Origin of infrared bands in neutron-irradiated silicon

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Infrared absorption measurements were made of the localized vibrational modes due to defects produced in Czochralski-grown Si material after irradiation with fast neutrons and subsequent thermal treatments. The investigation was focused, in particular, on three satellite bands in the region of the A center, located at 839, 833 and 824 cm^{-1} respectively, the annealing behavior of which was carefully monitored. Correlation of our results with previous infrared, electron paramagnetic resonance and positron annihilation studies favors attributing these bands to the V_2O, V_3O_2 and V_2O_2 defects respectively. In addition, semiempirical calculations were carried out for the vibrational frequencies of these defects, and the predicted values are in agreement with the above assignments. © *1997 American Institute of Physics.* [S0021-8979(97)05804-0]

I. INTRODUCTION

An interesting feature of oxygen in Si, especially in irradiated materials, is that it forms complexes with lattice vacancies leading to the creation of V_nO_m defects, as has been established by a variety of experimental techniques, particularly by electron paramagnetic resonance[1] (EPR), infrared (IR) spectroscopy[2] and positron annihilation studies[3] (PAS). In the last three decades IR spectroscopy has played a significant role in the study of these defects giving valuable information about their structure and properties.

The VO pair, the so-called A center, is the main defect induced in irradiated Czochralski (Cz)-grown Si. In its neutral charge state, it gives rise to an infrared band at about 828 cm^{-1}. After thermal treatment there is evidence of a number of weak bands[2,4,5] in the region of the A center. These bands appear as shoulders on either side of the dominant A center band and they are termed satellites. Their origin has been correlated[4] with multiple vacancy-oxygen defects.

Bearing in mind the above results, we have ventured to find the exact identity of the satellite bands. To this end, Si was subjected to irradiation by neutrons. In our studies, three bands at 839, 833 and 824 cm^{-1} were located and associated with V_2O, V_3O_2 and V_2O_2 defects respectively. Semiempirical calculations of the localized vibrational mode (LVM) frequencies for the structures of V_2O, V_3O_2 and V_2O_2 defects, as suggested from EPR data,[6] are in agreement with our experimental observations.

II. EXPERIMENTAL DETAILS

Cz-grown Si samples with typical dimensions of $20 \times 12 \times 2$ mm were used without being subjected to any post-growth heat treatment. The samples, purchased from MEMC, were initially p type (B doped) with resistivity $\rho_0 \approx 10 \ \Omega$ cm. The carbon concentration was $[C_s] < 1 \times 10^{16} \ cm^{-3}$. Their initial oxygen concentration $[O_i]_0$ was $\approx 1.1 \times 10^{18} \ cm^{-3}$ as was found by measurements of the 9 μm absorption band according to the relevant American Society for Testing and Materials (ASTM) procedures.[7]

Float-zone (Fz) samples with $[O_i]_0 \approx 10^{16} \ cm^{-3}$ were also used in these studies for the sake of comparison.

Fast neutron irradiations were performed inside a pool of water at ≈ 40 °C, with a dose of $\approx 1 \times 10^{17}$ n cm^{-2}. The samples were wrapped in cadmium foil to eliminate the effect of thermal neutrons and were put in sealed quartz tubes to avoid water contamination.

Fifteen minute isochronal anneals, in ≈ 10 °C increments, over the range from room temperature (RT) to 600 °C were performed with the samples in air. The annealing temperatures were accurate to $\approx \pm 2$ °C. Measurements were carried out in RT, with a JASCO-IR 700 double beam dispersive spectrometer. The two phonon absorption was always subtracted by using reference samples from Fz material of equal thickness.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 presents the region of the A center in the spectra of the Cz-grown material at various isochronal annealing temperatures. Upon annealing at ≈ 230 °C a weak line at the high frequency side of the 828 cm^{-1} band of the VO defect, with a LVM frequency of $\approx 839 \ cm^{-1}$, begins to emerge. Subsequently, we can make out two other weak lines of $\approx 824 \ cm^{-1}$ and 833 cm^{-1} appearing at annealing temperatures about 320 °C and 340 °C, respectively. All these lines appear as shoulders of the much stronger A center band and they have been designated in the literature[4] as satellites. Apparently, there is an obvious requirement to identify these lines. The overlapping of different peaks is an extra obstacle to their identification. In order to recover the individual contribution of each line we have made computer deconvolutions using Lorentzian profiles. Figure 2 presents the annealing behavior of the three satellite bands at 839, 833 and 824 cm^{-1} together with the evolution of the VO, VO_2 [887 cm^{-1} (Ref. 2)] and O_i (1106 cm^{-1}) bands.

