 \times 10^{16}\,cm^{-3})$, M_4 $([O_i] = 7.65 \times 10^{17}\,cm^{-3}$, $[C_s] = 9.35 \times 10^{16}\,cm^{-3})$, M_5 $([O_i] = 7.195 \times 10^{17}\,cm^{-3}$, $[C_s] = 1.52 \times 10^{17}\,cm^{-3})$, M_7 $([O_i] = 8.625 \times 10^{17}\,cm^{-3}$, $[C_s] = 4 \times 10^{16}\,cm^{-3})$. The samples were irradiated with fast neutrons at a temperature $T \sim 40°C$, with a fluence of $D = 1 \times 10^{17}\,n/cm^2$. After the irradiation the samples were subjected to 15 min isochronal anneals of $\sim 10°C$ steps, in open furnaces, in the range of room temperature up to 750°C. The defects produced were investigated by means of IR spectroscopy.

3. Experimental results and discussion

Immediately after the fast neutron irradiation a weak band at 544 cm^{-1} appears in the IR spectra of the carbon-doped material (Fig. 1). Accumulated evidence stated below led us to correlate the band with the C_iC_s center. Firstly, the band appears only in carbon-rich material. Its amplitude depends on the carbon content of the Si material (Fig. 2), an indication that the 544 cm^{-1} band is carbon-related. Secondly, 15 min isochronal anneals show that the band is stable up to $T \sim 250°C$ (Fig. 3a), in agreement with previous reports [1] concerning the C_iC_s center. Thirdly, we notice that the di-carbon center is expected to appear stronger in neutron-irradiated than in electron-irradiated Si. Actually, during irradiation the main fraction of vacancies and self-interstitials formed annihilate

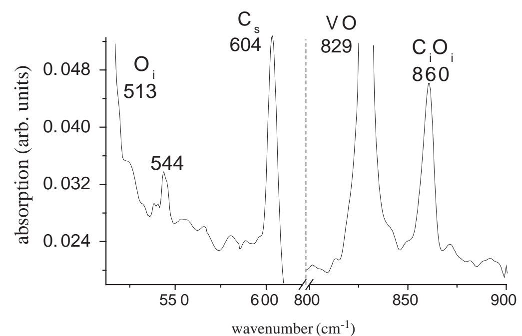

Fig. 1. The IR spectrum of sample M_5 after neutron irradiation.

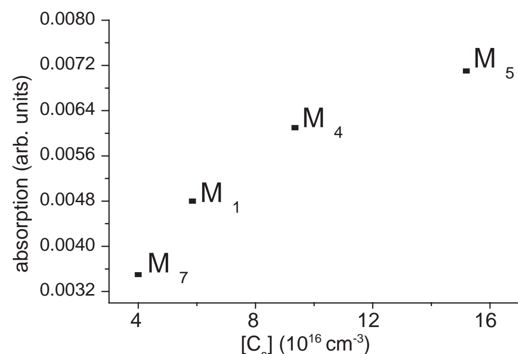

Fig. 2. The amplitude of the 544 cm^{-1} band versus the carbon concentration of the material.

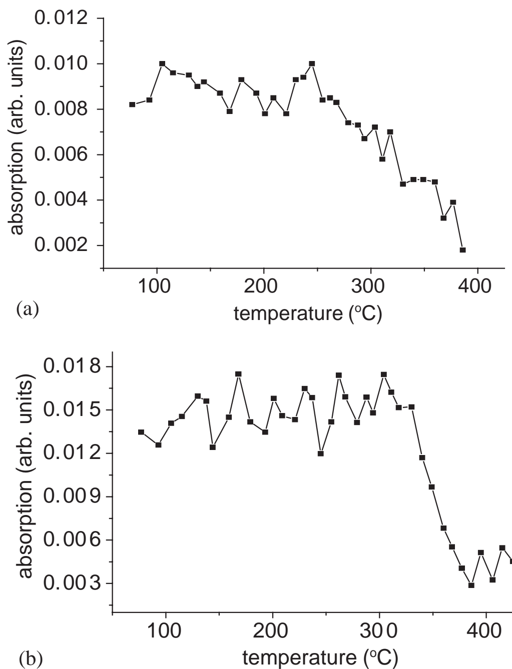

Fig. 3. (a) The thermal evolution curve of the $544\,cm^{-1}$ band and (b) the thermal evolution curve of the $860\,cm^{-1}$ band of the C_iO_i defect.

