# Kinetic study of the 830- and 889-cm<sup>-1</sup> infrared bands during annealing of irradiated silicon

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Electron-irradiated Czochralski-grown silicon samples have been isothermally annealed at four different temperatures in the range of 300 to 350 °C. The irradiation was performed at nominal room temperature with use of 2.0-MeV electrons and the bombardment dose was  $1.0 \times 10^{18} e^{-/cm^2}$ . After the irradiation, a dominant infrared (ir) band appears at 830 cm<sup>-1</sup> which is attributed to a vacancy-oxygen (VO) complex. The 830-cm<sup>-1</sup> band is stable up to temperatures of about 300°C where its strength decreases and a new prominent band at 889 cm<sup>-1</sup> develops. The decrease of the 830-cm<sup>-1</sup> band can be divided into one fast and one slow component. The fast component dominates at the initial stage of the annealing process and its relative influence is related to electron bombardment dose. The slow component dominates at a later stage and is usually the major term. Moreover, the growth of the 889-cm<sup>-1</sup> band is proportional to the slow component. Activation energies and frequency factors for the loss of the 830-cm<sup>-1</sup> band and the growth of the 889-cm<sup>-1</sup> band are determined and, finally, some different reaction models are discussed and compared with the experimental data. A model where the fast component is treated as a second-order reaction and the slow component is assumed to consist of two first-order processes with different rate constants shows good agreement with the experimental values.

#### I. INTRODUCTION

Oxygen is a main impurity in silicon material grown by the Czochralski method. The configuration of an isolated oxygen atom in the silicon lattice is nowadays well established.<sup>1</sup> The oxygen atom bonds to two neighboring silicon atoms in an interstitial position [Fig. 1(a)] and a Si<sub>2</sub>O molecule is formed with an angle between the two Si—O bonds of about 160°. The main oxygen infrared (ir) absorption band is located at 1106 cm<sup>-1</sup> for measurements performed at room temperature.<sup>2-4</sup> As indicated in Fig. 1(a) the band is assigned to an antisymmetric stretching mode of the Si<sub>2</sub>O configuration.

When a crystalline solid material is bombarded by particles with sufficiently high energies, vacancies and selfinterstitials are created. In silicon, interstitial oxygen atoms ( $O_i$ ) have been found to capture vacancies, which results in the formation of vacancy-oxygen complexes (VO). This defect, the so-called A center, was first reported more than 25 years ago<sup>5,6</sup> and its atomic configuration is illustrated in Fig. 1(b). The oxygen atom does not occupy a truly substitutional position. It is displaced from the central tetrahedral substitutional site in a (100) direction and bonds to two silicon atoms.

The VO center gives rise to two ir bands at 830 and 877 cm<sup>-1</sup>,<sup>7,8</sup> corresponding to neutral and negative charge state, respectively. At low sample temperatures ( $\leq$ 70 K) the positions of the bands shift to higher frequencies, 835 and 885 cm<sup>-1</sup>, respectively. The vibrational frequencies are significantly lower than for interstitial oxygen and reflect the more roomy substitutional environment of the vibrating oxygen atom. In the present measurements only the band at 830 cm<sup>-1</sup> was observed, i.e., all the VO centers were in the neutral charge state.

In contrast to interstitial oxygen, the VO center is electrically active with an acceptor level in the band gap located ~0.18 eV below the conduction band.<sup>9</sup> When the level is filled, i.e., when the center is in the negative charge state, the VO pair gives rise to an electron paramagnetic resonance (EPR) spectrum labeled the Si-A center resonance, which was the first reported experimental observation of the VO center.<sup>5,6</sup>



FIG. 1. Configuration of (a) an interstitial oxygen atom, (b) a vacancy-oxygen complex, and (c) a vacancy-dioxygen complex. The dashed circles in (b) and (c) indicate the position of the vacancy. In all the figures the vibrational frequencies are included.

