



The influence of thermal treatments under hydrostatic pressure prior to irradiation on the annealing characteristics of the VO defect in Si

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ABSTRACT

Cz-Si samples, initially subjected to thermal treatments under high hydrostatic pressure, were subsequently irradiated by fast neutrons. This paper describes a series of infrared spectroscopy measurements that enabled us to determine the effect of the pre-treatments on the annealing characteristics of the VO defect in Si. We found that the activation energies of the two main annealing reactions: $\text{VO} + \text{O}_i \rightarrow \text{VO}_2$ and $\text{VO} + \text{Si}_i \rightarrow \text{O}_i$ that the defect participates, are comparatively smaller than those of initially untreated samples, correspondingly. We argue that the pre-treatments reduce the potential barrier for the migration of the VO defect ($\text{VO} + \text{O}_i \rightarrow \text{VO}_2$) and also reduces the binding energy of the Si_i 's, bound at large defect clusters ($\text{VO} + \text{Si}_i \rightarrow \text{O}_i$).

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1. Introduction

A-center, that is the vacancy-oxygen (VO) pair, is among the dominant defects produced in Cz-grown Si material subjected to any kind of irradiation at room temperature. The main reasons are that the monovacancies produced by irradiation (i) are too mobile to survive at such temperatures and (ii) that they are selectively trapped by oxygen atoms being at large concentrations in Cz-Si. The structure and the properties of the center have been meticulously studied by various experimental techniques such as electron paramagnetic resonance (EPR), deep level transient spectroscopy (DLTS), infrared spectroscopy (IR), etc. In the negative charge state the defect gives rise [1] to an EPR spectrum labeled Si-A. The suggested model [2] for its structure is a nearly substitutional oxygen atom, and more specifically an oxygen atom located in an off-center substitutional site in the $\langle 100 \rangle$ direction. DLTS measurements have associated [3] with the A-center an acceptor level in the band gap at $E_c - 0.18$ eV. IR spectroscopy which has been proven a powerful technique in investigating oxygen-vacancy related defects in Si, has associated [4,5] two localized vibrational mode bands at 830 and 877 cm^{-1} related to the neutral and the negative charge states of the VO defect, respectively.

Upon heating the samples, the VO defect participates in numerous reaction channels [6]. It may be associated with an oxygen atom to form the VO_2 defect, with a lattice vacancy to form the

V_2O defect or even with another VO defect to form the V_2O_2 complex. It may also dissociate or being destructed by self-interstitial atoms. Obviously, the contribution of all these reactions in the VO annealing is not the same. In neutron irradiated Cz-Si, the two reactions $\text{VO} + \text{O}_i \rightarrow \text{VO}_2$ and $\text{VO} + \text{Si}_i \rightarrow \text{O}_i$ are considered [6] as the most important reactions involved in the annealing process of the VO defect. An important parameter of each reaction process that a defect participates is the activation energy. Its knowledge is significant not only for the basic physics of defect studies but also as a crucial piece of information for defect control and defect engineering processes. On the other hand, pressure is an important external parameter besides temperature which affects the behavior and properties of defects. The present work is focused on the study of the influence of thermal treatments under hydrostatic pressure on the activation energies of the processes that govern the annealing of the VO defect and the growth of the VO_2 defect. It is well known [7,8] that thermal treatments at 450°C introduce thermal donors, while thermal treatments at 650°C introduce new donors which are associated to some kind of oxygen precipitates. In addition, the application of high hydrostatic pressure can induce [9] changes in the structure of defects. Thermal treatments under high hydrostatic pressure reduce [10] significantly the concentration of oxygen, thus enhancing the formation of thermal donors at 450°C and promoting oxygen precipitation at 650°C . We note that oxygen dimer, which is the first stage of oxygen precipitation process, is not expected [11] to survive at the above temperatures. Thus, the formation of the VO_2 defect as a result of the reaction $\text{V} + \text{O}_2 \rightarrow \text{VO}_2$ is not expected to occur in irradiated Si initially subjected to thermal treatment under high hydrostatic pressure. Only the VO defect is

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formed, which is expected to convert to the VO_2 defect at $\sim 300^\circ\text{C}$. The particular aim of this work is to study the evolution of the VO defect and its conversion to the VO_2 defect in a crystal environment which is different from that of an initially untreated material, due to the pre-treatments, and calculate the activation energies of the involved processes. Their values are expected, in general, to be different than those of the initially untreated material.