($V + Si_I \rightarrow \varnothing$). This annihilation is less efficient in neutron-irradiated material due to the space separation of the primary defects. As a result, more Si_I's would participate, in general, in reactions with impurities present in the silicon crystal lattice. Consequently, stronger signals of the corresponding Si_I-related defects are expected. In C-doped material more C_i atoms are produced in the case of neutron irradiations and consequently more di-carbon defects form. Thus, a presumably weak signal from the di-carbon center is more likely to be seen in the spectra of neutron-irradiated Si. In neutron-irradiated Si the Fermi level is shifted to the middle of the gap and the defect can exist in the neutral charge state, which corresponds to the B configuration of its structure. Our $544\,cm^{-1}$ band recorded at room temperature could be considered as the combination of the two weak bands of the C_iC_s center in the B configuration at 540.3 and $543.3\,cm^{-1}$, recorded [2] at liquid helium temperature. Its amplitude therefore, becomes stronger allowing its detection at room temperature. Noticeably, a weak band at $\sim 540\,cm^{-1}$ detected at cryogenic temperatures was tentatively associated [6] with the C_iO_i complex mainly because the band has the same annealing behavior as that of the C_iO_i-related lines. However, in our case the $544\,cm^{-1}$ band decays faster than the $860\,cm^{-1}$ band, as seen in Fig. 3b.

Fig. 4 shows the IR spectrum in the region of $920–1030\,cm^{-1}$. Seven bands could be seen: $943\,cm^{-1}$, (935 and $1018\,cm^{-1}$), (953 and $960\,cm^{-1}$) and (987 and $993\,cm^{-1}$). The band at $943\,cm^{-1}$ will be discussed separately below. The first and the second pair of bands has been previously reported [1] in the literature and attributed to the defects $C_iO_i(Si_I)$ and $C_i(Si_I)$, respectively. They form when Si_I's are captured by the C_iO_i and the C_i centers, correspondingly. The third pair of bands has not been reported so far. However, in irradiated material at high doses also the center $C_iC_s(Si_I)$ is expected to be produced according to the reaction $C_iC_s + Si_I \rightarrow C_iC_s(Si_I)$. The formation of the center was inferred [5] as a result of the analysis of experimental data concerning carbon-related processes in irradiated Si. If the concentration of the center is small then the corresponding bands may pass undetected in the spectra. This may be the case of electron-irradiated Si. However, in neutron-irradiated silicon, where the percentage of the available Si_I's is larger the corresponding signal of the center would be stronger and therefore more easily detected in the spectra. In this line of thought, we attribute the two bands at 987 and $993\,cm^{-1}$ to the $C_iC_s(Si_I)$ complex. Preliminary studies of the thermal

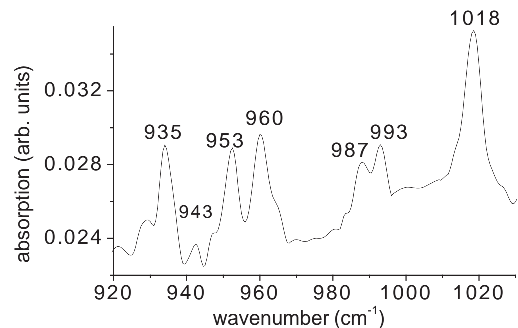

Fig. 4. The IR spectrum in the region $920–1030\,cm^{-1}$.

evolution of the two bands show that they appear immediately after the room temperature irradiation in the spectra and disappear together at around 300°C, an indication that they originate from the same defect.

