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ScienceDirect
Physica B 401–402 (2007) 483–486
PHYSICA B
www.elsevier.com/locate/physb

Properties and identification of the oxygen-related radiation defects in silicon

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Abstract

Properties of the recently reported deep-level radiation defects in oxygen-rich silicon (the M-center in p-type Si with the DLTS levels at $E_v + 0.36$ and $E_v + 0.12$ eV, and the X-center in n-type Si with the level at $E_c - 0.11$ eV, respectively) are investigated by means of DLTS and IR absorption. With a pre-irradiation heat treatment the linear correlation between the amount of oxygen dimers and the X- and M-center concentrations is established, indicating the oxygen dimer as the precursor of both radiation defects. The annihilation rates of the X- and M-centers in different charge states are measured in the temperature range of 295–350 K. The introduction rates and thermal stabilities of the M- and X-centers are found to be strongly different, which makes it difficult to correlate these levels with the same defect.

PACS: 61.72.Yx; 61.80.Az; 61.82.Fk; 71.55.Cn

Keywords: Silicon; Radiation defects; Oxygen

1. Introduction

Several new DLTS peaks have recently been reported in electron-irradiated oxygen-rich silicon [1–3]. In p-type boron-doped Si the levels located at $E_v + 0.36$ and $E_v + 0.12$ eV have been shown to belong to two different configurations of the same bistable negative-U defect referred below as the M-center. In n-type Cz–Si, irradiation forms the X-center with an acceptor level at $E_c - 0.11$ eV. Both the M- and X-centers anneal out in the temperature range of 80–130 °C. Based on the same range of annealing temperatures and absence of the both centers either in carbon-rich or oxygen-lean silicon, the whole set of levels has been ascribed to a complex of the self-interstitial with the oxygen dimer [3].

The oxygen dimer is believed to play the decisive role in the processes of oxygen diffusion and agglomeration [4,5]. Till now it has been observed only by IR absorption [6], however application of the technique is limited in this case due to the low dimer concentration even in the crystals with the highest oxygen content. If the oxygen dimer is the precursor of the M- and X-centers, the detection of these centers is a tool to study the dimers with highly sensitive electrical methods. Therefore, a correct identification of the X- and M-centers is very important.

The theoretical model of the IO_{2i} complex reproduces the most prominent features of the M-center which includes the charge-driven bistability and the negative Hubbard correlation energy [3]. However, neither identity of the X- and M-centers nor their relation to oxygen dimers have been experimentally demonstrated. In this paper we report on the preliminary experiments aimed at verification of the model. The introduction rates of the complexes are correlated with the oxygen dimer concentration, and the defect annealing kinetics are analyzed.

2. Experimental

The initial n- and p-type Cz–Si crystals ([P] = 9×10^{14}, [O] = 7×10^{17}, and [B] = 7×10^{14}, [O] = 9×10^{17} cm^{-3}, respectively) were annealed for different times in the

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doi:10.1016/j.physb.2007.09.004

temperature range of 400–750 °C. The annealing was terminated by quenching in liquid nitrogen, and the amount of oxygen dimers was characterized by the integral intensity of the 1012 cm^{-1} absorption line at 80 K [6]. The pre-treated samples were irradiated with the 5 MeV electrons ($\Phi = 7 \times 10^{14}$ cm^{-2}) at room temperature, Schottky diodes were fabricated by Au or Al evaporation on n- and p-type samples, respectively, and the deep-level spectra were studied using the DLTS technique.

3. Results and discussion

The deep-level spectra measured on the p-type crystal irradiated with high-energy electrons are shown in Fig. 1. The presence of a bistable defect can be revealed from the differences in the DLTS spectra measured with and without bias applied during cooling down from room temperature. The temperature position of the corresponding DLTS peak as well as the kinetics of growth and disappearance of the peak during bias/temperature manipulations coincide with those parameters of the bistable negative-U center (M-center) reported earlier [3].

In the following, we report on the annealing behavior of the M-center in different charge states and study its introduction rate as a function of the oxygen dimer concentration.

3.1. Thermal stability

The M-center has been found to anneal out at relatively low temperatures of 350–420 K [2]. This allows to measure its thermal stability in different charge states. Indeed, according to the model [3] the center is neutral in the space charge region (SCR) of a Schottky diode and double positive in the neutral p-type region, when the Fermi level is located below the M-center occupancy level at $E_v + 0.255$ eV. Although the last statement is only an approximation for the used low-doped crystals in the temperature range indicated above, the diodes have been subjected to reverse bias annealing (RBA). The reverse bias has been chosen to allow the measurements of the M-center concentration after the annealing step at both sides of the SCR boundary.

The results of such experiment are presented in Fig. 2. It is seen that the depth profiles of divacancies and C_iO_i complexes, which are stable at 340 K, are flat and reveal no peculiarities at the SCR boundary. In contrast, the M-center concentration shows a prominent step at the position of SCR boundary during annealing, indicating that the M-centers located inside SCR are significantly more stable as compared to those situated in the neutral region.

