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Isochronal Annealing Studies of the Oxygen–Vacancy Centres in Neutron-Irradiated Si

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The infrared spectra of room-temperature, neutron-irradiated, Czochralski-grown Si were investigated. During annealing, the 827 cm^{-1} VO defect band decreases, and another band at 885 cm^{-1} generally attributed to the VO_2 centre increases. The kinetics of the evolution of these two defects was investigated. The decay of VO is dominated by a second-order reaction ($VO + Si_i \rightarrow O_i$) with an activation energy 1.70 eV. The growth of VO_2 exhibits two stages. Below 360 °C, a first-order reaction ($VO + O_i \rightarrow VO_2$) with an activating energy of 1.46 eV or a second-order reaction ($VO + VO \rightarrow VO_2 + V$) with an activation energy of 1.96 eV could fit the data. The two cases are considered and discussed. The analysis goes further taking into account the more realistic case that both reactions occur in parallel. Values of 2.1 and 2.0 eV were derived, respectively. Above 360 °C, the phenomenon is not well understood, as other factors might also be at work which manifest their presence more profoundly above this temperature.

1. Introduction

The A-centre (VO) is one of the most common defects encountered in irradiated Si. Although a lot of information has been gathered about the structure and the electronic and optical properties of the centre, its exact annealing behaviour has not been completely clarified so far. The main reason for this is that the annealing of A-centres can follow simultaneously more than one reaction channel, as for example:

(i) Destruction [1] of A-centres by silicon self-interstitials emitted from defect clusters:

$$VO + Si_i \rightarrow O_i\,. \tag{1}$$

(ii) Association [2] of VO with O_i atoms:

$$VO + O_i \rightarrow VO_2 \tag{2}$$

and/or complexing [3] with another VO centre:

$$VO + VO \rightarrow V_2O_2 \rightarrow VO_2 + V\,. \tag{3}$$

(iii) Dissociation of A-centres:

$$VO \rightarrow V + O_i\,, \tag{4}$$

(iv) Association of VO with V:

$$VO + V \rightarrow V_2O \tag{5}$$

and/or V_2:

$$VO + V_2 \rightarrow V_3O \tag{6}$$

are also possible reaction channels. In principle, all these processes could occur in parallel. However, it depends on the dose and the kind of irradiation, the oxygen content of the material, the examined temperature range etc., which mechanism will prevail. It is therefore evident that the annealing process of the A-centre is compounded and complicated. Consequently, experimental data should be treated very carefully in order to distinguish the effect of the various processes and avoid misleading conclusions. Activation energies, for example, reported from Arrhenius plots where only one process has been considered, may not represent true values if one or more competing processes with different activation energies occur in parallel. The scatter of reported values of activation energies cited in the literature reflects the above complexities as a result of the fact that a consensus among researchers has not been reached concerning the exact kinetics describing the phenomenon [2 to 5].

In IR studies the decay of the $827\ \mathrm{cm}^{-1}$ signal from A-centres is accompanied by the growth of an $885\ \mathrm{cm}^{-1}$ signal attributed to VO_2 defects [2]. In this paper, we shall examine the annealing kinetics of A-centres and the correlated growth kinetics of VO_2 defects using data taken from isochronal annealing studies of fast neutron-irradiated Cz-grown Si. We shall consider three cases of combining processes for the decay of VO and the growth of VO_2 defects mainly connected with reactions (1), (2) and (3) in an attempt to establish which are the most suitable, but also physically meaningful mechanisms, that could explain the experimental data.

2. Experimental

Cz-grown Si samples, initially n-type ($[P] \approx 10^{14}\ \mathrm{cm}^{-3}$) with undetectable levels of substitutional carbon C_s ($[C_s] < 10^{16}\ \mathrm{cm}^{-3}$) and $[O_i] \approx 10^{18}\ \mathrm{cm}^{-3}$ were irradiated ($T_{\mathrm{irr}} < 50\ ^\circ\mathrm{C}$) by fast neutrons at a dose equal to $10^{17}\ \mathrm{cm}^{-2}$. The samples were wrapped in Cd foils to eliminate the effect of thermal neutrons. The heat treatments for annealing studies were carried out in open furnaces. The infrared absorption spectra were recorded at room temperature by using a JASCO-IR 700 dual beam spectrometer. Control samples of equal thickness from float-zone material were used during the measurements in order to subtract the two-phonon inherent absorption of the Si lattice.