In the following, we shall deal with the origin of the 943 cm^{-1} band, the thermal evolution of which is presented in Fig. 5 together with that of the 829 cm^{-1} band of the VO center. It is well-known that the oxygen impurity can interact with both vacancies and self-interstitials, produced by the irradiation. As a result centers as for example VO and O_iSi_I, form. For the carbon impurity, however, the situation is different since it occupies substitutional sites in the Si lattice. Although it is well established that the C_s atoms interact with self-interstitials to form C_i atoms, the interaction of the C_s atom with a silicon vacancy is still an open issue. While classical calculations [7] do not favor the formation of carbon–vacancy centers, ab initio calculations [8] predict their formation. Note that, a lot of complexes of the vacancy with substitutional impurities (i.e. phosphorous [9], arsenic [10], antimony [10], boron [11], aluminum [12], germanium [13] and tin [14]) have been reported so far. It is therefore reasonable to expect complexing of the vacancy with substitutional carbon, especially in neutron-irradiated Si, where a larger number of vacancies is available. In our studies the 943 cm^{-1} band appearing only in carbon-doped Si may be considered as a potential candidate for the C_s–V complex. Firstly, if carbon–vacancy centers were formed, their strength should be higher in samples with less oxygen content since the latter impurity pairs strongly with the vacancy. In our spectra the 943 cm^{-1} band appears clearly immediately after the irradiation in the oxygen-low Si material (sample M_1). Secondly, we observe that in samples with higher oxygen content only traces of it could be detected after the irradiation, and the band appears clearly in the spectra at $T \sim 250^{o}$C, where a release [15] of vacancies takes place from large defect complexes existing in neutron-irradiated Si. This is verified by the simultaneous increase of the intensity of the 829 cm^{-1} band of the VO center in the spectra (Fig. 5). On the other hand, one would expect the vibrational frequencies of such centers to be smaller [16] than that of the C_s center, due to the loss of the C–Si bond. However, the 943 cm^{-1} frequency is much larger than that of the C_s impurity. Another possibility is that the 943 cm^{-1} band is related to a C_I–V center, with the vacancy trapped nearby. The C_i defect, which has two LVM bands [1] at 922 and 932 cm^{-1}, is mobile during neutron irradiation and thus its complexing with the vacancy, is possible. Such a defect, is expected to form immediately after the irradiation in C-rich Si. However, one would reasonably expect two LVM bands correlated with the C_I–V defect in contrast with the one detected here. Of course, other structures related to the 943 cm^{-1} band should be considered. One could not exclude for example the possibility that the band is related to a second generation defect cluster, like $C_i(Si_I)_2$, $C_iO_i(Si_I)_2$, $C_iC_s(Si_I)_2$.

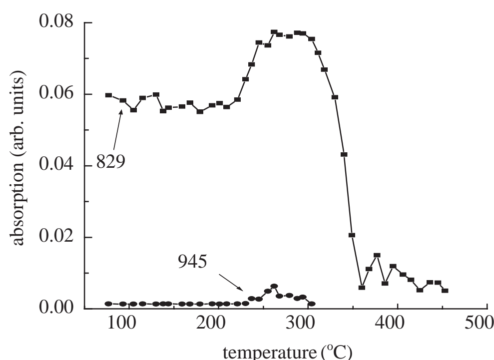

Fig. 5. The thermal evolution of the 943 cm^{-1} and the 829 cm^{-1} bands.

4. Conclusions

By means of IR spectroscopy we have investigated carbon-related complexes in neutron-irradiated Si. A band at 544 cm^{-1} was correlated with the C_iC_s center. Two bands at 987 and 993 cm^{-1} were correlated with the $C_iC_s(Si_I)$ complex. The origin of a band at 943 cm^{-1} is discussed in relation with either a carbon–vacancy complex or with any of the $C_iO_i(Si_I)_2$, $C_i(Si_I)_2$ and $C_iC_s(Si_I)_2$ complexes.

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