The appearance in the spectra of the 839 cm^{-1} band from 230 °C onwards coincides generally with the temperature range where divacancies, which are the main species of defects besides VO, are expected to become mobile.[6,8] On the other hand O_i is the main impurity in Cz-grown Si. The following reaction therefore could be put forward:

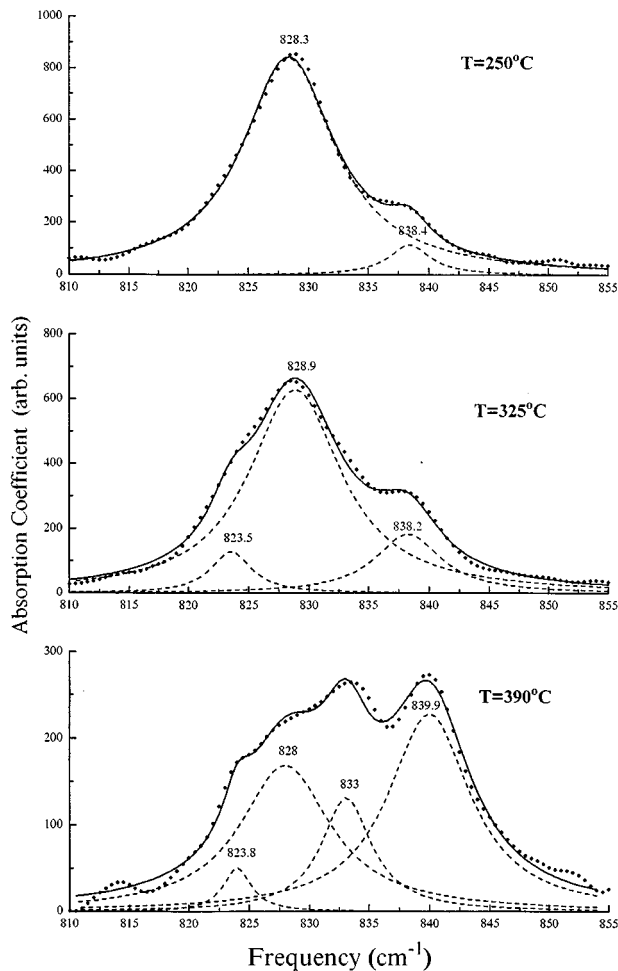[a]Electronic mail: nsarlis@atlas.uoa.gr

FIG. 1. Deconvolution of the A center region infrared bands into Lorentzian profiles at various selected isochronal annealing temperatures. Dotted lines represent experimental results; solid lines the best fitting curves; dashed lines the Lorentzian profiles

FIG. 2. Absorption coefficient of LVM bands: VO (828 cm^{-1}), O$_i$ (1106 cm^{-1}), VO$_2$ (887 cm^{-1}), 824 cm^{-1}, 833 cm^{-1} and 839 cm^{-1} bands as a function of the isochronal annealing temperature. VO and VO$_2$ curves are displaced vertically for the sake of clarity. For the same reason, the evolution of the bands of the VO$_3$ defect, appearing in the spectra when VO$_2$ begins to decay, are not shown.

V$_2$+O$_i$→V$_2$O. Thus, at first glance, it seems not unreasonable to pursue a correlation of the 839 cm^{-1} line with the V$_2$O defect. The loss of O$_i$ during annealing between 230 and 300 °C (Fig. 2) covers the increase of VO indicating that the main reaction at this temperature range is V+O$_i$→VO. Notice, however, that after irradiation the concentration of divacancies is expected to be considerably lower than the VO concentration, maybe by a factor of 10. Thus, V$_2$O concentration after annealing would be even lower than that of VO, a fact that is consistent with the experimentally observed intensities of the lines. The oxygen concentration loss seems sufficient to account for the observed increase of the VO and creation of the V$_2$O defect.