2. Experimental details

We used three groups of samples Cz-Si A_0 , A_3 , A_7 with initial oxygen content $1.4 \times 10^{18} \text{ cm}^{-3}$. The samples labeled A_0 are initially untreated. The samples A_3 and A_7 were subjected to thermal treatments with the application of hydrostatic pressure: A_3 (450°C , 10.65 kbar, 10 h), A_7 (650°C , 11 kbar, 10 h). After the above treatments all the samples were irradiated by fast neutrons with a fluence of $8 \times 10^{16} \text{ n/cm}^2$ at $T_{\text{irr}} \approx 50^\circ\text{C}$. Afterwards, 30 min isochronal anneals were carried out in steps of $\sim 10^\circ\text{C}$, in the range from 50 to 550°C . After each annealing step the IR spectra were taken at room temperature by employing a Jasco IR spectrometer of dispersive kind.

3. Experimental results and discussion

Fig. 1 shows fragments of the IR spectra of the A_0 , A_3 and A_7 samples after the pre-treatments, after the irradiations and after

the anneal at 350°C , in the course of the isochronal annealing sequence starting from 50°C . After the irradiation only the VO defect (828 cm^{-1}) is produced, as expected.

Fig. 2 shows the evolution with temperature of the amplitude of the O_i (1104 cm^{-1}), VO (828 cm^{-1}) and VO_2 (885 cm^{-1}) defects in the temperature range of 50 – 550°C , during the isochronal anneal sequence, of the samples A_0 , A_3 and A_7 . As it is seen from the evolution curves there is a gradual increase in the amplitude of the VO band between 200 and $\sim 300^\circ\text{C}$. This inverse annealing stage, occurring prior to the onset of the decay of the VO defect and its conversion to the VO_2 defect, is apparently due to the additional formation of VO defects. In fact, in the course of the annealing sequence, vacancies are liberated in this temperature range which are captured by oxygen atoms to form the VO defects. Sources of these vacancies are large clusters of defects [11,12], divacancies [13] and disordered regions [14]. The decrease of the O_i signal in the same temperature range, supports the interpretation for the additional VO formation.

The annealing of the VO defect is a rather complicated process. At least two main mechanisms should be considered [6]. At first, we observe that, the decrease of the amplitude of the 830 cm^{-1} band of the VO defect is accompanied by the emergence and growth in the spectra of the 885 cm^{-1} band of the VO_2 defect. The reaction that describes the phenomenon [15] is the $\text{VO} + \text{O}_i \rightarrow \text{VO}_2$, which is a first order process considering that $[\text{O}_i]$ is more than one order of magnitude larger than that of the $[\text{VO}]$. The corresponding differential