3. Experimental Results and Discussion

As expected, the A-centre band at $827\ \mathrm{cm}^{-1}$ appears in our IR spectra, immediately after irradiation. On increasing the temperature, as the isochronal anneal is carried out, the shape of the band is distorted by the emergence of satellite bands previously reported in the literature [6, 7]. To extract the individual contribution of each component, the data were analyzed by computer deconvolution using Lorentzian profiles for each band. Fig. 1 shows the annealing behaviour of the A-centre band after subtracting the contributions of the satellite bands. The growth of the $885\ \mathrm{cm}^{-1}$ band attributed to the VO_2 centre is also shown. The study of the evolution of these two defects will be the subject of this investigation.

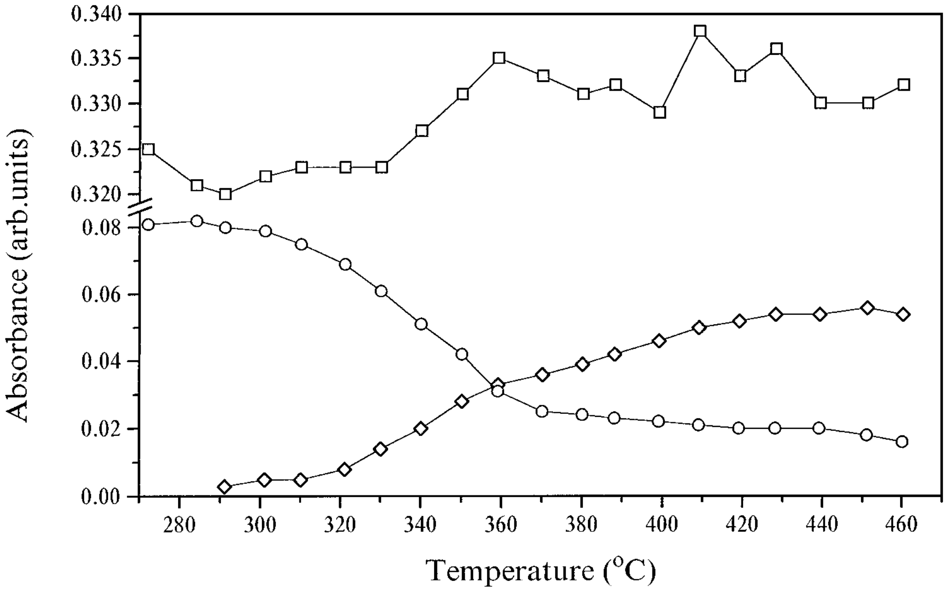

Fig. 1. The evolution of VO (○), VO_2 (◇) and O_i (□) defects as a function of temperature in a 15 min isochronal annealing sequence

3.1 The decay of VO

As already mentioned there are many reactions, Eqs. (1) to (6), that could take place on this temperature range. However, the irradiation is rather heavy and the isochronal annealing time $\tau = 15$ min is rather small. One would expect, therefore, that the contribution of some of the reactions will be negligible in comparison with some others [3]. In an attempt to determine the order of the reaction that dominates the decay of VO we assume that it generally follows γ-order kinetics described by the equation

$$\frac{\mathrm{d}[\mathrm{VO}]}{\mathrm{d}t} = -k_\gamma [\mathrm{VO}]^\gamma \,, \tag{7}$$

and we shall calculate the proper value of γ that fits best our experimental data. Eq. (7) leads to the following expressions [8] of the rate constant k:

$$k_\gamma \,\Delta t = \ln \frac{[\mathrm{VO}]_t}{[\mathrm{VO}]_{t+\Delta t}} \quad \text{for} \quad \gamma = 1 \tag{8}$$

and

$$k_\gamma \,\Delta t = \left(\frac{1}{[\mathrm{VO}]_t^{\gamma-1}} - \frac{1}{[\mathrm{VO}]_{t+\Delta t}^{\gamma-1}} \right) \quad \text{for} \quad \gamma \neq 1 \,. \tag{9}$$