The 830-cm<sup>-1</sup> band is stable up to temperatures somewhat below 300 °C where it declines while new absorption bands emerge. A prominent growing band appears at 889  $cm^{-1}$ .<sup>10,11</sup> Corbett *et al.*<sup>10</sup> assigned tentatively this band to a complex consisting of two oxygen atoms sharing one substitutional site, a vacancy-dioxygen pair (VO<sub>2</sub>) [Fig. 1(c)]. Recently, Lindström *et al.*<sup>12</sup> presented quantitative results indicating that the 889-cm<sup>-1</sup> band originates from a complex involving two oxygen atoms. They reported a linear correlation between the strength of the 889-cm<sup>-1</sup> band and the square of the interstitial oxygen concentration in a number of annealed electron-irradiated samples with strongly varying oxygen content [ $\sim (1-8) \times 10^{17}$ atoms/cm<sup>3</sup>]. Recently, Stein<sup>13</sup> published results from ox-ygen isotope studies indicating that the 889-cm<sup>-1</sup> mode is determined by a single oxygen bonded to Si. Thus, if two oxygens are occupying a single vacancy then the O-O interactions must be weak or nonexistent. This is consistent with theoretical calculations for the  $VO_2$  pair by DeLeo et al.<sup>14</sup> indicating that the two oxygens are only weakly coupled to each other.

Experimental observations reported in the literature of the electrical activity for the 889-cm<sup>-1</sup> defect are scarce. Recent results suggest that it is a neutral defect.<sup>15</sup> Calculations by DeLeo *et al.*<sup>14</sup> show no electrical levels in the band gap for the equilibrium configuration of the  $VO_2$  center.

Although no definite assignment of the 889-cm<sup>-1</sup> band can be made, a  $VO_2$  pair with two weakly interacting oxygen atoms accounts for the experimental observations made by various authors and is regarded as the prime candidate.

In this paper we examine quantitatively the loss of VO centers and the corresponding growth of the 889-cm<sup>-1</sup> band during isothermal annealing using infrared spectroscopy. Activation energies and frequency factors are extracted from the annealing curves. The results show conclusively that more than one defect reaction is occurring during the annealing process, which can be divided into one fast and one slow component. The fast component dominates at the initial stage and may account for more than 50% of the loss of VO centers. The slow component dominates at a later stage and is usually the major term. The growth of the 889-cm<sup>-1</sup> band is proportional to the slow component. Finally, in order to describe the annealing process some different reaction models are discussed and compared with the experimental data using computer simulations.

#### **II. EXPERIMENTAL PROCEDURE**

In the experiments Czochralski silicon single crystals grown in the  $\langle 100 \rangle$  direction were used. Both phosphorus- and boron-doped materials with nominal resistivities of 10 and 28  $\Omega$  cm, respectively, were investigated. Six samples with dimensions of  $3.0 \times 0.5$  cm<sup>2</sup> and a thickness of about 1.7 mm were cut from the middle of different wafers with diameters of 2.25 in. The samples were then mechanically polished to an optical surface on two sides.

According to room-temperature ir measurements the interstitial oxygen concentration  $[O_i]$  was between 7.7 and  $8.7 \times 10^{17}$  atoms/cm<sup>3</sup> in all the samples and the substitutional carbon concentration  $[C_s]$  was below  $5 \times 10^{16}$  atoms/cm<sup>3</sup> (Deutsche Industrie Normeu calibration constants). A survey of the samples is given in Table I.

The irradiation was performed with 2.0 MeV electrons at nominal room temperature (<40 °C) using a current density of about 3  $\mu$ A/cm<sup>2</sup>. In order to avoid beam heating during the irradiation the samples were mounted on a water-cooled block. All the samples were bombarded by a dose of  $1.0 \times 10^{18} \ e^{-}$ /cm<sup>2</sup>. Every sample was then cut into four small specimens, one for each of the four isothermal annealing temperatures applied, 304, 320, 335, and 350 °C. Within each group of four small specimens the relative variation of [O<sub>i</sub>] was less than 5% and the spread in VO concentration below 10%.