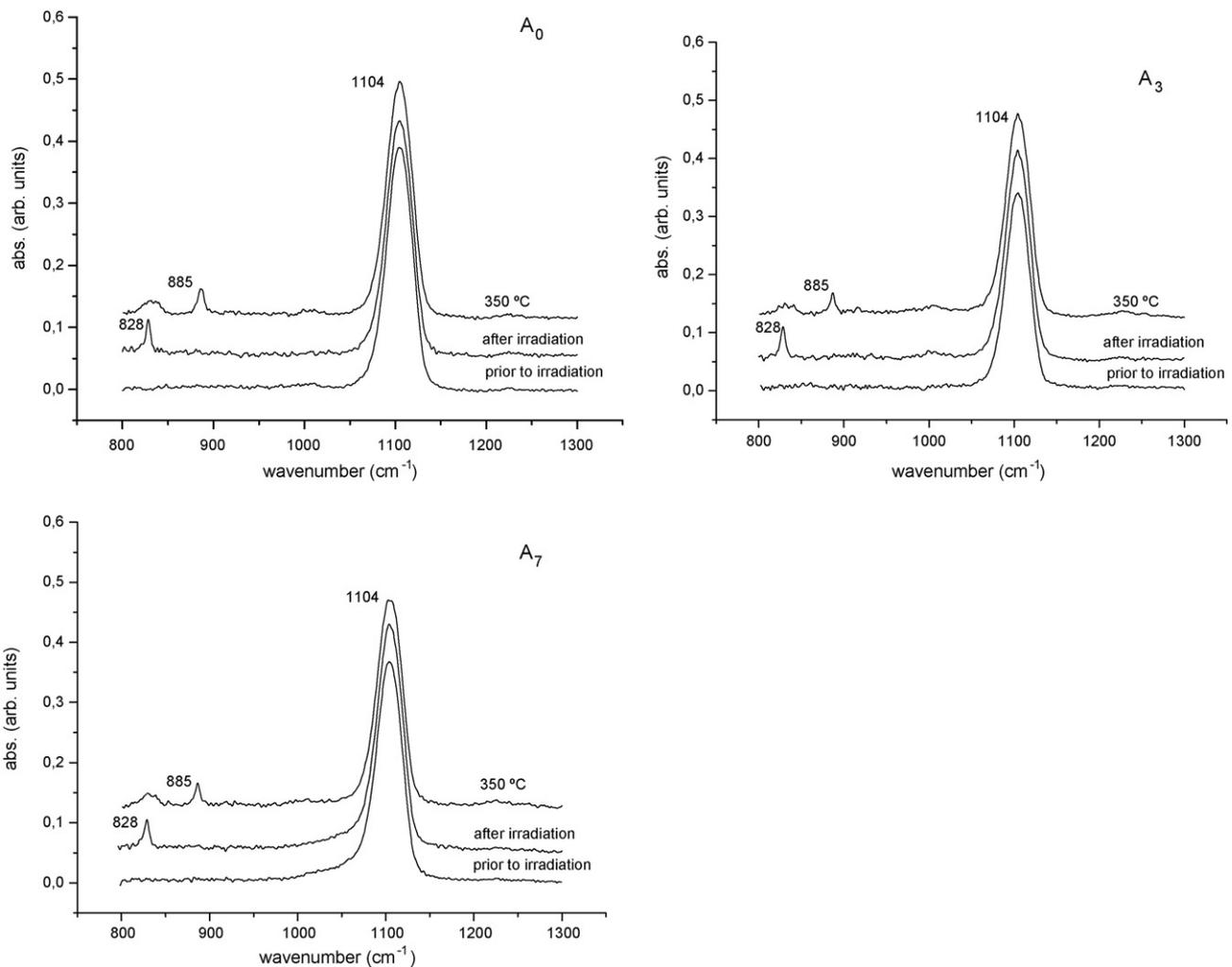


Fig. 1. Fragments of the IR spectra of the samples A_0 , A_3 and A_7 after the pre-treatments, after the irradiation and after the isochronal anneal at 350°C , correspondingly.