Equations (8) and (9) provide values of the rate constant k_γ for each annealing temperature T. These values change with the value of the reaction order γ. For any arbitrary value of γ, we can make the Arrhenius plot $\ln(k_\gamma) = f(1/T)$, which is a straight line with a slope equal to the activation energy E_a of the process divided by the Boltzmann constant k. In order to find the proper reaction order γ, we calculate the correlation coefficient r_γ of the linear regression for any value of γ. r_γ is defined [9] by the expression

$$r_\gamma = \frac{n \sum \frac{1}{T} \ln(k_\gamma) - \sum \frac{1}{T} \sum \ln(k_\gamma)}{\sqrt{\left[n \sum \left(\frac{1}{T}\right)^2 - \left(\sum \frac{1}{T}\right)^2\right] \left[n \sum (\ln(k_\gamma))^2 - \left(\sum \ln(k_\gamma)\right)^2\right]}}\,, \tag{10}$$

where n is the number of points used in the regression. Reasonably, the most acceptable value of γ is that for which r_γ becomes maximum [8]. In Fig. 2, we plot the correlation coefficient r_γ as a function of γ. As is shown in this figure, the maximum value of r_γ is obtained for $\gamma = 1.8$ with a corresponding activation energy of $E_a = (1.56 \pm 0.05)$ eV. Moreover, we can also see from the figure that the change in r_γ between $\gamma = 1.8$ and 2 is negligible, indicating that the decay of VO is dominated by an almost second-order reaction.

Such a reaction is actually that described by equation (1). Notice at first, that in neutron-irradiated Si large clusters of defects are formed, which are expected [1] to liberate silicon self-interstitials in the temperature range under consideration. Thus the process described by the reaction $\mathrm{VO} + \mathrm{Si_i} \rightarrow \mathrm{O_i}$ is the most likely one to occur and account for the decay of VO. Such a process is also in agreement with the corresponding increase of the $\mathrm{O_i}$ concentration shown in Fig. 1 that was found to accompany the decrease of VO concentration. Noticeably, reaction (1) is described by the rate equation

$$\frac{\mathrm{d[VO]}}{\mathrm{d}t} = -k_1 [\mathrm{VO}]\,[\mathrm{Si_i}] \tag{11}$$

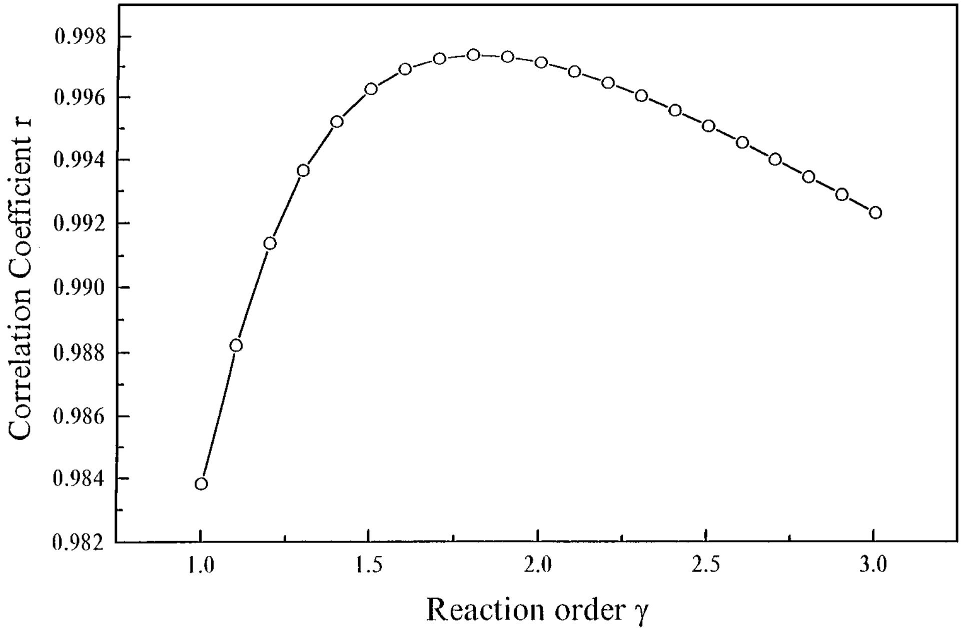

Fig. 2. Correlation coefficient for data concerning the VO decay as a function of the reaction order

which, however, could be approximated, with a small error, by a second-order reaction. In fact, this is reasonable since immediately after irradiation [V] ≈ [$\mathrm{Si_i}$], and assuming that almost all the vacancies are captured by oxygen atoms to form VO pairs, i.e. [VO] ≈ [V], we finally have [VO] ≈ [$\mathrm{Si_i}$] leading to the rate equation

$$\frac{\mathrm{d[VO]}}{\mathrm{d}t} = -k_1 [\mathrm{VO}]^2 . \tag{12}$$

In the above analysis other contributions to the decay of VO have been ignored. This is however a plausible assumption which is further supported by the obtained value of 1.8 for the reaction order of the rate equation (7).