In order to assist the overall interpretation we further studied spectra received from Fz-Si material subjected to the same irradiation and subsequent heat treatment procedures. No evidence emerged for the 828 cm^{-1} and 839 cm^{-1} bands (or for the 824 cm^{-1} and 833 cm^{-1} bands), indicating oxygen involvement in the structure of the corresponding defects. It is worth noting at this point that results from positron ann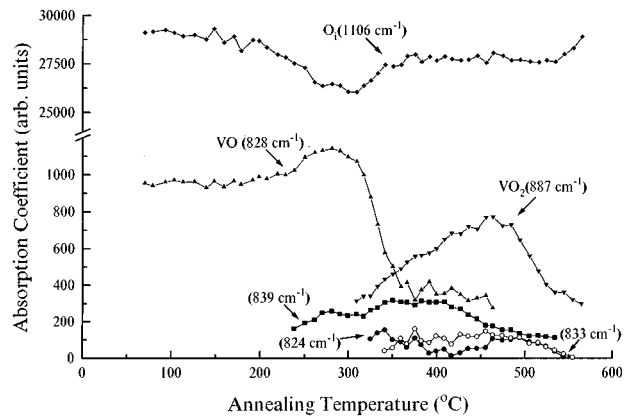ihilation studies[3,9] also indicate that secondary defects observed above 200 °C should be correlated with vacancy-oxygen complexes.

In addition, the V$_2$O defect due to its suggested structure,[6] is expected to give rise to a LVM frequency close to that of the VO center. A picture therefore emerges favoring the notion that the V$_2$O defect gives rise to the 839 cm^{-1} line. To support this we have performed a semiempirical calculation of the LVM frequency of the V$_2$O defect that is presented below.

The VO pair is characterized by a ⟨001⟩ off-center configuration[10–13] where the oxygen atom is displaced about 1 Å (see Table I) towards the two Si atoms to which it is bonded. The LVM frequency located at about 828 cm^{-1} in our studies arises from the oscillation along the ⟨110⟩ axis of the oxygen atom placed near the substitutional (vacancy V) site. Figures 3(a) and 3(b) exhibit the atomic configurations of VO and V$_2$O defects as suggested by Lee and Corbett[6] from EPR investigations. We shall try to calculate the LVM frequency of the V$_2$O defect from that of the VO defect by using the modification caused on the Si-O-Si bond in the V$_2$O structure, as a result of the attachment of an extra vacancy next to the Si-O-Si unit of the VO. According to the covalent bond theory,[14,15] the oxygen atom in the Si-O-Si unit interacts with each of the two neighboring Si atoms by a power law potential of the form

$$V = \epsilon \left[\left(\frac{\sigma}{R} \right)^4 - \left(\frac{\sigma}{R} \right)^2 \right], \tag{1}$$

TABLE I. Theoretical results for the off-center displacement of the oxygen atom in the VO defect, according to various investigations.