The isothermal heat treatments were interrupted at certain time intervals in order to follow the strengths of the 830- and 889-cm<sup>-1</sup> bands. Before every ir analysis the samples were etched in HF and then rinsed in deionized water. All the ir measurements were performed at room temperature using a Bruker 113 V Fourier-transform infrared (FTIR) spectrometer. The spectral resolution was set to 2.0 cm<sup>-1</sup> and as a reference sample a float-zone (FZ) crystal was used where both  $[O_i]$  and  $[C_s]$  were below  $5 \times 10^{15}$  atoms/cm<sup>3</sup>. The size of the analyzed area was ~12 mm<sup>2</sup>. Special care was taken when mounting the samples in order to obtain highly reproducible conditions during the ir measurements.

TABLE I. Survey of the samples used in the present work. The values given for  $[O_i]$  were obtained after electron irradiation and before heat treatment. Activation energies and frequency factors for the loss of the 830-cm<sup>-1</sup> band and the growth of the 889-cm<sup>-1</sup> band are included.

		830-cm <sup>-1</sup> band		889-cm <sup>-1</sup> band	
Sample No.	$[O_i]$ 10 <sup>17</sup> atoms/cm <sup>3</sup>	$E_a$ (eV)	$c_0 (s^{-1})$	$E_a$ (eV)	$c_0 (s^{-1})$
1 ( <i>n</i> -type)	7.3	2.30	3×10 <sup>15</sup>	1.86	6×10 <sup>11</sup>
2 ( <i>p</i> -type)	8.2	2.30	3×10 <sup>15</sup>	1.96	4×10 <sup>12</sup>
3 ( <i>p</i> -type)	7.4	2.27	$2 \times 10^{15}$	1.79	$2 \times 10^{11}$
4 ( <i>p</i> -type)	7.9	2.22	6×10 <sup>14</sup>	1.95	$3 \times 10^{12}$
5 ( <i>p</i> -type)	7.1	2.29	2×10 <sup>15</sup>	1.86	6×10 <sup>11</sup>
6 ( <i>p</i> -type)	7.0	2.24	9×10 <sup>14</sup>	1.79	2×10 <sup>11</sup>

## **III. EXPERIMENTAL RESULTS**

## A. General annealing characteristics

In Figs. 2(a)-2(d) typical results obtained for the absorption coefficients  $\alpha$  of the 830- and 889-cm<sup>-1</sup> bands are plotted as a function of annealing time at 350, 335, 320, and 304°C, respectively. The solid lines are polynomial fits of the experimental points. The polynomials g(t) are of the form

$$g(t) = a_0 + a_1 t^{1/3} + a_2 t^{2/3} + a_3 t + a_4 t^2$$
,

where t is the annealing time and  $a_0$ ,  $a_1$ ,  $a_2$ ,  $a_3$ , and  $a_4$  are fitting constants.

The concentration of VO centers decreases rapidly during the initial stage of the annealing and then more slowly at longer times. For example, at 350 °C 50% of the VO pairs are lost after only 10 min, while it takes about 100 min to obtain a concentration below the detection limit. The absorption coefficient of the 889-cm<sup>-1</sup> band increases rapidly in the beginning of the heat treatment and then a gradual decrease in the rate of increase takes place, and finally  $\alpha_{889}$  reaches a saturation value. It may be noticed that the asymptotic value of  $\alpha_{889}$  shows a downward dependence as a function of annealing temperature.

## B. The 830-cm<sup>-1</sup> band (vacancy-oxygen center)

In Figs. 3(a) and 3(b) the logarithm of  $\alpha_{830}$  is depicted versus annealing time at 350 and 335 °C. The values are

normalized with respect to  $\alpha_{830}$  (t=0). Figure 3 shows conclusively that the entire annealing process of VO centers cannot be described by an exponential decay. Only at long enough times a linear dependence is obtained.

In a first approximation, the relative number of VO centers lost by the exponential decay can be estimated by extrapolating the linear relationship between  $\ln[\alpha_{830}/\alpha_{830}(t=0)]$  and time to t=0, as indicated by the dashed lines in Fig. 3. In the following, this exponential part of the annealing process will be labeled the second component, while the initial fast loss of VO centers will be referred to as the first component.