By integration, one gets

$$[\mathrm{VO}]\,(t) = \frac{[\mathrm{VO}]_0}{1 + [\mathrm{VO}]_0\, k_1 t} , \tag{13}$$

and therefore

$$k_1 \tau = \frac{1}{[\mathrm{VO}]'} - \frac{1}{[\mathrm{VO}]_0} , \tag{14}$$

where k_1 has a temperature dependence of the form $k_1 \propto \mathrm{e}^{-E_1/kT}$, E_1 being the activation energy of the process, $[\mathrm{VO}]_0$ is the initial concentration of A-centres, $[\mathrm{VO}]'$ the concentration of VO after annealing for time τ at temperature T, and $[\mathrm{VO}](t)$ the concentration of VO at any time during the isochronal annealing at T. By fitting ln k_1 versus

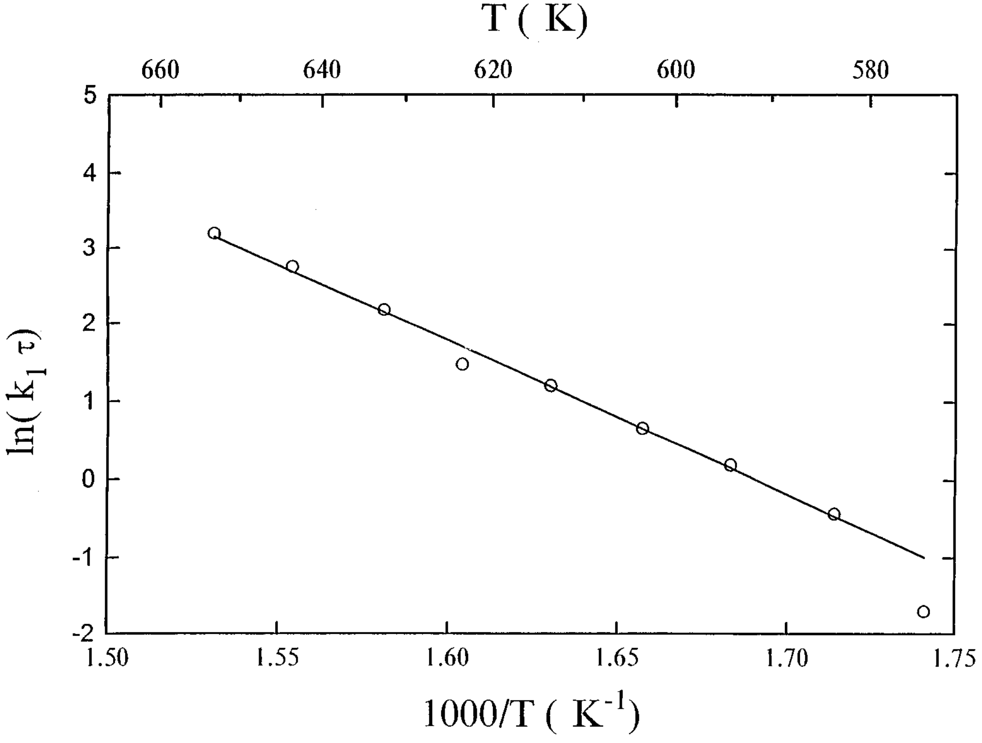

Fig. 3. Arrhenius plot for the decay of VO

$1/T$ in the range 310 to 380 °C (Fig. 3), we find an activation energy of $E_1 = (1.70 \pm 0.05)$ eV with a correlation coefficient of $r = 0.997$.

In what follows, we shall assume that the decay of VO is dominated by the reaction $\mathrm{VO} + \mathrm{Si_i} \rightarrow \mathrm{O_i}$, so that all other reactions are only minor disturbances in terms of the VO concentration. According to this assumption, the concentration of VO is given at any temperature by (13).

3.2 The growth of VO_2

As is seen from Fig. 1 the growth of $\mathrm{VO_2}$ is concomitant with the decay of A-centres. A simple way to study the relation between the two processes is by combining equation (1), either with equation (2) or with equation (3). Dissociation is not considered to affect significantly the decay of A-centers [10] especially in the temperature range of 300 to 360 °C where the rapid decrease appears, and therefore equation (4) is not taken into account in this study. Other reaction channels expressed by equations (5) and (6) are also excluded from the present analysis. In the following, we shall firstly proceed with each case independently while afterwards both cases will be considered in combination.

