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Vacancy-related complexes in neutron-irradiated silicon

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Abstract

Electrically active defects induced by neutron irradiation in n-type Czochralski-grown (Cz) Si crystals have been studied by means of capacitance transient techniques. These neutron-induced defects are compared with those created by electron irradiation and self-ion implantation. Four electron traps with the activation energies for electron emission of 0.12, 0.16, 0.24 and 0.42 eV were observed after neutron irradiation in phosphorous-doped Cz Si crystals. It is inferred that the E(0.12) and E(0.16) traps are related to the single-acceptor states of the silicon self-interstitial–oxygen dimer complex (IO_{2i}) and the vacancy–oxygen pair (VO), respectively. The E(0.24) trap is associated with the electron emission from the double-acceptor state of the divacancy (V_2). However, an asymmetric peak with its maximum at around 220 K and an activation energy for electron emission of 0.42 eV dominated the spectra. We used high resolution Laplace DLTS to investigate the structure of E(0.42) and found that this signal is complex, consisting of contributions from several defects. From the annealing behaviour, it was revealed that as some of these defects anneal out they are sources of vacancies evidenced by an increase in the concentration of VO and V_2. It is suggested that some of the defects contributing to the E(0.42) peak are related to small vacancy clusters.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

It is evident from recent studies that there are profound differences in the density distribution of defect energy levels produced by electron irradiation and ion implantation in silicon (Svensson *et al* 1991, Peaker *et al* 2000, Evans-Freeman *et al* 2002). The principal reason for this is the

high damage rate near the end of range of the implanted particle, which results in clustering of vacancies and self-interstitials. Reverse modelling of annealing and *ab initio* calculations (Hastings *et al* 1997, Cowern *et al* 1999, Staab *et al* 2002) predict stable clusters of small numbers of vacancies and/or interstitials but it has been proved extremely difficult to study these experimentally by techniques which give detailed electronic and structural information. Among the many reasons for this is that ion damage is extremely inhomogeneous, resulting in a wide spatial distribution of different cluster sizes. To overcome this problem we have utilized fast neutrons to produce more uniform damage in silicon. In the work reported here we have used irradiation temperatures and flux densities which were expected to produce mostly small vacancy clusters in silicon. These were studied by conventional and Laplace DLTS. The evolution of defects has been investigated upon isochronal anneals.

2. Experimental details

The materials used in our experiment were phosphorus-doped Czohralski-grown (Cz) silicon crystals with initial resistivities of (1–2) Ω cm. The samples were irradiated with 1 MeV neutrons at the Imperial College Reactor, London, UK. The samples were enclosed in a cadmium shield to filter out thermal neutrons and so avoid the transmutation reaction of Si into P. The temperature of the samples during irradiation did not exceed 30 °C and the flux was about 9×10^{11} n° cm^{-2} s^{-1}. The accumulated dose of fast neutrons was 2×10^{14} cm^{-2}. The sample surfaces were cleaned after irradiation and Schottky barriers were fabricated by thermal evaporation of Au. Electronic traps were characterized with conventional deep level transient spectroscopy (DLTS) and high resolution Laplace DLTS (LDLTS) techniques (Dobaczewski *et al* 2004).

The irradiated samples were subjected to 60 min isochronal annealing in the temperature range 100–200 °C with temperature increments of 50 °C.

3. Experimental results

Figure 1 shows a DLTS spectrum of an n-type Czochralski-grown silicon sample, which was irradiated with 1 MeV neutrons. For comparison, DLTS spectra for similar crystals, which were irradiated with either 4 MeV electrons or 800 keV Si ions, are shown. The spectra have been normalized to the equal intensity of a peak with its maximum at about 90 K.

Four traps with their DLTS peak maxima at about 72, 90, 130 and 222 K for an emission rate window of 80 s^{-1} are observed in the spectrum of the electron-irradiated sample. These traps are referred to as E–E1 to E–E4 in the following text. In this labelling the first letter denotes the type of irradiation ('E' for electrons, 'N' for neutrons, and 'I' for ions) and the second letter (E) with a number denotes an electron trap with a number assigned to it. Activation energies of electron emission for the E–E1 to E–E4 traps have been determined from Arrhenius plots of T^2-corrected electron emission rates as 0.129, 0.163, 0.239, and 0.424 eV, respectively. The DLTS spectrum for the electron irradiation case resembles those reported in the literature for Cz Si crystals irradiated with electrons (Kimerling 1977, Brotherton and Bradley 1982, Lindström *et al* 2001). On the basis of comparison of the measured trap parameters (activation energies for electron emission and values of electron capture cross section) with the known values for defects induced by electron irradiation (Kimerling 1977, Brotherton and Bradley 1982, Lindström *et al* 2001), we assign the E–E1 peak to an acceptor level of the self-interstitial–dioxygen complex (Lindström *et al* 2001), the E–E2 peak to an acceptor level of the vacancy–oxygen (VO) complex (Watkins and Corbett 1961), the E–E3 peak to the second acceptor level