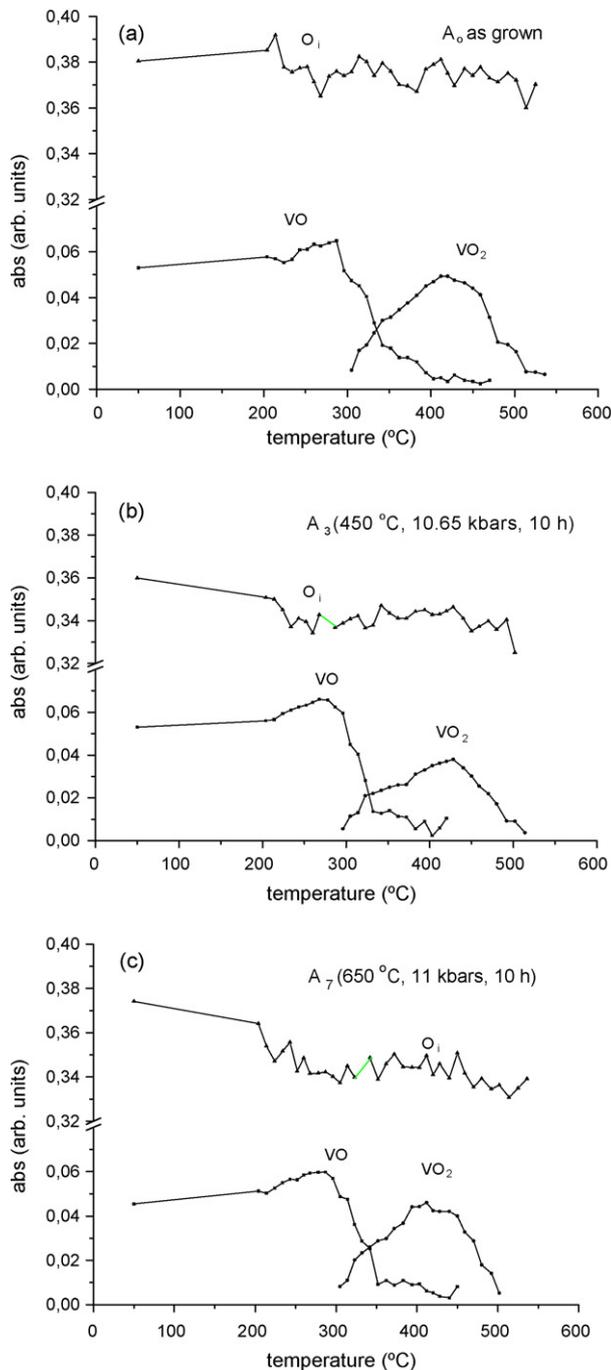


Fig. 2. The thermal evolution of the O_i , the VO and the VO_2 defects in Si, during the course of a 30 min isochronal anneals sequence for the samples (a) A_0 , (b) A_3 and (c) A_7 , correspondingly.

equation is:

$$\frac{d[VO]}{dt} = -k_1[VO] \quad (1)$$

The rate constant k_1 of the process is given by the equation $k_1 = k_{10} \exp(-E/KT)$, where k_{10} is a frequency factor and E the activation energy of the process. Secondly, we observe that the initial stage of the decrease of the VO signal is accompanied by an increase in the O_i amplitude. Actually, the evolution curves of O_i are too noisy and at first look it is difficult to make any definite statement about increases of the O_i amplitudes. However, on closer inspection, for the temperatures above 300 °C where VO defect begins to decay,

the oxygen concentration shows a general tendency to increase, especially for the pre-treated samples A_0 and A_7 . This stage of VO was attributed [11] to the reaction $VO + Si_i \rightarrow O_i$, where the Si_i 's atoms are released from large defect clusters formed by the irradiation, especially in the neutron-irradiated samples. The increase of the O_i concentration could be also related to the VO dissociation: $VO \rightarrow V + O_i$. However, experimental observations strongly suggest that the latter reaction should not be taken into account [11,16].

The $VO + Si_i \rightarrow O_i$ reaction is approximately a second order process [11,17] described by the reaction:

$$\frac{d[VO]}{dt} = -k_2[VO]^2 \quad (2)$$

where we have assumed that $[Si_i] \approx [V] \approx [VO]$. Actually, after the irradiation most of the produced vacancies (V) and the self-interstitials (Si_i) are annihilated ($V + Si_i \rightarrow \emptyset$). The remaining V and Si_i 's are of about the same concentrations, i.e., $[V] = [Si_i]$. Almost all of the remaining V are expected to be trapped by O_i atoms to form VO defects. On the other hand, almost all of the remaining Si_i 's are expected to be incorporated at large interstitial clusters, especially in a material with very low carbon content like our samples. Upon annealing, these Si_i 's are liberated and react with VO. Reasonably therefore we can assume that $[VO] = [Si_i]$. According to the above, the annealing process of the VO defect could be divided [11] into two stages. The first stage describes the initial decay of the VO defects in the temperature range 300–350 °C, where the reaction $VO + Si_i \rightarrow O_i$ predominates. Actually, below 350 °C the VO_2 signal is weak indicating that the reaction $VO + Si_i \rightarrow O_i$ prevails over the reaction $VO + O_i \rightarrow VO_2$. Above ~350 °C the increase of the O_i concentration is practically terminated. No further production of O_i atoms seems to occur. At a later stage of the anneal the release of Si_i 's from the agglomerates is expected [11] to be reduced and thus the regeneration of O_i atoms due to the reaction $VO + Si_i \rightarrow O_i$ also reduces. At higher temperatures, here ~350 °C, the production of O_i atoms due to the reaction $VO + Si_i \rightarrow O_i$ is balanced [11,17] by the loss of O_i atoms due to the reaction $VO + O_i \rightarrow VO_2$. The second stage refers to the temperature range 350–410 °C, where the reaction $VO + O_i \rightarrow VO_2$ is considered to prevail. Notice that Eq. (1) that describes this process has the same activation energy with the process that describes the growth of the VO_2 defect, which follows the equation:

$$\frac{d[VO_2]}{dt} = k_1[VO] \quad (3)$$

considering that almost all the VO defects at this stage are converted to VO_2 defects ($VO + O_i \rightarrow VO_2$). The results of the fittings together with the Arrhenius plots and the extracted activation energies are exhibited in Figs. 3–5.

The calculated values for the activation energies of the samples A_3 and A_7 pre-treated under high hydrostatic pressure at 450 and 650 °C, respectively, are lower than the corresponding values of the activation energy of the initially untreated sample A_0 , for both stages of the annealing process. Actually, changes in the activation energies were expected due to the fact that the pre-treatments under pressure have induced changes in the crystalline environment of the defects of the Si material. As a result, the migration of the VO defect towards the O_i atoms and/or of the Si_i 's atoms towards the VO defects take place in a different surrounding in comparison with that of the initially untreated sample. We argue that thermal treatments under high pressure create conditions inside the crystal that facilitate the reaction processes, that VO participates. Quantitatively, this is expressed by the lower values of the activation energies of the two annealing processes that VO defect participates.