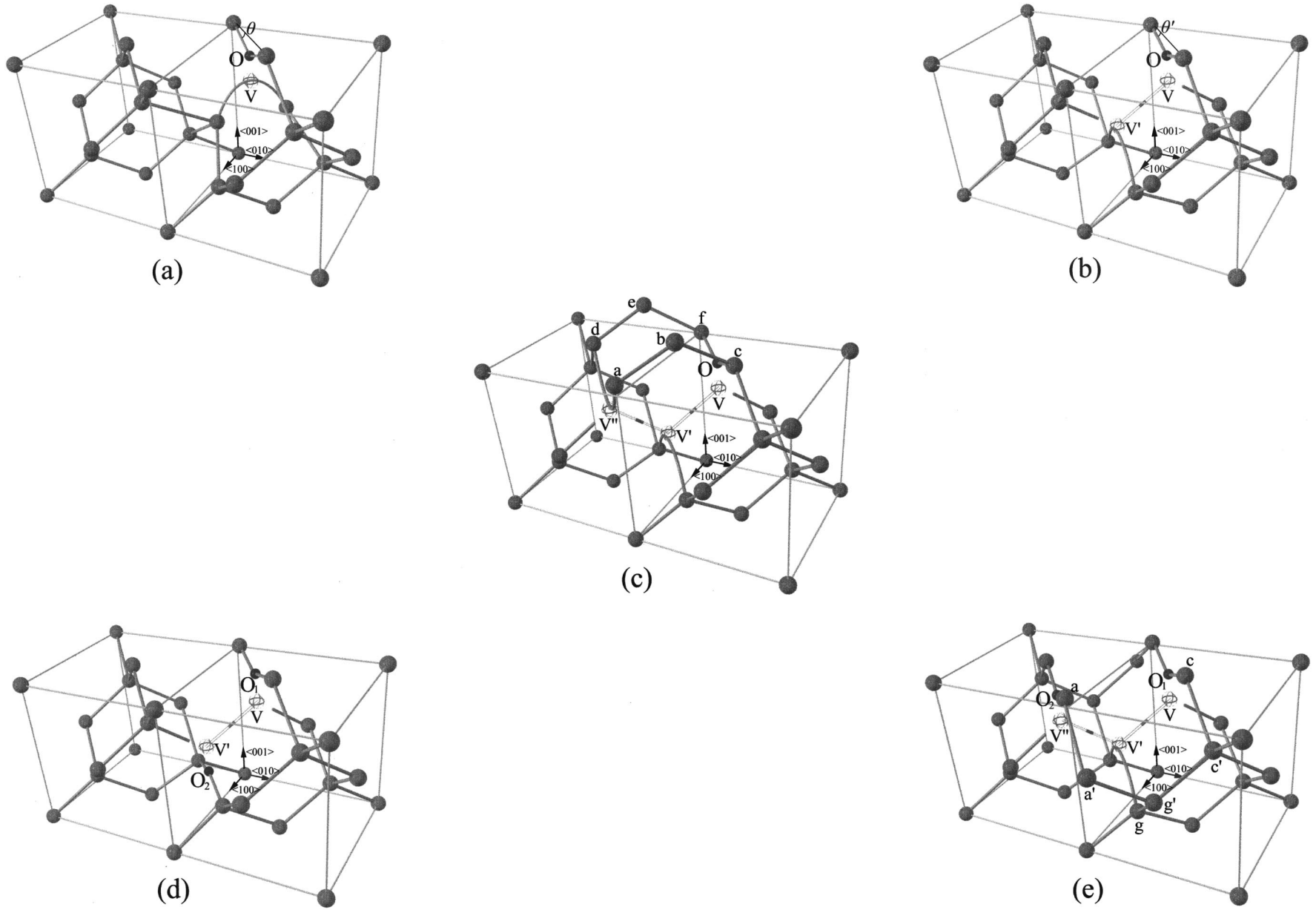| Off-center displacement (Å)	Reference
1.1	10
1.1	11
1.03	12
0.934	13

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FIG. 3. The structural models for (a) VO, (b) V_2O, (c) V_3O, (d) V_2O_2, and (e) V_3O_2 centers.

where ϵ, σ are empirical parameters and R the length of the Si-O bond. Employing this power law potential, the dependence of the force constant κ on the equilibrium length R_0, for small oscillations, is found to be

$$\kappa = \frac{2\epsilon}{R_0^2}. \tag{2}$$

Using a molecular XY_2 model,[16] the frequency of the oscillation of the oxygen atom in the Si-O-Si unit is related to κ and to the angle θ between the $\langle 110 \rangle$ axis and the Si-O bond (Fig. 3(a)) according to the formula

$$\omega = \sqrt{\frac{\kappa}{m_{Si}}\left(1 + 2\frac{m_{Si}}{m_O}\cos^2 \theta\right)}, \tag{3}$$

where m_{Si} and m_O are the masses of the silicon and oxygen atoms respectively. Substituting the ratio of the atomic masses and using Eq. (2), we obtain

$$\omega = \sqrt{\frac{2\epsilon}{m_{Si}}}\frac{\sqrt{1 + 3.5 \cos^2 \theta}}{R_0}. \tag{4}$$

This relation also holds for the Si-O-Si unit in the V_2O defect. If R_0' and θ' are the structural parameters of the latter defect and ω' its LVM frequency, we finally have

$$\omega' = \omega \frac{R_0}{R_0'}\frac{\sqrt{1 + 3.5 \cos^2 \theta'}}{\sqrt{1 + 3.5 \cos^2 \theta}}, \tag{5}$$

where R, θ and ω refer to the VO defect. A recent,[13] first principles cluster calculation analysis gave the values, $R_0 = 1.754$ Å, $\theta = 21°$ for the VO defect and $R_0' = 1.725$ Å, $\theta' = 18.5°$ for the V_2O defect, which when inserted into Eq. (5) together with our experimental value of ω lead to a value for ω' equal to 852 cm^{-1}.

