Pressure assisted evolution of defects in silicon

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The effect of enhanced hydrostatic pressure following heat treatment on the evolution of point defects in neutron-irradiated Czochralski-grown silicon is investigated using infrared spectroscopy. The behavior of oxygen-related defects, particularly of the VO and the VO_2 centers, is mainly studied using samples subjected to heat treatment under hydrostatic pressure. It is observed that (1) pressure accelerates the annealing process of the VO defects and enhances the growth of the VO_2 complexes and (2) the VO_2 concentration is larger than expected from the corresponding decay of the VO defects. The faster decay of the VO defects is attributed to a pressure-induced decrease of their migration energy. The larger VO_2 concentration is also discussed. One possible explanation is that pressure stimulates an additional mechanism for the formation of the VO_2 defects, which involves the reaction of oxygen dimers with vacancies.

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1 Introduction

It is well-known that by the irradiation of Si at room temperature primary mobile defects are produced, i.e vacancies and self-interstitials, giving rise to the formation of secondary defects: V_2, Si di-interstitials, various vacancy-pairs with dopants and other impurities, larger complexes and other extended defects. The radiation-induced defects and their annealing behavior has been the subject of extensive investigations employing techniques [1-3] such as DLTS (Deep Level Transient Spectroscopy), EPR (Electron Paramagnetic Resonance), IR absorption (Infrared Spectroscopy), and others. However, there remains a number of open questions concerning the properties and the behavior of these defects. Some problems [4] related to the annealing processes, reaction paths and mechanisms involved, even problems associated with the identification of some defects are to an extent still under discussion [see, e.g., Ref. 5 and references therein].

In Cz-Si material, where oxygen is in abundance, the most important vacancy-impurity complex is the VO pair: the well-known A-center. This center is detected in IR spectra immediately after irradiation, giving rise [6] to the 828 cm^{-1} Localized Vibrational Mode (LVM) band. Upon annealing at elevated temperatures, the center becomes mobile at about 300° C. The decay of the 828 cm^{-1} band is accompanied [6-8] by the emergence of another band at 887 cm^{-1} attributed to the VO_2 defect, according to the reaction $VO + O_i \rightarrow VO_2$. Actually, the VO centers become mobile at about 300° C and upon being captured by oxygen interstitial atoms result in the formation of the VO_2 defects. However, when interpreting experimental data, there are some difficulties [7,9] concerning the assignment of the 887 cm^{-1} band to the VO_2 defect. Also, the annealing behavior of the VO defect is not completely understood and a number of reactions taking place separately, or in parallel, have been

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considered in the literature [10] in order to account for the said annealing behavior. The most important of these reactions is the direct production of the VO_2 defect ($VO + O_i \rightarrow VO_2$), the destruction of the VO defect by silicon self-interstitials ($VO + Si_I \rightarrow O_i$), the production of the VO_2 defect through pairing of two VO defects ($VO + VO \rightarrow V_2O_2 \rightarrow VO_2 + V$), the dissociation of the VO defect ($VO \rightarrow V + O_i$), the trapping of VO defects by vacancies ($VO + V \rightarrow V_2O$) and divacancies ($VO + V_2 \rightarrow V_3O$). Another suggested [11] reaction worthy of mention is $V + O_2 \rightarrow VO_2$, where vacancies encounter oxygen dimers to form VO_2 complexes. It will also be useful for a later discussion to note that the V_3O defect formed by the encounter of VO and V_2 centers has [12] an LVM frequency, at 887 cm^{-1}, which is very close to that of the VO_2 center. Thus, practically, one would expect their corresponding signals to more or less coincide in the IR spectra.

Previous investigations [13-17] have revealed that enhanced hydrostatic pressure could alter the diffusion kinetics of various dopants, affect precipitation processes and influence the formation and evolution of various defects in Si following heat treatment. In this context, it will be of interest to study the effect of pressure on oxygen-related defects in Si. In particular, in this article our aim is to investigate the effect of pressure on the evolution of A-centers and VO_2 defects upon annealing. It is not unreasonable to think that pressure would affect the various mechanisms involved in the annealing of VO centers and the concomitant growth of VO_2 centers. Moreover, it will affect each mechanism in a different way. This would enable one to distinguish the degree of contribution of each mechanism in the evolution of the VO and VO_2 defects and therefore to cast some new light on the phenomena.

2 Experimental

Cz-grown Si samples with initial oxygen concentration $[O_i]_o \sim 9.5 \times 10^{17}$ cm^{-3} were irradiated with fast neutrons of 5 MeV energy, at temperatures around 40-50 °C. The dose of the irradiation was $D = 1.1 \times 10^{17}$ $n \cdot cm^{-2}$. Then, half of the samples were subjected to a sequence of successive runs of heat treatment at 325 °C for 45 min under hydrostatic pressure of 10.5 kbars and the other half at atmospheric pressure. The treatments under high pressure were performed in argon atmosphere in a specially designed apparatus described elsewhere [18]. The defects were studied by IR spectroscopy using a Jasco-700 dispersive kind spectrometer operating in the frequency range 400-5000 cm^{-1}. The spectra were registered at room temperature. Two phonon absorption was subtracted by using a reference sample from float-zone material of the same thickness.