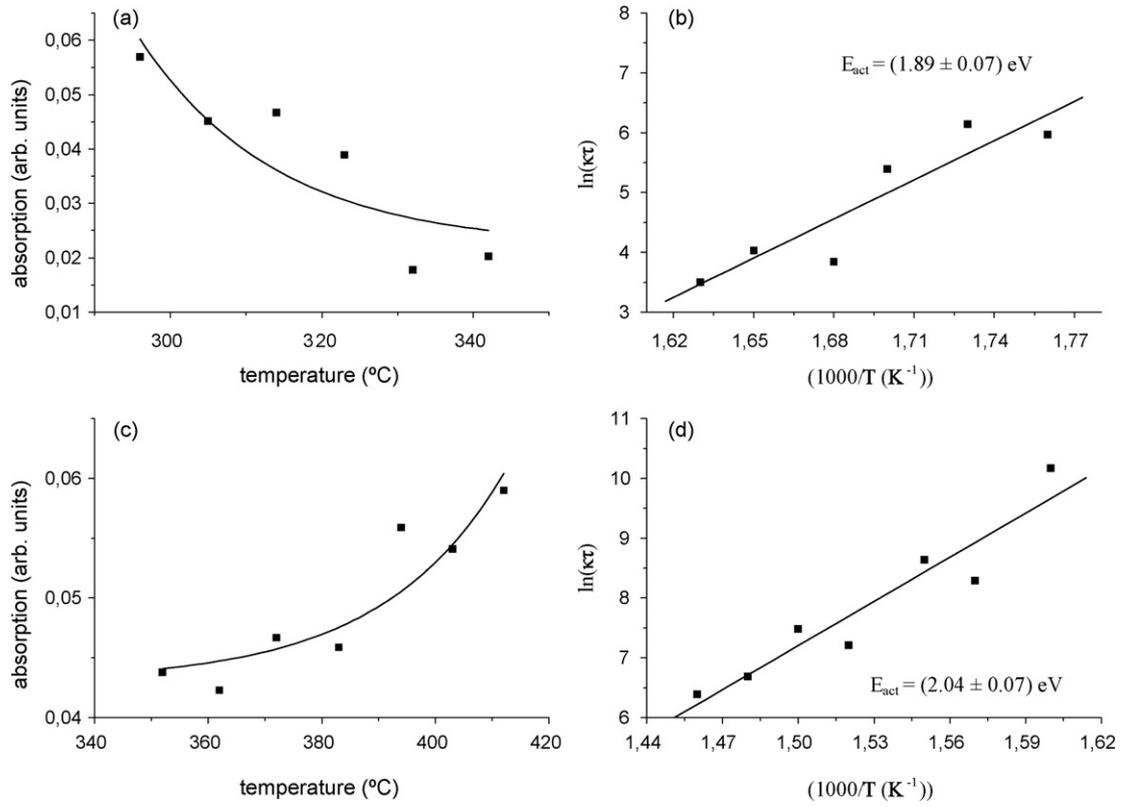


Fig. 3. Simulation curves describing the annealing of the VO defect (a) and the growth of the VO₂ defect (c) for the sample A₀. Arrhenius plots for the decay of the VO defect (b) and the growth of the VO₂ defect (d).