Normally, 65 to 75% of the decrease of VO centers is due to the second component. However, in samples with a lower oxygen content and a higher carbon content than in the samples used in the present investigation the fast component may account for more than 50% of the decrease.<sup>16</sup> Moreover, the relative influence of the first component depends on bombardment dose. In Fig. 3(c) the annealing curve for sample no. 1 at 320°C is compared with that for a similar sample irradiated by half the dose  $(5 \times 10^{17} e^{-}/cm^{2})$ . In the low-dose sample the strength of the 830-cm<sup>-1</sup> band after irradiation was about 60% of that in sample no. 1 and, as revealed in Fig. 3(c) by extrapolating the second component to t = 0, the relative contribution of the first component was reduced by almost a factor of 2.

In deep-level transient spectroscopy (DLTS) studies of the annealing sequence the complete process was exponen-



FIG. 2. Absorption coefficients of the ir bands at 830 and 889 cm<sup>-1</sup> as a function of annealing time for sample no. 4. (a)  $350^{\circ}$ C, (b)  $335^{\circ}$ C, (c)  $320^{\circ}$ C, and (d)  $304^{\circ}$ C.

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TABLE II. Average values at different temperatures of the rate constants $c$ , $c_1$ , and $c_2$ . The proportionality constant $p$ and the corresponding correlation coefficient $r$ are also included.						
Temp. (°C)	c (s <sup>-1</sup> )	$c_1 (s^{-1})$	$c_2 (s^{-1})$	p	r	
350	7.1×10 <sup>-4</sup>	2.4×10 <sup>-4</sup>	4.7×10 <sup>-4</sup>	0.68	0.993	
335	$2.5 \times 10^{-4}$	$1.1 \times 10^{-4}$	$1.5 \times 10^{-4}$	0.84	0.988	
320	$8.7 \times 10^{-5}$	$4.2 \times 10^{-5}$	$4.5 \times 10^{-5}$	0.96	0.992	
304	$2.2 \times 10^{-5}$	$1.1 \times 10^{-5}$	1.1×10 <sup>-5</sup>	1.0	0.995	



FIG. 3. Logarithm of the absorption coefficient of the 830-cm<sup>-1</sup> band versus annealing time: (a) 350 °C, (b) 335 °C, and (c) 320 °C. The values are normalized with respect to the initial value of  $\alpha_{830}$ . The solid lines represent a least-squares fit of the experimental points. In (c) a comparison is made between sample no. 1 and a similar sample irradiated by only half the dose  $(5 \times 10^{17} e^{-}/cm^2)$ .



FIG. 4. Logarithm of the rate constant of the second component for the decrease of  $\alpha_{830}$  versus the reciprocal absolute annealing temperature. The solid line shows a least-squares fit of the experimental points and the slope corresponds to an activation energy of 2.27 eV.

tial and no first component was observed.<sup>17</sup> The concentration of VO centers in the DLTS studies was two to three orders of magnitude smaller than in the present ir experiments.

The rate constants of the second component c are given in Table II for the different annealing temperatures. The tabulated values are averages of the individual values for each specimen. The individual values were extracted by a least-squares fit of the data points. No electron fluence dependence of the rate constants was found. The values for the two samples in Fig. 3(c) are identical within 1%.

Activation energy  $E_a$  and frequency factor  $c_0$  for the second component are determined. In Fig. 4 the logarithm of the rate constant is depicted versus the reciprocal absolute annealing temperature for all the specimens used. The values are normalized with respect to the rate constant at 335 °C and, therefore, c(335 °C)=1. The average value of  $E_a$  was found to be 2.27 eV and the corresponding  $c_0$  value was  $1.6 \times 10^{15} \text{ s}^{-1}$ . The individual  $E_a$  and  $c_0$  values for the six samples are given in Table I. All the values of  $E_a$  lie within  $2.27 \pm 0.05 \text{ eV}$ .

#### C. The 889-cm<sup>-1</sup> band

Activation energy and frequency factor for the growth of the 889-cm<sup>-1</sup> band have been reported in a previous paper<sup>11</sup> and were found on the average to be 1.86 eV and  $6 \times 10^{11}$  s<sup>-1</sup>, respectively. The individual values for the samples are listed in Table I.