Repeating the depth profiling after each RBA step, kinetics of the M-center annealing are measured. The M-center decay in the neutral p-type region is found to be well described by the first-order kinetics, and the corresponding rates are shown in Fig. 3 with filled circles. Obviously, the two experimental points cannot be directly used to determine the activation energy and pre-exponential factor of the annealing process, as the proper account of the average charge state at different temperatures has to be taken.

The M-center annealing proceeds much slower inside SCR. Small reduction of the M-center concentration

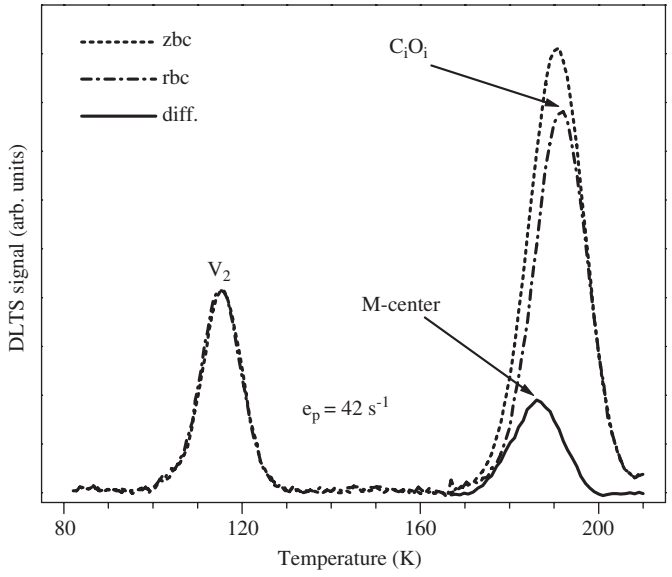

Fig. 1. DLTS spectra of the p-type boron-doped Cz–Si irradiated with 5 MeV electrons ($U_R = 15$ V, $U_P = 6$ V, $t_p = 1$ mS). The dashed and dash-dotted curves are measured after cooling the diode under zero (zbc) and reverse bias (rbc), respectively. The solid line is calculated as a difference between the two measured curves.

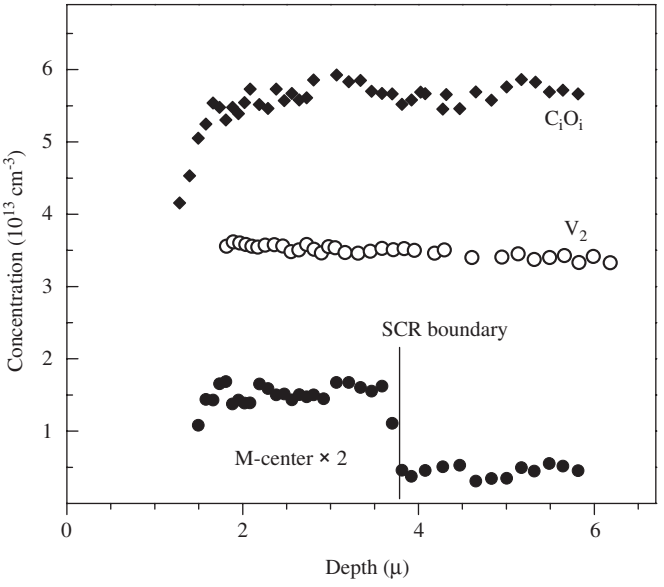

Fig. 2. Depth profiles of the deep-level centers in the Schottky diode on p-type electron-irradiated Cz–Si after the annealing at 340 K under reverse bias of 6 V for 110 min. The M-center concentration is multiplied by a factor of two for better comparison. Vertical line indicates the SCR boundary position calculated from the diode capacitance at annealing temperature.

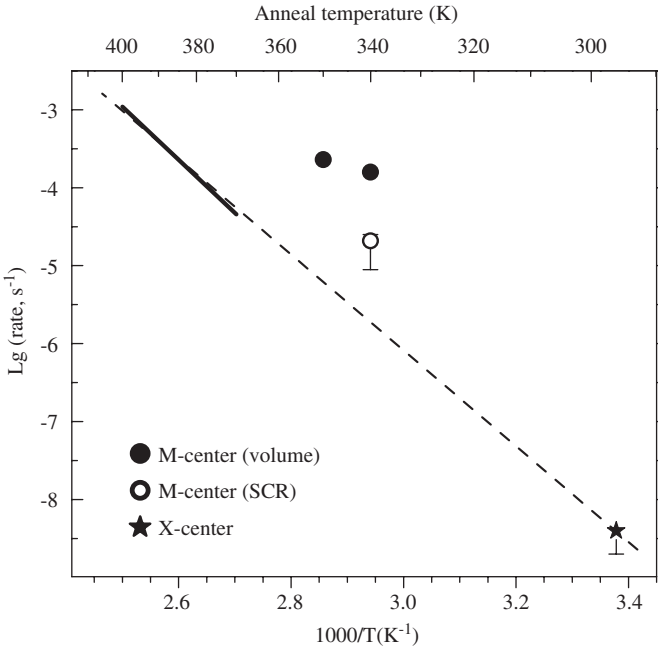

Fig. 3. Annihilation rates of the X-center and the M-center in different charge states. Solid line represents the X-center annealing data from Ref. [2].