A significant point of the above analysis is that the addition of an extra vacancy in the VO structure, in order to form the V_2O defect, results in an increase of the corresponding LVM frequency. This increase is in accord with previously reported experimental findings[17] that the compression of the Si-O-Si unit of the VO, along the $\langle 110 \rangle$ axis, leads to an increase of the vibrational frequency. Indeed, the distance $2R_0' \cos \theta'$, between the Si atoms of the unit in the V_2O structure is smaller than the distance $R_0 \cos \theta$ in the VO defect. In this sense, the association of the 839 cm^{-1} band with the V_2O defect is in general agreement with both theoretical and experimental predictions.

Another potential candidate for the 839 cm^{-1} band is the V_3O defect. Its formation may be related to a reaction process like $V_2 + VO \rightarrow V_3O$. The structure[6] of the V_3O defect is shown in Fig. 3(c). In order to estimate its LVM frequency we shall consider the effect of the attachment of the extra vacancy V'' to a V_2O defect. Due to this attachment, an additional modification in the structure of the Si-O-Si unit should be considered with respect to that of the V_2O defect. Notice that the formation of a neutral vacancy in Si is accompanied by a Jahn-Teller distortion that displaces its nearest neighbors.[8,12,18] The weak bond that is formed by the elimination of the dangling bonds that remain after the vacancy formation makes atoms a and d of Fig. 3(c) approach each other. Bonds a-b and d-e will then converge towards

each other by rotation, tending to drag along with them bonds b-c and e-f in order to keep the coupling between the sp^3 hybrids[14] of atoms b and e minimal. This tension is equivalent to the application of additional compressive stress along the $\langle 110 \rangle$ axis to the Si-O-Si unit of the V_3O defect. Thus, the V_3O LVM frequency is expected to be even higher than that of the V_2O defect. However, the concentration of V_3O defects created through the reaction $V_2 + VO \rightarrow V_3O$ is expected to be even smaller than the concentration of V_2O defects created through the reaction $V_2 + O_i \rightarrow V_2O$ since $[O_i] \gg [VO]$. This adds more weight to the argument that the V_2O defect is the most likely candidate to be related to the 839 cm^{-1} IR band.

The appearance of the 824 cm^{-1} line at ≈ 320 °C may be correlated to reaction processes related to the decay of the VO signal. The decrease of the VO signal in neutron irradiated material is probably dominated especially at the initial stages by the destruction of VO pairs by Si self-interstitials released from clusters of defects (VO + Si$_i \rightarrow O_i$), in agreement with the observed increase of oxygen concentration (see Fig. 2). Other reaction channels are related to the migration of VO pairs as entities where either they are captured by O_i to form the VO$_2$ center[2] giving rise to the 885 cm^{-1} band and/or they act as traps for each other leading to the formation of the V_2O_2 defect. The latter defect, due to its structure,[6] is expected to have a LVM frequency close to that of the A center. Consequently, it seems reasonable to pursue the correlation of the V_2O_2 defect with the 824 cm^{-1} band.

To estimate the vibrational frequencies of the V_2O_2 structure[6] (Fig. 3(d)), we shall assume that the two oxygen atoms are located 1 Å off-center from the corresponding vacancy sites, as in the case of the VO. The motion of the oxygen atom of the VO defect is described by an effective Hamiltonian:

$$H = \frac{1}{2}M_O\dot{q}^2 + \frac{1}{2}k_O q^2, \tag{6}$$

where $M_O = 16$ amu is the mass of the oxygen and $k_O = 40.4$ eV/Å^2 is the force constant.[19] In the case of the V_2O_2 defect, the two oxygen atoms oscillate along the same direction. Modification of the frequencies of the oxygen atoms in V_2O_2 is related to the polarity of the Si-O-Si bond. Due to the dipole moment of this bond, the two oxygen atoms are coupled through a dipole-dipole interaction. The dipole moments of each Si-O-Si bond in the V_2O_2 structure are given by the formulae