In Fig. 5 the growth of the 889-cm<sup>-1</sup> band is plotted versus the second component of the loss of the 830-cm<sup>-1</sup> band, and within the experimental accuracy a proportionality is obtained. The proportionality constant p reveals, however, a downward dependence as a function of annealing temperature as shown in Table II. In Table II

are also included correlation coefficients r, which are a quantitative measure of how well the data points can be described by a straight line.<sup>18</sup> The maximum value of r is 1.0.

The 889-cm<sup>-1</sup> band is stable up to temperatures of about 450 °C where it develops into new bands at 905, 969, and 1001 cm<sup>-1</sup>.<sup>10,15</sup> This development is probably caused by interaction with mobile interstitial oxygen atoms.<sup>15</sup>

## D. Variation of oxygen and carbon concentrations

The concentrations of interstitial oxygen and substitutional carbon were monitored after every annealing step. In Fig. 6  $[O_i]$  is depicted versus annealing time at 335 °C.



FIG. 5. Growth of the 889-cm<sup>-1</sup> band versus the second component of the decrease of the 830-cm<sup>-1</sup> band. (a) 350 °C, (b) 320 °C. All experimental values at the given temperatures are included and the solid lines were obtained by a least-squares fit of the data.



FIG. 6. Interstitial oxygen concentration as a function of the annealing time at 335 °C.

The oxygen content increases significantly in the beginning of the heat treatment, e.g., in sample no. 2  $[O_i]$  increases by more than  $3 \times 10^{16}$  atoms/cm<sup>3</sup>. After the initial growth  $[O_i]$  stays almost constant during the complete annealing sequence. It should be noted that the increase of  $[O_i]$  appears in the same time interval as where the first component of the loss of VO centers dominates. After the irradiation  $[C_s]$  was below  $1 \times 10^{16}$  atoms/cm<sup>3</sup> in all the samples and during the annealing no significant variations were found.

## **IV. REACTION KINETICS**

## A. General outline

The rate equation for a defect N which disappears through a first-order process is given by

$$\frac{-\partial[N]}{\partial t} = k_1[N] , \qquad (1)$$

where  $k_1$  is a rate constant. A characteristic feature of a first-order process is that each individual defect complex anneals out independently of the rest. Dissociation is an example of such a process. A second example is the following reaction:

$$N + X \rightarrow NX$$
, (2)

where X is a defect and/or impurity of such a high concentration that  $[X]_{t=0} \gg [N]_{t=0}$  and, consequently,  $[X]_{t=0} \approx [X]_{t=\infty}$ . According to the theory for diffusionlimited processes,<sup>19</sup> the corresponding rate equation becomes

$$\frac{-\partial[N]}{\partial t} = 4\pi R D[X]_{t=0}[N] , \qquad (3)$$

where R is a capture radius and D is the sum of the diffusion coefficients for X and N. Normally, D is dominated by one of the two contributions, i.e.,  $D \approx D_X$  or  $D \approx D_N$ . Comparing Eqs. (1) and (3), the rate constant  $k_1$  equals  $4\pi RD[X]_{t=0}$ . Usually,  $k_1$  is expressed in the form<sup>20</sup>

$$k_1 = k_0 \exp(-E_a / k_B T) ,$$

where  $k_0$  is a frequency factor and  $E_a$  an activation energy for the process. The temperature dependence in Eq. (3) is attributed to D and identification gives  $k_0 = 4\pi R D_0 [X]_{t=0}$ , where  $D_0$  is the preexponential factor of the diffusion coefficient. Equation (3) is readily integrated to

$$[N] = [N]_{t=0} \exp(-k_1 t) .$$
(4)

Let us label the defect resulting from the reaction (2) as Y, i.e., Y = NX. Utilizing Eq. (4) the time dependence of Y can be expressed as

$$[Y] = [N]_{t=0} [1 - \exp(-k_1 t)].$$
(5)

An interesting case occurs if N is destroyed by two first-order processes with comparable but different rate constants, e.g., a reaction as in Eq. (2) and dissociation  $(k_2)$ ,

$$\frac{\partial [N]}{\partial t} = -k_2[N] - 4\pi R D[N][X]_{t=0} = -[N](k_1 + k_2).$$
(6)