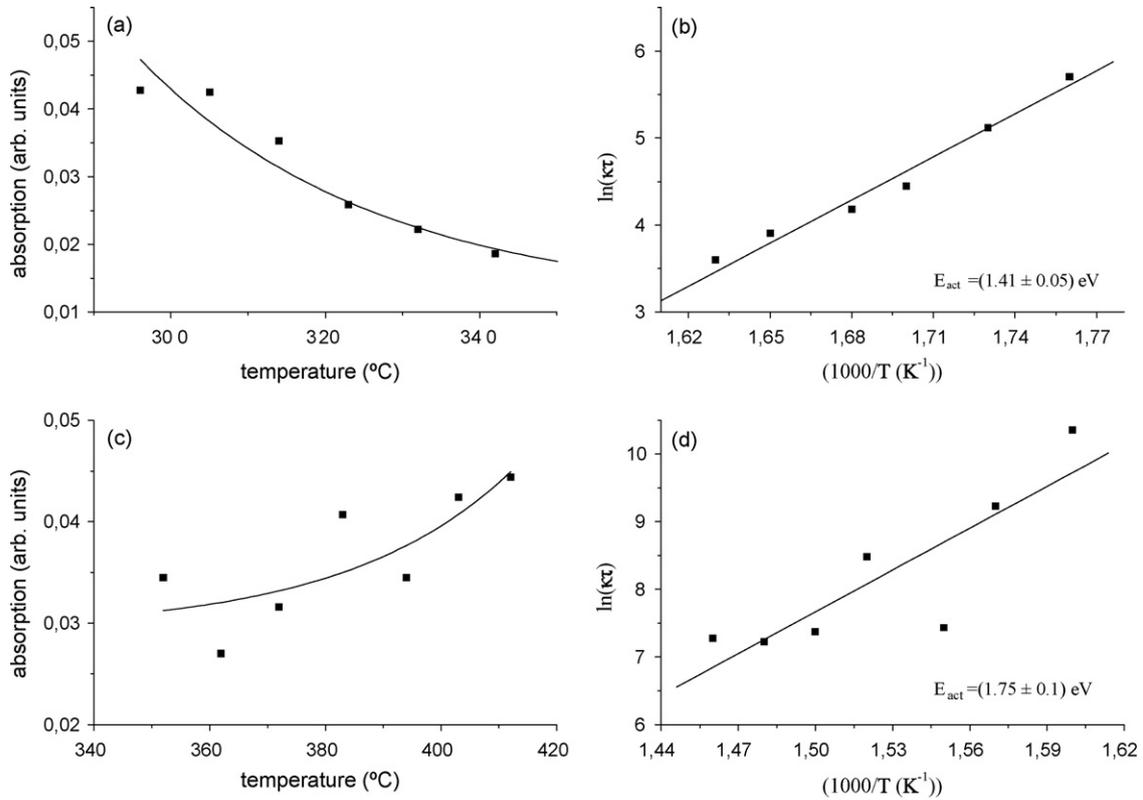


Fig. 4. Simulation curves describing the annealing of the VO defect (a) and the growth of the VO₂ defect (c) for the sample A₃. Arrhenius plots for the decay of the VO defect (b) and the growth of the VO₂ defect (d).

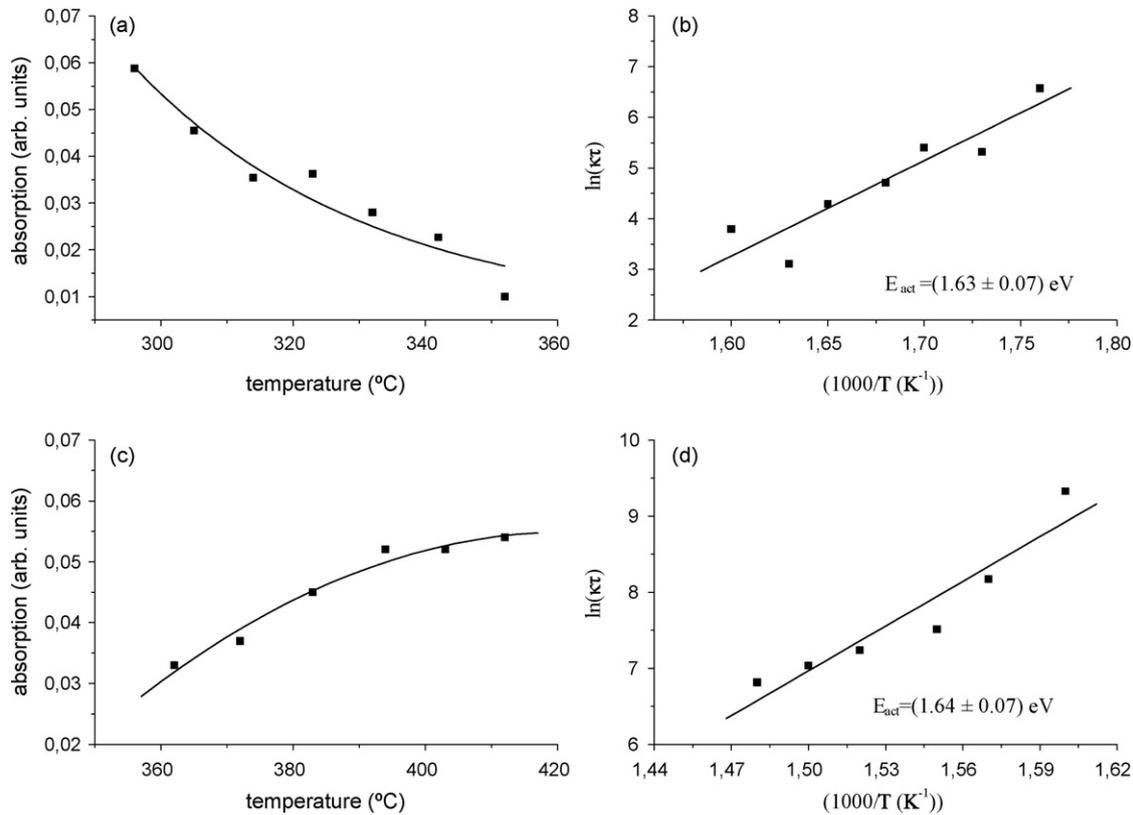


Fig. 5. Simulation curves describing the annealing of the VO defect (a) and the growth of the VO₂ defect (c) for the sample A₇. Arrhenius plots for the decay of the VO defect (b) and the growth of the VO₂ defect (d).