(i) In the first alternative the production of $\mathrm{VO_2}$ follows a first-order reaction described by the equation

$$\frac{\mathrm{d}[\mathrm{VO_2}]}{\mathrm{d}t} = k_2[\mathrm{VO}]\,, \tag{15}$$

where $[\mathrm{VO}](t)$ is given by equation (13). By integration, one gets

$$k_2 = k_1\,\frac{[\mathrm{VO_2}]' - [\mathrm{VO_2}]_0}{\ln\left([\mathrm{VO}]_0/[\mathrm{VO}]'\right)}\,, \tag{16}$$

where $[\mathrm{VO_2}]_0$ and $[\mathrm{VO_2}]'$ are defined in the same way as $[\mathrm{VO}]_0$ and $[\mathrm{VO}]'$, respectively. By substituting equation (14) into (16) the following expression for k_2 is obtained

$$k_2\tau = \left(\frac{1}{[\mathrm{VO}]'} - \frac{1}{[\mathrm{VO}]_0}\right)\frac{[\mathrm{VO_2}]' - [\mathrm{VO_2}]_0}{\ln\left([\mathrm{VO}]_0/[\mathrm{VO}]'\right)}\,. \tag{17}$$

The Arrhenius plot for the rate constant k_2 is shown in Fig. 4. As is seen from this graph two stages possibly exist. In the first stage, below 360 °C, the logarithm of the rate constant can be fitted to a linear expression of $1/T$, and an activation energy of $E_2 = (1.46 \pm 0.29)$ eV is obtained, with a correlation coefficient $r = 0.962$. Temperatures above ≈360 °C will be discussed later.

(ii) In the second alternative, the production of $\mathrm{VO_2}$ follows a second-order reaction, described by the equation

$$\frac{\mathrm{d}[\mathrm{VO_2}]}{\mathrm{d}t} = k_2'[\mathrm{VO}]^2\,, \tag{18}$$

where $[\mathrm{VO}](t)$ is given by equation (13). By integration one gets

$$k_2' = k_1\,\frac{[\mathrm{VO_2}]' - [\mathrm{VO_2}]_0}{[\mathrm{VO}]_0 - [\mathrm{VO}]'}\,. \tag{19}$$

By substituting equation (14) into (20) the following expression for k_2' is obtained

$$k_2'\tau = \left(\frac{1}{[\mathrm{VO}]'} - \frac{1}{[\mathrm{VO}]_0}\right)\frac{[\mathrm{VO_2}]' - [\mathrm{VO_2}]_0}{[\mathrm{VO}]_0 - [\mathrm{VO}]'}\,. \tag{20}$$

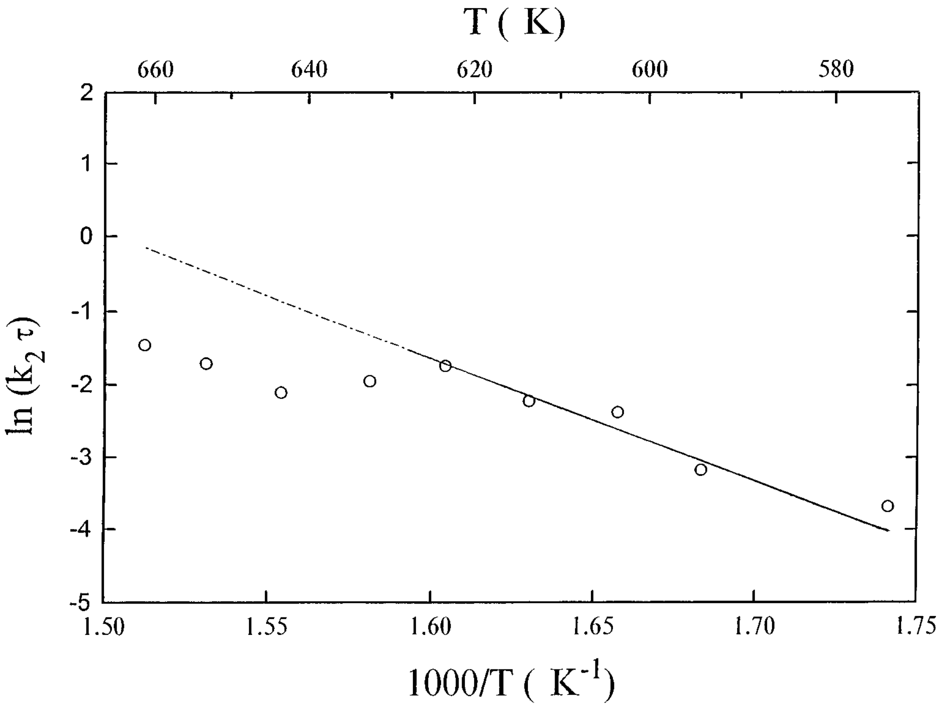

Fig. 4. Arrhenius plot for the growth of VO_2 (first case)