The solution becomes

$$[N] = [N]_{t=0} \exp[-(k_1 + k_2)t], \qquad (7)$$

and for the reaction product Y,

$$[Y] = [N]_{t=0} \{1 - \exp[-(k_1 + k_2)t]\} / (1 + k_2/k_1) .$$
(8)

It may be noticed that the maximum value of [Y] varies with temperature if  $k_1$  and  $k_2$  have different activation energies. In a second-order reaction the rate equation for N becomes

$$\frac{-\partial[N]}{\partial t} = k_3[N]^2 \tag{9}$$

and the corresponding solution is directly obtained by integration

$$[N] = [N]_{t=0} / (1 + [N]_{t=0} k_3 t) .$$
<sup>(10)</sup>

An important feature of Eq. (10) is that the fractional decay,  $[N]/[N]_{t=0}$ , depends on the initial concentration of N. This is in contrast to first-order kinetics where the fractional decay is independent of  $[N]_{t=0}$ ; see, e.g., Eq. (4). At long enough times  $([N]_{t=0}k_3t \gg 1)$  the fractional decay depends inversely on  $[N]_{t=0}$ , while at short times  $([N]_{t=0}k_3t \ll 1)$ , a linear dependence is obtained and  $\ln([N]/[N]_{t=0}) = -k_3[N]_{t=0}t$ .

#### B. Comparison with experiment, second component

An important issue when modeling the defect kinetics is the origin of the 889-cm<sup>-1</sup> band. As mentioned in Sec. I, a number of studies have recently been presented concerning this subject.<sup>12-15</sup> Based on these studies a  $VO_2$ pair with two weakly interacting oxygens [Fig. 1(c)] is considered as the prime candidate, and in the following this assignment will be utilized. The results in Fig. 5 show a proportionality between the second component of the decay of VO centers, which can be described as a predominantly first-order process, and the increase of  $\alpha_{889}$ . This suggests strongly that the 889-cm<sup>-1</sup> defect is formed through a first-order reaction involving VO. An alternative is that the vacancy dissociates from the isolated oxygen and is subsequently trapped by oxygen atoms in other configurations which give rise to the 889-cm<sup>-1</sup> band. In order to account for the observed intensities and the kinetics, the concentration of such oxygens has to be at least ~ 10<sup>17</sup> cm<sup>-3</sup>. However, in that case, the 889-cm<sup>-1</sup> band should have been observed directly after irradiation. A second and more promising alternative is to assume that the following reaction occurs:

$$VO + O_i \rightarrow VO_2$$
. (11)

Equation (11) can be viewed as a first-order reaction since the interstitial oxygen concentration is about one order of magnitude higher than the estimated value of the initial concentration of VO centers. This estimate is based on an "oscillator strength" of  $1 \times 10^{-17}$  cm<sup>2</sup> for the VO center,<sup>21</sup> i.e.,  $[VO] = 1 \times 10^{17} \alpha_{830}$  (RT) cm<sup>-3</sup>, and as a result,  $[O_i]$  may be treated as a constant.

As revealed in Table II the proportionality constant between the growth of  $\alpha_{889}$  and the loss of  $\alpha_{830}$  decreases with temperature. This may indicate that the second component involves not only reaction (11) but also additional processes with kinetic properties that can be regarded as first order. In a first attempt, let us assume that dissociation takes place:

$$VO \rightarrow V + O_i$$
 . (12)

Applying Eq. (7) this gives for decrease of VO centers

$$[VO] = [VO]_{t=0} \exp\{-(4\pi R(D_{VO} + D_{O_i})[O_i] + D_d)t\},$$
(13)

where  $D_{VO}$  and  $D_{O_i}$  are the diffusion coefficients for VO centers and interstitial oxygens, respectively, and  $D_d$  the rate constant for dissociation. Using Eq. (8) the relation for the corresponding growth of VO<sub>2</sub> centers becomes

$$[VO_2] = [VO]_{t=0} \{1 - \exp[-(c_1 + c_2)t]\} / (1 + c_2/c_1),$$
(14)