The extracted value for the activation energy of the reaction $\text{VO} + \text{Si}_i \rightarrow \text{O}_i$ is 1.89 eV for the initially untreated sample A₀. This value is found to be 1.41 eV for the A₃ sample and 1.63 eV for the A₇ sample. Assuming that the activation energy for the migration of the Si_i's is negligible, the activation energy of the reaction $\text{VO} + \text{Si}_i \rightarrow \text{O}_i$ in essence refers to the energy of a self-interstitial atom to break away from the agglomerate. Due to the treatments under pressure this binding energy for the samples A₃ and A₇ is apparently smaller than that of the A₀ sample. Additionally, the binding energies are expected to be different between the samples treated under pressure at different temperatures since the size and the structure of the agglomerates is expected to be different. The analysis of the experimental data indicates that the binding energy of the Si_i's of the A₃ sample is smaller than that of the A₇ sample.

The extracted value for the activation energy of the reaction $\text{VO} + \text{O}_i \rightarrow \text{VO}_2$ is 2.04 eV for the initially untreated sample A₀. This value is found to be 1.75 eV for the A₃ sample and 1.64 eV for the A₇ sample. The application of high hydrostatic pressure has a permanent effect on the treated crystals. Thus, the pre-treated samples under pressure are stressed materials. Notice now that theoretical calculations [18] predict an increase in the diffusivity of vacancy-dopant pairs in Si material under compressive stress. Thus, a larger diffusivity is expected for the VO defect. Additionally the diffusivity of O_i defect is larger [19] under stress. For applied pressures around 10 kbar the changes in the Si lattice constant are small [19]. Thus, any changes in the pre-exponential coefficient D_0 in the expression of the diffusivity $D = D_0 \exp(-E/KT)$ is expected to be negligible and the variation of D is mainly determined by the variation of the activation energy E . Larger diffusivities means smaller activation energies. The difference in the values of the activation energies of the samples A₃ and A₇ reflects to the different temperatures of the high-pressure treatment and therefore the different effect

of the compressive stress at the corresponding temperatures. It is worth stating that the balance between the two main reactions $\text{VO} + \text{O}_i \rightarrow \text{VO}_2$ and $\text{VO} + \text{Si}_i \rightarrow \text{O}_i$ contributing in the anneal process of VO is affected by the pre-treatments. In other words the contribution of the two reactions in the VO anneals is different for different pre-treatments.

It worth noting that by looking at the evolution curves of the VO and the VO₂ defects in Fig. 2, for the samples A₀, A₃ and A₇ it is difficult to notice any significant difference between them. The effect of pre-treatment under pressure is not well pronounced. Thus, it may be argued that the differences of the activation energies, derived by the analysis shown in Figs. 3–5, arise simply from the scatter of the points. Though there is indeed a large scatter of the points, the results of the least-square-fits (mean values and standard deviations) in Figs. 3–5 unambiguously demonstrate a decrease in the activation energies of the pre-treated samples. Additionally, we notice that in this experiment we used three samples from each group A₀, A₃ and A₇ and the received values of the activation energies were similar to those reported in the text, correspondingly.

4. Conclusions

We studied the reaction kinetics of the conversion of the VO to the VO₂ defect in neutron-irradiated Si samples, pre-treated at 450 and 650 °C under high hydrostatic pressure. Two main annealed reactions were considered: $\text{VO} + \text{Si}_i \rightarrow \text{O}_i$ and $\text{VO} + \text{O}_i \rightarrow \text{VO}_2$. The activation energies of the two processes were found smaller in the pre-treated samples than those of the untreated samples, correspondingly. We argue that the pre-treatments result in the reduction of (i) the binding energy of the Si_i's at the agglomerates and (ii) the potential barrier characterising the movement of the VO defect in the Si lattice.

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