$$\mathbf{p}_1 = Z^*(-r\hat{\mathbf{k}} + q_1\hat{\mathbf{q}}), \quad \mathbf{p}_2 = Z^*(r\hat{\mathbf{k}} + q_2\hat{\mathbf{q}}), \tag{7}$$

where $\hat{\mathbf{k}}, \hat{\mathbf{q}}$ are the unit vectors along the $\langle 001 \rangle$ and $\langle 110 \rangle$ axis and r is the vertical distance of the oxygen atom from the straight line that connects the two Si atoms in the Si-O-Si unit. The effective charge Z^* concentrated on the oxygen atom of the Si-O-Si bond, assuming an angle θ of about 18° (this is the mean value of $\theta = 15.5°$ from Ref. 12 and $\theta = 21°$ from Ref. 13), is found[20] to be $Z^* \approx 1.1e$, where e is the electron charge. The mutual potential energy of these two dipoles is given by[21]

$$W = \frac{\mathbf{p}_1 \cdot \mathbf{p}_2 - 3(\hat{\mathbf{n}} \cdot \mathbf{p}_1)(\hat{\mathbf{n}} \cdot \mathbf{p}_2)}{d^3}, \qquad (8)$$

where $\hat{\mathbf{n}}$ is the unit vector along the direction that connects the two dipoles, and d the distance between them. Assuming the dipoles to be on the oxygen sites, we easily find that $d = 3.9$ Å. The q-dependent part of the dipole-dipole interaction is found by combining Eqs. (7) and (8) to be equal to $[(Z^*)^2/d^3]q_1 q_2$. This interaction introduces a coupling between the two oscillating oxygen atoms in the effective Hamiltonian that describes their motion

$$H = \frac{1}{2} M_O \dot{q}_1^2 + \frac{1}{2} k_O q_1^2 + \frac{1}{2} M_O \dot{q}_2^2 + \frac{1}{2} k_O q_2^2 + \lambda q_1 q_2, \quad (9)$$

where $\lambda = (Z^*)^2/d^3 = 0.3$ eV/Å². This well-known Hamiltonian has two normal modes: a symmetric one, $(q_1 + q_2)/2$, with a frequency $\omega_{sym} = \sqrt{(k_0 - \lambda)/M_O}$, and an antisymmetric one, $(q_1 - q_2)$, with a frequency $\omega_{antisym} = \sqrt{(k_0 + \lambda)/M_O}$. Substituting the values of k_0, λ and M_O, we get $\omega_{sym} = 826$ cm⁻¹ and $\omega_{antisym} = 832$ cm⁻¹.

In the dipole approximation, the coupling energy U of the V_2O_2 defect with a plane electromagnetic wave $\mathbf{E}(\mathbf{r},t) = \mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \Omega t)}$ is given by

$$U = -\mathbf{E}(\mathbf{r_1},t) \cdot \mathbf{p}_1 - \mathbf{E}(\mathbf{r_2},t) \cdot \mathbf{p}_2. \qquad (10)$$

Substituting Eq. (7) into Eq. (10), we obtain the following expression for the q-dependent part H_1 of the interaction Hamiltonian

$$H_1 = -Z^* \mathbf{E}_0 \cdot \hat{\mathbf{k}} e^{i(\mathbf{k} \cdot \mathbf{r_0} - \Omega t)}[\cos(\mathbf{k} \cdot \mathbf{d}/2)(q_1 + q_2)$$
$$+ i \sin(\mathbf{k} \cdot \mathbf{d}/2)(q_1 - q_2)], \qquad (11)$$

where $\mathbf{r}_0 = (\mathbf{r}_1 + \mathbf{r}_2)/2$, $\mathbf{d} = \mathbf{r}_1 - \mathbf{r}_2$, and $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of the two dipoles respectively. Apparently from Eq. (11), the ratio of the coupling constants of the antisymmetric and symmetric modes is proportional to $\tan(\mathbf{k} \cdot \mathbf{d}/2)$. For electromagnetic waves in the region of the IR (≈ 10 μm), $\tan(\mathbf{k}_{IR} \cdot \mathbf{d}/2)$ is smaller than 1.3×10^{-4}. Therefore the antisymmetric mode of the V_2O_2 defect is expected to be much weaker than the symmetric one. Thus our semiempirical calculations agree well with the correlation of the 824 cm⁻¹ infrared band to the V_2O_2 defect.