where  $c_1 = 4\pi R (D_{VO} + D_{O_i})[O_i]$  and  $c_2 = D_d$ . From the exponential part of the annealing curve the sum of  $c_1$  and  $c_2$  is extracted and from the proportionality constant between the growth of  $\alpha_{889}$  and the decrease of  $\alpha_{830}$  (second component) the ratio  $c_2/c_1$  can be determined. In the calculations of  $c_2/c_1$  it was accounted for that the 889-cm<sup>-1</sup> band is attributed to a center containing two weakly interacting oxygen atoms that contribute independently to the infrared absorption by using an oscillator strength of twice that for the VO centers. In Table II the extracted average values of  $c_1$  and  $c_2$  are given at different temperatures and the activation energies obtained for  $c_1$  and  $c_2$  are 2.06 and 2.51 eV, respectively.

#### C. Comparison with experiment, complete process

As indicated in Fig. 3(c) the fast annealing process (first component) depends on the initial concentration of VO centers. In accordance with Eq. (10) this suggests that the process obeys second- or higher-order reaction kinetics. In a first approximation, a second-order process appears most likely and a reaction of the form

TABLE III. Simultaneous differential equations for the reactions (11), (12), and (15) and numerical values of the input parameters used in the computations.

Simultaneous differential equations	$\frac{\partial [VO]}{\partial t} = -4\pi R (D_{VO} + D_{O_i}) [VO][O_i] - D_d [VO] - 4\pi R (D_{VO} + D_Z) [VO][Z]$
	$\frac{\partial [VO_2]}{\partial t} = 4\pi R (D_{VO} + D_{O_i}) [VO][O_i]$
	$\frac{\partial [O_i]}{\partial t} = -4\pi R (D_{VO} + D_{O_i}) [VO] [O_i] + D_d [VO] + 4\pi R (D_{VO} + D_Z) [VO[Z]]$
	$\frac{\partial [Z]}{\partial x} = -4\pi R (D_{VO} + D_Z) [VO][Z]$
	$\frac{\partial [Z']}{\partial t} = 4\pi R (D_{VO} + D_Z) [VO] [Z]$
	$\frac{\partial [V]}{\partial t} = D_d[VO]$
Capture radius	R = 5 Å
Diffusion coefficients	$D_{VO} = 5.0 \times 10^{-16} \text{ cm}^2 \text{s}^{-1}$ ,
and dissociation rates at 350°C	$D_Z = 1.26 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1},$ $D_{O_1} = 5.0 \times 10^{-22} \text{ cm}^2 \text{ s}^{-1}, D_d = 4.4 \times 10^{-4} \text{ s}^{-1}.$
Initial values of defect	r
initial values of defect	[10] (7, 10] (7, 10] (7, 10)
and impurity concentrations	$[VO] = 6.7 \times 10^{10} \text{ cm}^{-3}, [Z^{+}] = 0$
	$[VO_2] = 0, [V] = 0$
	$[O_i] = 7.25 \times 10^{17} \text{ atoms/cm}^3$
	$[Z] = 1.5 \times 10^{16} \text{ cm}^{-3}$

$$Z + VO \rightarrow Z' + O_i \tag{15}$$

is proposed. Z represents some irradiation-induced defect, which may be carbon related, or a constituent from such a defect, e.g., a self-interstitial. Z' is a reaction product. The reaction  $VO+VO \rightarrow V_2O_2$ , which also is a second-order process, is not proposed because of the following reasons.

(i) It does not account for the experimentally observed increase of  $[O_i]$  during the fast process.

(ii) It is expected to be of minor importance compared with the reaction  $VO+O_i \rightarrow VO_2$  since  $[O_i] \gg [VO]$ .

(iii) The resulting defect,  $V_2O_2$ , is, because of its atomic configuration,<sup>22</sup> expected to give rise to an ir band with a position close to the 830-cm<sup>-1</sup> band, and no such major band was observed.

In Figs. 7, Eqs. (11), (12), and (15) are compared with experimental data at 350 °C. The coupled rate equations corresponding to these reactions are given in Table III together with the input values used. The equations were solved numerically using a computer.

### V. DISCUSSION AND CONCLUSIONS

The annealing process of vacancy-oxygen centers can be divided into two components, one fast component occurring during the initial stage of the heat treatment and one slow component which dominates at the intermediate and final stages of the annealing sequence.