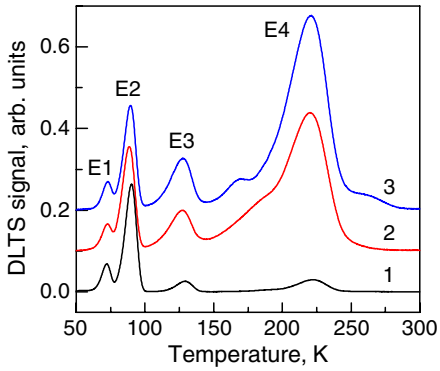

Figure 1. DLTS spectra of n-type Czochralski-grown Si crystals after irradiation with (1) 4 MeV electrons ($F = 1 \times 10^{15}$ cm^{-2}), (2) 1 MeV neutrons ($F = 2 \times 10^{14}$ cm^{-2}), and (3) 800 keV Si ions ($F = 1 \times 10^{9}$ cm^{-2}). Measurement settings were $e_n = 80$ s^{-1} and pulse duration 1 ms. The spectra have been normalized to the equal intensity of the E2 DLTS peak and shifted on the vertical axis for clarity.

of the divacancy (Watkins and Corbett 1965), and the E–E4 peak to the first acceptor level of the divacancy with an admixture of another level with small concentration. This minor level disappeared completely after annealing at 100 °C.

Low temperature (35–150 K) parts of the DLTS spectra for the neutron- and ion-irradiated samples are very similar to that for the electron-irradiated sample, and activation energies of electron emission for the N–E1 to N–E3 and I–E1 to I–E3 traps have been found to be nearly identical to those for the E–E1 to E–E3 traps. This identity suggests the same origin of the E1–E3 traps for all types of irradiation. The only difference is that the ratio of E3 to E2 (and E1) peak intensities for the cases of neutron irradiation and ion implantation is higher compared to that for the electron irradiation.

In the temperature range of 150–300 K the DLTS spectra for Cz Si samples irradiated with different high energy particles differ significantly. Firstly, the N–E4 and I–E4 DLTS peaks are much more intense compared to the E–E4 one. Secondly the N–E4 and I–E4 peaks are broader than the E–E4 one, and finally the structure of satellite peaks around the main E4 peak is different for different irradiations. These differences can be seen more clearly in figure 2, which shows fragments of the conventional DLTS spectra in the temperature range 150–300 K. The spectra have been normalized to the equal intensity of the E4 signals. It should be mentioned that the ratio of intensities of the satellite peaks to the main E4 peak is essentially higher for the ion- and neutron-irradiated samples than for the electron-irradiated one. The origin of the minor DLTS peaks (E5–E8) in irradiated Cz Si is not clear. With regards to the main E4 peak, in electron-irradiated Cz Si samples it is related to the first acceptor level of the divacancy with very small admixture from the acceptor level of the vacancy–phosphorus pair (Kimerling 1977, Brotherton and Bradley 1982). Obviously, the electron emission from the first acceptor level of the divacancy contributes to the E4 DLTS peak in the neutron-irradiated and Si-ion-implanted samples, as the divacancy is thought to be one of the main types of radiation-induced damage for the cases of neutron irradiation and ion implantation and has been observed experimentally after such irradiations by a number of experimental techniques (e.g., see Newman 1982 and references therein). There are, however, some indications that electron emissions from other defects contribute to the E4 peak in the case of ion implantation (Peaker *et al* 2000, Evans-Freeman *et al* 2002) as well as in the case of neutron irradiation (Moll *et al* 1997). It should be pointed out that the distribution of defects is not uniform both

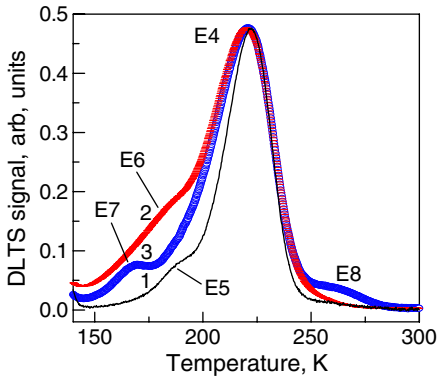

Figure 2. Fragments of DLTS spectra of n-type Cz Si crystals after irradiation with (1) 4 MeV electrons ($F = 1 \times 10^{15}$ cm^{-2}), (2) 1 MeV neutrons ($F = 2 \times 10^{14}$ cm^{-2}), and (3) 800 keV Si ions ($F = 1 \times 10^{9}$ cm^{-2}). Measurement settings were $e_n = 80$ s^{-1} and pulse duration 1 ms. The spectra have been normalized to the equal intensity of the E4 DLTS peak.