The Arrhenius plot for the rate constant k_2' is shown in Fig. 5. We observe again the existence of two characteristic stages below and above 360 °C. The activation energy, extracted from fitting the data of the first stage, has a value $E_2' = (1.96 \pm 0.27)$ eV, with a correlation coefficient $r = 0.981$. Again we defer our discussion for temperatures above ≈360 °C for later on.

The results are summarized in Table 1. Apparently, an activation energy of 1.46 eV for the movement of the A-center, as derived in the first case, is difficult to accept, whereas an activation energy of 1.96 eV, as derived in the second case, is more reasonable. Moreover, judging from the values of the correlation coefficients, the experimental data for the growth of VO_2 fit better with a second-order reaction. That raises a question, since the reaction $VO + O_i \rightarrow VO_2$ cannot be excluded due to the fact that $[O_i]$ is about two orders of magnitude larger than [VO]. Consequently, migrating VO defects would be expected to be trapped readily by oxygen atoms. In our opinion, both reactions (2) and (3) do occur in parallel. This is corroborated by Fig. 6 which is the analogue to Fig. 2 but for the growth of the VO_2 band. In this case, the correlation coefficient monotonously increases with reaction order γ, especially in the range of $1 \le \gamma \le 3$, where γ is more physically meaningful. This fact is an indication of mixed kinetics. In line with the above, the most possible selection is a combination of a first-order reaction process with a second-order reaction process.

(iii) In the third case we proceeded by taking into account reactions (2) and (3) simultaneously. The growth of $[VO_2]$ is now described by the equation

$$\frac{\mathrm{d}[VO_2]}{\mathrm{d}t} = k_2[VO] + k_2'[VO]^2 \,. \tag{21}$$

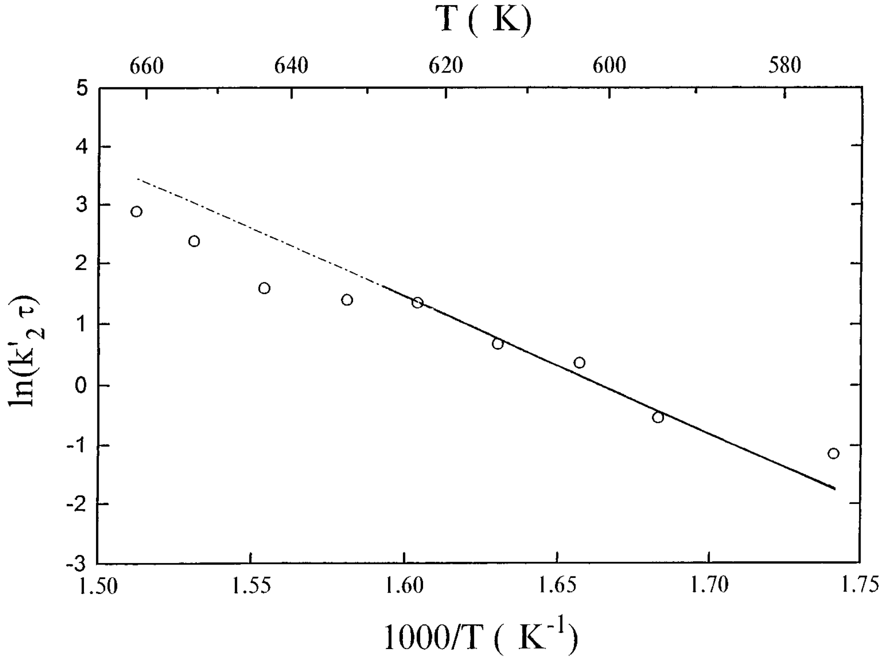

Fig. 5. Arrhenius plot for the growth of VO_2 (second case)