3 Results and Discussion

Fig. 1 shows the IR spectra of a Cz-Si sample obtained after irradiation (Fig. 1a) and after subsequent isothermal anneals at 325 °C under hydrostatic pressure of 10.5 kbars for 45 min (Fig. 1b - d). In the same figure we present the IR spectra of another similar sample registered after irradiation (Fig. 1a′) and after subsequent isothermal anneals at 325 °C under atmospheric pressure for 45 min (Fig. 1b′ - d′). As is obvious, Fig. 1a and Fig. 1a′, obtained after irradiation, are the same.

Comparing Fig. 1b and 1b′ we immediately note that the decay of the VO defect (828 cm^{-1} band) is faster in sample S (annealed under high pressure) than in sample S′ (annealed at atmospheric pressure). Simultaneously, we observe that the growth of the VO_2 defect (887 cm^{-1} band) is more enhanced in sample S. The same observation holds after comparing Figs. 1c and 1c′. What is finally obtained by comparing Figs. 1d and 1d′ is that the peak of the VO band is diminished to a higher degree in sample S than in sample S′. Correspondingly, the peaks of the VO_2 band are more intense in sample S. Therefore, we conclude that pressure accelerates the decay of VO defects and enhances the formation of VO_2 defects. Additionally, as is seen by comparing the spectra shown in the left handside column with those shown in the right handside column of Fig. 1, the satellite bands [19] in the frequency range of VO centers appear more pronounced in the samples subjected to thermal anneals under high pressure. These satellite bands were previously detected and correlated with certain V_nO_m defects. In particular, the bands at 839, 833 and 824 cm^{-1} have been attributed [19] to the V_2O, V_3O_2 and V_2O_2 defects, respectively. Thus, a more general conclusion arrived at is that pressure induces a faster growth of all the multivacancy multioxygen-related defects V_nO_m, and not only of the VO_2 defect.

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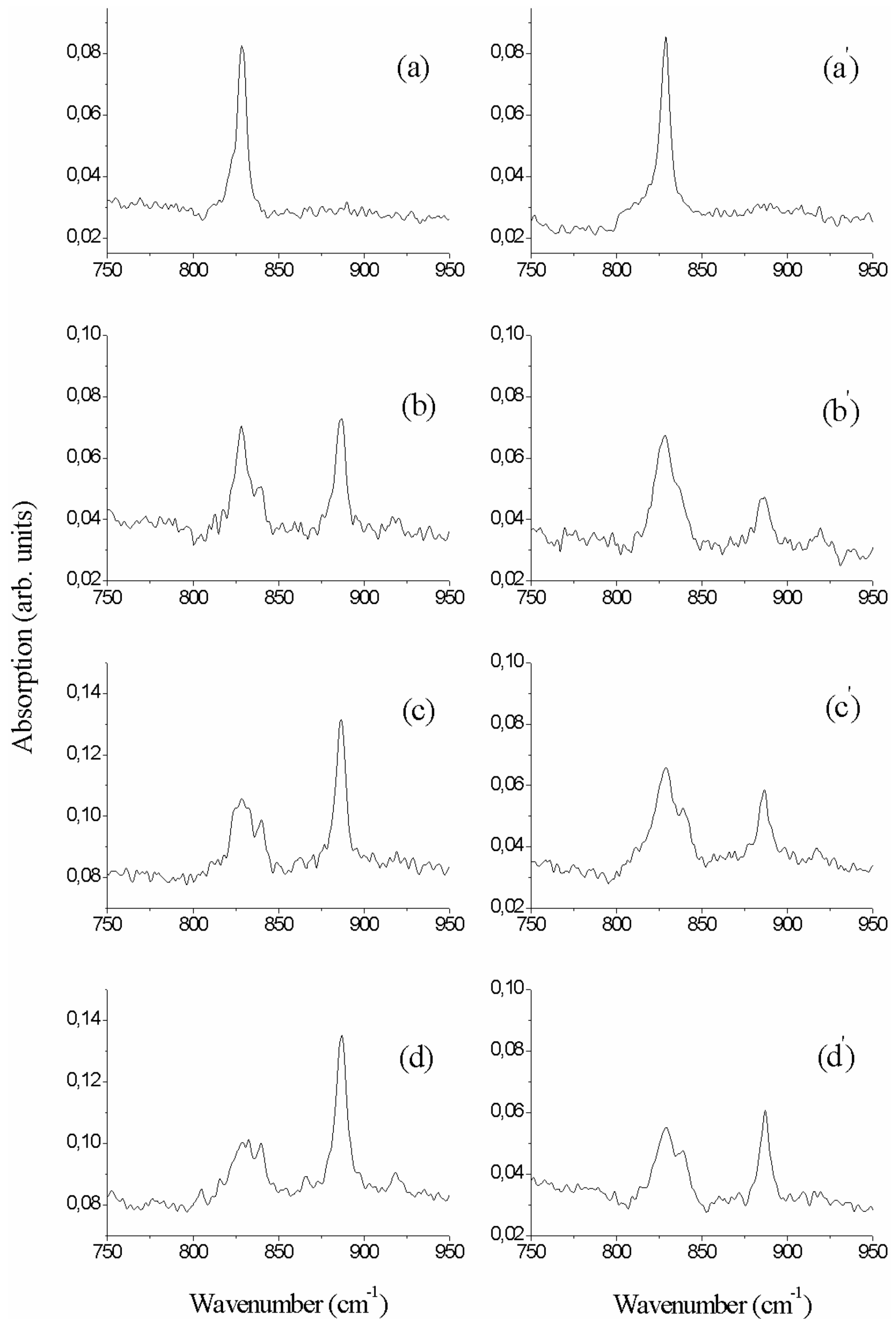