It is worth noting that the emergence in the spectra of 824 cm⁻¹ occurs at about the same temperature as that of the 887 cm⁻¹ band of the VO_2 defect. This is consistent with the assignment of the 824 cm⁻¹ band to the V_2O_2 defect considering that in both cases the moving agent is the same defect i.e., the VO center which in the case of 887 cm⁻¹ band is trapped by an isolated oxygen interstitial atom to form the VO_2 defect[2] ($VO + O_i \rightarrow VO_2$), whereas in the case of the 824 cm⁻¹ band it is paired with another VO center to form the V_2O_2 defect.

In principle, one would also expect in this temperature range signals arising from the V_3O_2 defect.[3] An attempt to calculate the LVM frequencies of this defect is given below. In the present analysis, it is sufficient to consider that the two equivalent[6] oxygen atoms of the V_3O_2 defect oscillate along the $\langle 110 \rangle$ axis with a frequency of 833.5 cm⁻¹. This frequency is the average $(828 + 839)/2$ cm⁻¹ of the VO and

V_2O LVM frequencies vibrating independently, considering that the bonds g-g′-a′-a and g-g′-c′-c (Fig. 3(e)) allocate the distortion, due to the vacancy attachment, equivalently on each of the two oxygen atoms in the V_3O_2 geometry. Again, a dipole-dipole interaction is established between the two oxygen atoms originating from the polar Si-O-Si bonds. The situation is similar to that of the V_2O_2 defect, and the distance between the two oxygen atoms is found to be $d = 3.8$ Å leading to a value for λ equal to 0.3 eV/Å². The corresponding effective Hamiltonian now has the form

$$H' = \frac{1}{2} M_O \dot{q}_1^2 + \frac{1}{2} k'_O q_1^2 + \frac{1}{2} M_O \dot{q}_2^2 + \frac{1}{2} k'_O q_2^2 + \lambda q_1 q_2, \tag{12}$$

where $k'_O = 40.9$ eV/Å² is the force constant corresponding to the 833.5 cm⁻¹ frequency. This Hamiltonian has a symmetric $(q_1 + q_2)/2$ mode with a LVM frequency at 831 cm⁻¹ and an antisymmetric mode $(q_1 - q_2)$ with a LVM frequency at 837 cm⁻¹. Again, due to the long, with respect to d, wavelength of the IR radiation only the low frequency symmetric mode is expected to be detected in our spectra. We attribute, therefore, the 833 cm⁻¹ satellite band to the V_3O_2 structure.

In summing up, we have tried to calculate the LVM frequencies of V_2O, V_3O_2 and V_2O_2 defects. First, for the V_2O defect, we have made use of a molecular XY_2 model of the Si-O-Si unit together with a power law potential for the interaction between the O and Si atoms, and calculated the LVM frequency shift of the V_2O defect with respect to the VO by using results for the defect structures obtained by first principles cluster calculations. In any case, it must be stressed that the molecular model used for the V_2O defect can only give qualitative indications. In the next step, for the V_2O_2 and V_3O_2 defects, a simple effective Hamiltonian that takes into account the dipole-dipole interaction between the polar Si-O-Si units of the defect has been used. Our theoretical analysis was extended to the case of the V_3O defect. Based on (i) the temperature of the appearance and the evolution curves of the bands, (ii) the absence of the signals in Fz-Si material, (iii) the results from previous IR, EPR, and PAS studies, and (iv) our calculations, we finally proposed a correlation of the 839 cm⁻¹ line with the V_2O defect, the 833 cm⁻¹ line with the V_3O_2 defect and the 824 cm⁻¹ line with the V_2O_2 defect.

IV. CONCLUSIONS

We have presented a study of defects in neutron irradiated Cz-grown Si material. Infrared spectra were examined as a function of isochronal annealing temperature. The signals from three satellite bands of the A center at 824, 833 and 839 cm⁻¹ were obtained by fitting data to Lorentzian functions. The bands were correlated with the V_2O_2, V_3O_2 and V_2O defects respectively. These assignments were corroborated by semiempirical calculations of the LVM frequencies caused by the vibration of the oxygen atoms in the above structures.

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