The determination of k_2 and k_2' of (21) from isochronal annealing data is no more a simple task since multiple regression is required. Considering that [VO] evolution obeys equation (13) (notice that $r_1 = 0.997$) the following integral form of (21) is obtained:

$$([VO_2]' - [VO_2]_0)\left(\frac{1}{[VO]'} - \frac{1}{[VO]_0}\right) = k_2\tau \ln\left(\frac{[VO]_0}{[VO]'}\right) + k_2'\tau([VO]_0 - [VO]') . \tag{22}$$

Table 1
The three cases for the decay of VO and the growth of VO_2 defects

	first case	second case	third case
reactions	$VO + Si_i \to O_i$ $VO + O_i \to VO_2$	$VO + Si_i \to O_i$ $VO + VO \to VO_2 + V$	$VO + Si_i \to O_i$ $VO + O_i \to VO_2$ $VO + VO \to VO_2 + V$
rate equations	$\frac{d[VO]}{dt} = -k_1[VO]^2$ $\frac{d[VO_2]}{dt} = k_2[VO]$	$\frac{d[VO]}{dt} = -k_1[VO]^2$ $\frac{d[VO_2]}{dt} = k_2'[VO]^2$	$\frac{d[VO]}{dt} = -k_1[VO]^2$ $\frac{d[VO_2]}{dt} = k_2[VO] + k_2'[VO]^2$
activation energies	$E_1 = (1.70 \pm 0.05)$ eV $E_2 = (1.46 \pm 0.29)$ eV	$E_1 = (1.70 \pm 0.05)$ eV $E_2' = (1.96 \pm 0.27)$ eV	$E_1 = (1.70 \pm 0.05)$ eV $E_2 = (2.1 \pm 0.2)$ eV $E_2' = (2.0 \pm 0.2)$ eV
cor. coefficients	$r_1 = 0.997$ $r_2 = 0.962$	$r_1 = 0.997$ $r_{2'} = 0.981$	$r_1 = 0.997$
normalized χ^2	1.000	0.107	0.076

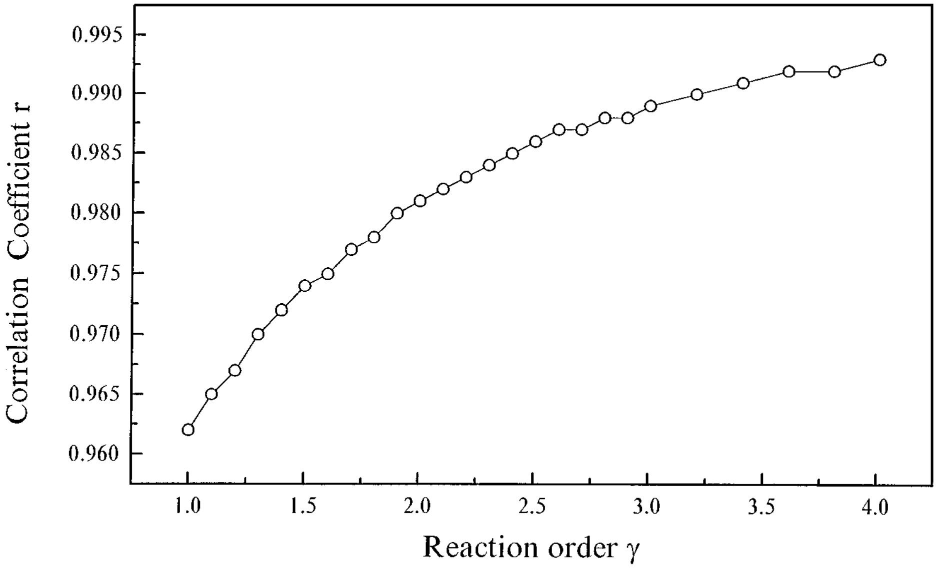

Fig. 6. Correlation coefficient for data concerning the growth of VO_2 as a function of the reaction order

Taking the usual temperature dependence $k = c\,e^{-E/kT}$ for each of the two rate constants, the corresponding pre-exponential factors c are obtained by fitting the experimental data to (22). Thus, for any pair E_2, E_2' of activation energies, an optimum pair c_2, c_2' of pre-exponential coefficients is obtained. Comparing the theoretical values of $[VO_2]_{th}$, expected from this set of rate constants, with the experimental values $[VO_2]_{exp}$, the set of activation energies that minimizes the quantity $\chi^2 = \sum([VO_2]_{exp} - [VO_2]_{th})^2$ could be derived. The values derived by this way of analysis are $E_2 = (2.1 \pm 0.2)$ eV and $E_2' = (2.0 \pm 0.2)$ eV and are also cited in Table 1. Notice that the value of χ^2 in this case was smaller than that obtained in the previous two cases (Table 1). The fit of the experimental data by the theoretical curves of the three considered cases is shown in Fig. 7. Apparently, the third case is more realistic in describing the phenomenon. Both activation energies E_2, E_2' refer to the movement of the VO defect which is trapped either by an isolated interstitial oxygen atom or/and by another VO defect. These values for the migration of the A-centre are in fair agreement with previous values reported in the literature [3].