Fig. 1 Left column: IR spectra of a sample (a) after neutron irradiation, (b - d) after successive runs of heat treatment at 325 °C, 10.5 kbars, 45 min. Right column: IR spectra of a sample (a′) after neutron irradiation, (b′ - d′) after successive runs of heat treatment at 325 °C, 1 bar, 45 min.

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Considering now the observed faster decay of VO defects, one could claim that the application of pressure causes changes in the bond lengths and angles within the crystal matrix. As a result, the surrounding environment inside the crystal, where the various defects move, also changes. In, a more or less, qualitative approach regarding the evolution of VO defects, this could be expressed by stating that high pressure induces changes in the migration path of VO defects, as these travel as an entity through the lattice before being captured by O_i atoms, thus producing VO_2 defects. The jump probability r, at which the VO defect hops from one position to the next during a migration event, could be given [20] by a relation of the form $r = r_o \exp(-\Delta E / kT)$, where r_o is an effective frequency and ΔE is the potential barrier for the formation of the VO defect. Assuming that the changes in r_o due to a thermal treatment under high pressure have a minor effect on the jump probability r (compared to changes in ΔE), it may be concluded that a reduction in the potential barrier due to the application of high hydrostatic pressure is responsible for the phenomenon. In other words, we believe that the application of high pressure results in a lower activation energy for the migration of VO defects. This appears in the spectra as a faster decay of the defect band peak. The easier the migration of the VO centers, the faster the formation of various V_nO_m defects.

Concerning now the growth of the VO_2 concentration in sample S (Fig. 1 left column, especially Fig 1c, and Fig. 1d) it is clear that it is larger than that expected from the corresponding decrease of the VO defect peak. This enhanced formation of VO_2 defects could indicate that another mechanism, which possibly operates in parallel to the usual reaction, $VO + O_i \rightarrow VO_2$, becomes more active, increasing the concentration of the VO_2 defects. We argue that this second mechanism could be the reaction $V + O_2 \rightarrow VO_2$. The idea of oxygen dimers, the fast diffusing species, was initially proposed [21] to explain the kinetics of oxygen aggregation processes in Si and the formation of thermal donors. In an earlier work [22] it has been shown that oxygen dimers form at temperatures around 350 ^{o}C and this process controls the formation kinetics of thermal donors. Additionally, it has been suggested [23] that pressure increases the oxygen diffusivity in silicon. It is worth noting at this point that pressures larger than 10 kbars affect the vibrational frequencies of the oxygen staggered dimers [24]. Thus, a faster diffusivity of oxygen in silicon entails an enhanced formation of oxygen dimers. Assuming, therefore, that high pressure enhances the formation of oxygen dimers at 325 ^{o}C, one would expect that vacancies encounter these dimers to form VO_2 defects. Mobile vacancies can be produced as a result of dissociation of divacancies and/or other multivacancy complexes, present in the damaged lattice. Other suggestions could also be put forward. As mentioned above, the V_3O defects with an LVM frequency at 887 cm^{-1}, are also produced in neutron-irradiated Si. Apart from the reaction $VO + V_2 \rightarrow V_3O$, reaction $V_2O + V \rightarrow V_3O$ could also be proposed [9,10]. Thus, if the concentration of V_3O defects increases due to annealing under high pressure, then the enhanced peak of the 887 cm^{-1} band in our spectra could be explained, assuming that both the VO_2 and V_3O defects are placed in the IR spectra at nearly the same position. This is also in agreement with the larger decrease of the VO peak under pressure. Naturally, such an explanation merits further investigation.

4 Conclusion

We have studied the effect of high hydrostatic pressure on the evolution of oxygen-vacancy related centers in neutron-irradiated Si. In particular, we have observed a faster disappearance of VO defects, tentatively attributed to the fact that high pressure reduces the activation energy for their migration. The observed enhanced growth of the VO_2 peak was attributed to the activation of another reaction, that is $V + O_2 \rightarrow VO_2$, in parallel to the usual formation reaction $VO + O_i \rightarrow VO_2$. Finally, we have observed that high pressure results in a faster formation of various V_nO_m defects, known as the satellite bands in the spectral region of A-centers.

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