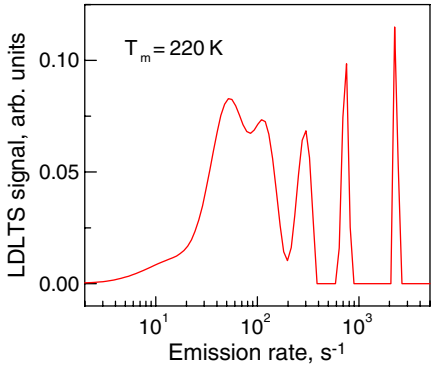

Figure 3. Laplace DLTS spectrum for a Cz Si:P sample, which was irradiated with fast neutrons. Measurements were carried at 220 K with the following measurement settings: bias $-5 \rightarrow -0.2$ V and pulse duration 1 ms.

in ion-implanted and in neutron-irradiated samples (Newman 1982) and special care should be taken to analyse electronic properties of the defects properly (Antonova *et al* 1988, Monakhov *et al* 2002). The Laplace DLTS technique has been applied to study the E4-related electron emission in neutron-irradiated samples and it has been found that the corresponding LDLTS spectrum is rather complex, consisting of several single emission lines (figure 3). We believe that the complex structure of the E4-related Laplace DLTS spectrum is associated mainly with the interference of electron emissions from a few traps with closely spaced energy levels in the range of 0.40–0.44 eV below the conduction band edge. In order to obtain additional information on the properties of neutron-irradiation-induced traps, transformations of the traps upon isochronal annealing have been studied.

Figure 4 shows the development of the DLTS spectra for a neutron-irradiated n-type Cz Si sample upon 60 min isochronal annealing. Anneals at 100 and 150 °C resulted in the disappearance of the N–E1 and N–E6 traps and significant decrease in the magnitude of the dominant N–E4 peak, while the magnitudes of the DLTS peaks related to the N–E2 and N–E3 traps increased. This can be clearly seen in figure 5, which shows the difference between

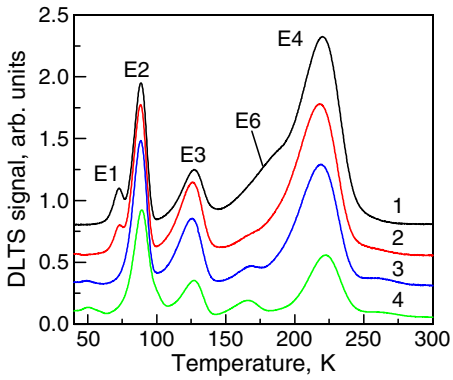

Figure 4. Development of DLTS spectra for a neutron-irradiated Cz Si:P sample upon 60 min isochronal annealing with temperature increments of 50 °C. The spectra were measured (1) after irradiation and after anneals at (2) 100 °C, (3) 150 °C, and (4) 200 °C. Measurement settings were $e_n = 80\ s^{-1}$, bias $-5 \rightarrow -0.5$ V, and pulse duration 1 ms. The spectra have been shifted on the vertical axis for clarity.

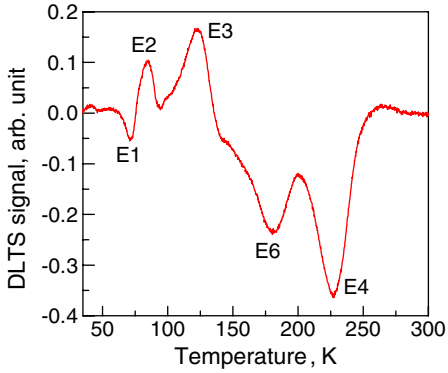

Figure 5. Difference between the DLTS spectra for a neutron-irradiated Cz Si:P sample after treatment at 100 °C for 60 min and in the as-irradiated state (spectra 2 and 1 in figure 4). Measurement settings were $e_n = 80\ s^{-1}$, bias $-5 \rightarrow -0.5$ V, and pulse duration 1 ms.

the DLTS spectra recorded after the treatment at 100 °C and in the as-irradiated state (spectra 2 and 1 in figure 4). The thermal stability of the N–E1 trap is consistent with that of the self-interstitial–dioxygen complex (Lindström *et al* 2001); this gives further support to our assignment of this trap to the IO_{2i} complex. The annealing behaviour of other traps will be discussed below.