Let us consider now the second stage, above 360 °C, of the growth of VO_2. As seen from both Figs. 4 and 5, the experimental points deviate from the straight lines which represent Arrhenius plots for temperatures below ≈360 °C. In other words, the experimental values of $\ln k_2$ or $\ln k_2'$ are not described adequately by these regression lines. More specifically, above 360 °C, a reduction in the production of VO_2 is observed, as is indicated in Fig. 7. This reduction has also been observed in [2], Fig. 3. It could be surmised that above this temperature other mechanisms are at work in the evolution of the VO_2 defect. It seems that the growth process of VO_2 is more complicated than it appears at first sight. It may be argued that more than one mechanism are involved in the whole process, which below 360 °C could be represented by the reaction kinetics we have described. However, above this temperature this kinetics fails to fit the data properly

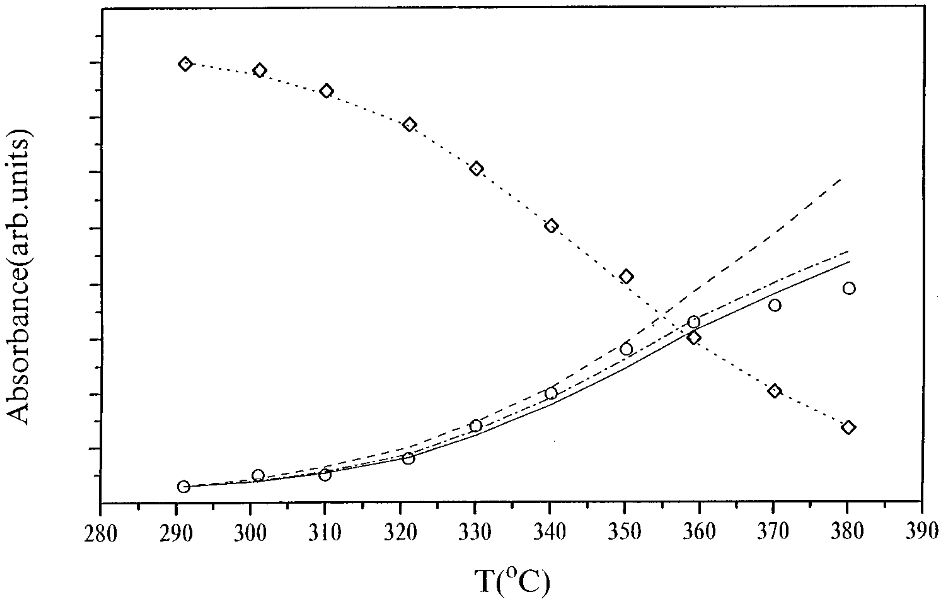

Fig. 7. Experimental data for the evolution of the defects VO (◇) and VO_2 (○) and the corresponding theoretical fitting curves for the first (dashed), second (dash-dotted), and third (full) cases

and our analysis deviates from the experimental data. Unfortunately, more definitive suggestions cannot be put forward from our data. Any speculations would not add anything to clear up the situation. This point needs further investigation for the VO_2 behaviour to become fully understood.

4. Conclusions

There are at least three processes that contribute to the demise of A-centres with increasing temperature above ≈360 °C. The first is related to the reaction $VO + Si_i \rightarrow O_i$ ($E_a = 1.70$ eV). The other two processes $VO + O_i \rightarrow VO_2$ and $VO + VO \rightarrow VO_2 + V$ are related to the parallel growth of VO_2 defects as well, through the migration of A-centres. Combining the first and the second processes an activation energy of 1.46 eV for the movement of VO was obtained. Combining the first and the third processes, a corresponding activation energy of 1.96 eV was obtained. Assuming that the second and the third processes occur simultaneously, something we believe that actually occurs, values of 2.1 and 2.0 eV, respectively, were obtained. Above 360 °C, the evolution of VO_2 is influenced by other factors, presently unknown, and the phenomenon is not clearly understood.

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