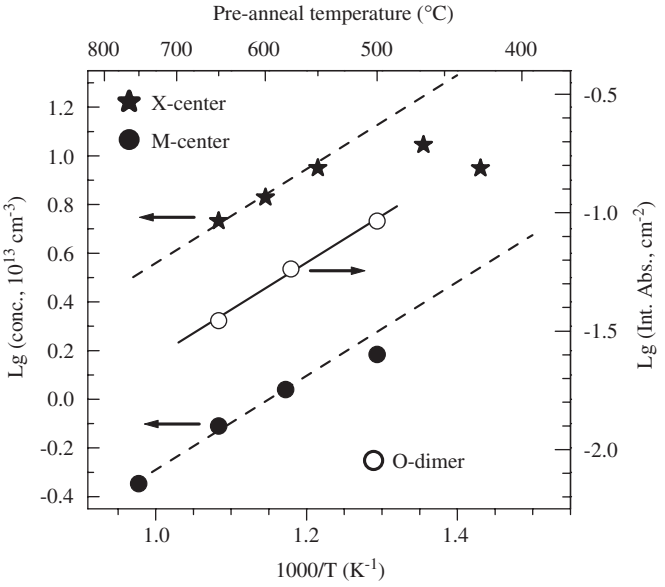

Fig. 4. The effect of pre-annealing on concentrations of the X- and M-centers formed by subsequent irradiation. Integral absorbance of the 1012 cm^{-1} oxygen dimer line in p-type samples is also shown (right scale). The dashed lines are parallel to the solid one, which is the best fit to the oxygen dimer data.

(~15%) impedes the detailed analysis of kinetics. The decay rate estimated assuming the first-order kinetics is shown in Fig. 3 with open circle.

It is interesting to compare the annealing rate of the neutral M-centers with that of the X-centers [1]. Since the X-center annihilation rates have been studied only at higher temperatures [2], we have measured the X-center stability at room temperature. Repeated measurements of the same diode in about five months indicate that the X-center concentration is reduced by few percent. The corresponding annihilation rate is shown in Fig. 3 with the star symbol. This value is seen to agree fairly good to the literature data for higher temperatures.

The annealing rates in Fig. 3 contradict a model which assumes the same chemical structure for the X- and M-centers. Indeed, according to the configuration-coordinate diagram in Ref. [3], the defect has to acquire the neutral B-form both in n-type material and inside the SCR of a Schottky diode on p-type sample. However, the decay rates of neutral X- and M-centers exhibit more than 10 times difference at 340 K.

3.2. Pre-irradiation annealing

It has been assumed that the oxygen dimers act as important traps for the mobile radiation defects and the X- and M-centers are the results of such interaction [2]. To verify this assertion we have compared concentrations of these centers in the samples containing different amounts of the oxygen dimers due to the pre-irradiation heat treatments at different temperatures. The preliminary results of these experiments are shown in Fig. 4.

The dimer concentration is seen to exhibit the expected exponential dependence on the annealing temperature (open circles in Fig. 4), the best linear fit to the data (solid line) corresponds to ~0.4 eV binding energy. The measured concentrations of the X- and M-centers are shown with the filled stars and circles, respectively. The dashed lines parallel to the solid one fit the data fairly good for higher pre-annealing temperatures. Indeed, taking into account that concentrations of the X- and M-centers in our samples are relatively low as compared to the most abundant radiation defects, the linear relationship is expected between the dimer amounts and concentrations of the dimer-related radiation defects. For pre-annealing temperatures below 500 °C the thermal donors are formed in our oxygen-rich crystals. The competition between thermal donors and oxygen dimers for the mobile radiation defects is believed to result in a saturation and further decrease of the X-center concentrations at lower pre-annealing temperatures.

It is seen in Fig. 4 that the introduction rate of the X-centers is about seven times higher than that of the M-centers, implying different structures of the two centers. Taking into account that the introduction rates for the X- and M-centers have been measured in n- and p-type samples, respectively, the remaining uncertainty is related to a possible effect of the Fermi level position on the defect reaction rates. Therefore, further experiments on the crystals with different doping levels are required to clarify the question.

4. Conclusion

The direct proportionality of the X- and M-center concentrations to the pre-irradiation amount of oxygen dimers indicates that oxygen dimer is the precursor of the both radiation defects. Although the introduction rates are not conclusive due to a possible Fermi level effect, the different annealing rates ask for a difference in the structure of the two centers.

Acknowledgements

The numerous discussions with E. Lavrov are highly appreciated. The work was supported by the Deutsche Forschungsgemeinschaft under Grant 436 RUS 17/22/06 and by the Russian Foundation for Basic Research (Grant 05-02-17730a).

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