4. Discussion and conclusions

As discussed above the E–E3 and E–E4 DLTS peaks in electron-irradiated Cz Si samples are related to the electron emission from the double- and single-acceptor states of the divacancy (Watkins and Corbett 1965). The E–E3 and E–E4 peak magnitudes, which can be considered as a measure of trap concentrations, are essentially the same for the case of electron irradiation, which confirms the previous assignment of the peaks to the same defect. However, the magnitudes of the E3 and E4 peaks differ significantly for the neutron-irradiated and self-ion-

implanted samples (spectra 2 and 3 in figure 1). Such differences were observed previously for Si samples implanted with different ions (Svensson *et al* 1991, Peaker *et al* 2000, Evans-Freeman *et al* 2002, Monakhov *et al* 2002) and also in samples irradiated with fast neutrons (Moll *et al* 1997). It should be pointed out that there is no consensus in the literature with regards to the origin of the difference between the magnitudes of the E3 and E4 peaks in ion-implanted samples. According to one point of view (Svensson *et al* 1991, Monakhov *et al* 2002), the E3 and E4 peaks in ion-implanted Si crystals are related only to the acceptor states of the divacancy. The difference between the magnitudes of the peaks was suggested to be associated with the suppression of electron emission from the double-acceptor state of the divacancy because of either

(i) a stronger effect on the double acceptor state of the divacancy, $V_2(=)$, than the single acceptor state, $V_2(-)$, in relation to the suppression of electronic bond switching (motional averaging) in distorted damage peak regions (Svensson *et al* 1991) or
(ii) a local compensation of the carrier concentration in highly disordered regions located within the collision cascades (Monakhov *et al* 2002).

On the other hand, it was argued that the difference can be explained by contributions to the E4 peak of electron emissions from several defects, of which $V_2(-)$ is only one, induced by either ion implantation or neutron irradiation (Moll *et al* 1997, Peaker *et al* 2000, Evans-Freeman *et al* 2002).

Let us consider now how our experimental results can be interpreted in the light of the above models. Laplace DLTS measurements have shown that the capacitance transients in the temperature range of electron emission from the double-acceptor state of the divacancy in neutron-irradiated samples (the N–H3 DLTS peak) is nearly exponential. Assuming that the N–H3-related electron emission comes from divacancies located partly in disordered regions and partly from the single divacancies in the bulk of the sample (Newman 1982), this result shows that the effect of strain in neutron-induced disordered regions on the electron emission from the $V_2(=)$ state is not very strong. On the other hand, the Laplace DLTS spectra in the temperature range of emission from the single-acceptor state of the divacancy (the N–H4 DLTS peak) are rather complex, consisting of several different mono-exponential electron emissions (figure 3). The combination of these two observations is not consistent with the hypothesis that the effect of strain on the electron emission from the $V_2(=)$ state is much greater than for the case of the $V_2(-)$ state in disordered regions created by either ion implantation or neutron irradiation.

The annealing behaviour of divacancies in an electron-irradiated phosphorus-doped Cz Si sample has been studied recently by Markevich *et al* (2003). It was argued that the divacancies annealed out in the temperature range 225–275 °C and the main mechanism of their disappearance in Cz Si crystals is related to the interaction of mobile V_2 with interstitial oxygen atoms. So, the very significant decrease in the magnitude of the N–E4 peak upon annealing in the temperature range of 100–200 °C can hardly be related to the usual mechanism of V_2 disappearance in Cz Si crystals. It is more likely that some of the traps whose electron emission interferes with that from the $V_2(-)$ state in the N–E4 peak disappear in the temperature range of 100–200 °C. The mechanisms of their disappearance are not clear at the moment; these could be related to annihilation or dissociation of defects, as well as to the association of some smaller centres to larger complexes. It is reasonable to suggest that the increase in magnitudes of the $VO(-/0)$ and $V_2(=/-)$-related signals (N–E2 and N–E3 peaks, respectively) is associated with the decrease in magnitudes of the N–E4 and N–E6 peaks. This assumes that some of the traps giving rise to the N–E4 and N–E6 peaks must be vacancy related, most likely to be associated with small vacancy clusters.

It should be noted that EPR signals associated with small vacancy clusters were observed in neutron-irradiated Si crystals, which were not subjected to any heat treatments after irradiation. In particular, the Si–P3 EPR signal associated with the {110}-planar tetravacancy was found to be present in neutron-irradiated Si samples and to anneal out at about 170 °C (Lee and Corbett 1974). It might be possible that this defect gives rise to the E4 or E6 electron traps in neutron-irradiated Cz Si samples studied in the present work.

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