The relative importance of the first component depends on the initial concentration of VO centers [Fig. 3(c)] and, therefore, a second-order reaction is suggested. This is also in agreement with the early work by Corbett et al.<sup>10</sup> who reported that the initial decay of the 830-cm<sup>-1</sup> band indicates a second-order reaction. During the first component a significant increase of the interstitial oxygen concentration occurs. This may indicate that an interstitial-related defect becomes mobile and/or releases self-interstitials. This causes annihilation of VO centers and a corresponding release of oxygen atoms. A second alternative is that dissociation takes place  $(VO \rightarrow V + O_i)$ . The dissociated vacancies may be trapped by some irradiation-induced defect which prevents the reforming of VO centers.

It is important to point out that interstitial oxygen atoms can be regarded as practically immobile at temperatures in the range of 300 to 350 °C. A jumping rate of only  $10^{-6}$  s<sup>-1</sup> is estimated at 350 °C using the wellestablished diffusion coefficient for interstitial oxygen motion.<sup>23</sup> Thus, interstitial oxygen motion can be ruled out as an annealing mechanism for VO centers since the concentration of VO is reduced below the detection limit during a heat treatment at 350 °C for 100 min.

As mentioned in Sec. IV, the second component can be regarded as a predominantly first-order process with a corresponding growth of the 889-cm<sup>-1</sup> band. However, the component involves probably more than one process since the proportionality constant between the increase of  $\alpha_{889}$  and the loss of  $\alpha_{830}$  decreases with temperature. The extracted value of the activation energy (2.27 eV) is believed to be due to a mixed process where motion of VO centers and a subsequent generation of  $VO_2$  pairs [Eq. (11)] constitute a main contribution. Under these assumptions, some features of the additional contribution(s) may be revealed.

(i) The relative importance increases with temperature in comparison with the motion of VO centers.

(ii) Interstitial oxygen atoms are released since  $[O_i]$  stays constant although  $VO_2$  centers are generated.

(iii) The kinetic properties can be approximated by first-order kinetics.

(iv) Due to the similarities between the values of c given in Table II and that found in DLTS studies<sup>17</sup> the reactions occurring during the second component are expected to be active over a wide range of concentration.

One candidate is dissociation, provided that it is attributed to a higher activation energy than motion of VO centers,  $\sim 2.5$  versus 2.06 eV. Figure 7 shows excellent agreement between experimental data and calculated curves based on Eqs. (11), (12), and (15).

Furthermore, Eqs. (13) and (14) provide an explanation for the difference between the extracted activation energy values for the increase of  $\alpha_{889}$  and the decrease of  $\alpha_{830}$ (second component). For the loss of  $\alpha_{830}$ ,  $E_a$  is determined by the temperature dependence of  $c_1 + c_2$ , while for the growth of  $\alpha_{889}$ , also the influence of the term  $1/(1+c_2/c_1)$  has to be taken into account. It can be shown that this lowers the temperature dependence of the increase of  $\alpha_{889}$ , and consequently, if it is assumed in the extraction procedure of  $E_a$  that only a single activation energy is involved, a lower value is obtained than for the decrease of  $\alpha_{830}$  (second component).

It may be noticed that the results from the calculations based on Eqs. (11), (12), and (15) imply different activa-



FIG. 7. A comparison between the experimental values of [VO] and  $[VO_2]$  for sample no. 3 at 350 °C and simulated values obtained from the reaction model described in Table III.

tion energies for complete and partial dissociation (motion of VO involves partial dissociation<sup>10</sup>), and do not account for the possibility that the "anomalous" oxygen diffusion observed by Stavola *et al.*<sup>23</sup> may be a vacancy-assisted process where a continuous dissociation and reforming of VO centers move all the oxygen atoms.<sup>11</sup>

The reactions (11), (12), and (15) are, however, only a first attempt to describe the kinetic properties of the annealing process and are not to be regarded as definite ones. Other proposals for reaction models will be discussed in a subsequent work where modeling of the annealing process

using computer simulations is the main subject<sup>16</sup> In particular, the influence of formation and annihilation of multivacancy-oxygen complexes on the process will be treated.

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