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 $V_n O_m$ defects, as has been established by a variety of experimental techniques, particularly by electron paramagnetic resonance (EPR), infrared (IR) spectroscopy, and positron annihilation studies (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$_p$ 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, which appear as shoulders 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 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 $V_2 O$, $V_2 O_2$ and $V_2 O_2$ defects respectively. Semiempirical calculations of the localized vibrational mode (LVM) frequencies for the structures of $V_2 O$, $V_2 O_2$ and $V_2 O_2$ defects, as suggested from EPR data, 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 $\rho_0 = 10$ $\Omega$ cm. The carbon concentration was $[C]_0 < 1 \times 10^{16}$ cm$^{-3}$. Their initial oxygen concentration $[O_2]_0$ was $11.1 \times 10^{18}$ cm$^{-3}$ as was found by measurements of the 9 $\mu$m absorption band according to the relevant American Society for Testing and Materials (ASTM) procedures.

Fast neutron irradiations were performed inside a pool of water at $\approx 40$ $^\circ$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 $\approx 10$ $^\circ$C increments, over the range from room temperature (RT) to 600 $^\circ$C were performed with the samples in air. The annealing temperatures were accurate to $\approx \pm 2$ $^\circ$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 $\approx 230$ $^\circ$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 $^\circ$C and 340 $^\circ$C, respectively. All these lines appear as shoulders of the much stronger A center band and they have been designated in the literature 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$_2$ (1106 cm$^{-1}$) bands.

The appearance in the spectra of the 839 cm$^{-1}$ band from 230 $^\circ$C onwards coincides generally with the temperature range where divacancies, which are the main species of defects besides VO, are expected to become mobile. On the other hand O$_2$ is the main impurity in Cz-grown Si. The following reaction therefore could be put forward:
V₂O₃ → V₂O. Thus, at first glance, it seems not unreasonable to pursue a correlation of the 839 cm⁻¹ line with the V₂O defect. The loss of Oᵢ 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₊Oᵢ → 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, V₂O 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 V₂O 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 annihilation studies³,⁹ also indicate that secondary defects observed above 200 °C should be correlated with vacancy-oxygen complexes.

In addition, the V₂O 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 V₂O defect gives rise to the 839 cm⁻¹ line. To support this we have performed a semiempirical calculation of the LVM frequency of the V₂O defect that is presented below.

The VO pair is characterized by a off-center configuration¹⁰–¹³ 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 V₂O defects as suggested by Lee and Corbett⁶ from EPR investigations. We shall try to calculate the LVM frequency of the V₂O defect from that of the VO defect by using the modification caused on the Si-O-Si bond in the V₂O 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

\[ V = \epsilon \left( \frac{\alpha}{R} \right)^{4} - \left( \frac{\alpha}{R} \right)^{2}, \]  

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

<table>
<thead>
<tr>
<th>Off-center displacement (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>10</td>
</tr>
<tr>
<td>1.1</td>
<td>11</td>
</tr>
<tr>
<td>1.03</td>
<td>12</td>
</tr>
<tr>
<td>0.934</td>
<td>13</td>
</tr>
</tbody>
</table>
FIG. 3. The structural models for (a) VO, (b) V₂O₃, (c) V₃O₇, (d) V₂O₅, and (e) V₃O₇ centers.
where $\epsilon, \sigma$ are empirical parameters and $R$ the length of the Si-O bond. Employing this power law potential, the dependence of the force constant $\kappa$ on the equilibrium length $R_0$, for small oscillations, is found to be

$$\kappa = \frac{2\epsilon}{R_0^2}. \quad (2)$$

Using a molecular $XY_2$ model the frequency of the oscillation of the oxygen atom in the Si-O-Si unit is related to $\kappa$ and to the angle $\theta$ between the $(110)$ axis and the Si-O bond (Fig. 3(a)) according to the formula

$$\omega = \sqrt{\kappa \left(1 + 2\frac{m_o}{m_Si} \cos^2 \theta \right)}. \quad (3)$$

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

$$\omega = \frac{\sqrt{2\epsilon \sqrt{1 + 3.5 \cos^2 \theta}}}{R_0}. \quad (4)$$

This relation also holds for the Si-O-Si unit in the $V_2 O$ defect. If $R'_0$ and $\theta'$ are the structural parameters of the latter defect and $\omega'$ its LVM frequency, we finally have

$$\omega' = \frac{R_0}{R'_0} \sqrt{1 + 3.5 \cos^2 \theta'}. \quad (5)$$

where $R, \theta$ and $\omega$ refer to the VO defect. A recent first principles cluster calculation analysis gave the values, $R_0 = 1.754$ Å, $\theta = 21^\circ$ for the VO defect and $R'_0 = 1.725$ Å, $\theta' = 18.5^\circ$ for the $V_2 O$ defect, which when inserted into Eq. (5) together with our experimental value of $\omega$ lead to a value for $\omega'$ 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 $V_2 O$ defect, results in an increase of the corresponding LVM frequency. This increase is in accord with previously reported experimental findings that the concentration of $V_2 O$ defects created through the reaction $V_2 + VO \rightarrow V_2 O$ is expected to be even smaller than the concentration of $V_2 O$ defects created through the reaction $V_2 + O_2 \rightarrow V_2 O$ since $[O_2]_{V_2 O}$. This adds more weight to the argument that the $V_2 O$ 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 $\approx 320$ °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$_i$→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 giving rise to the 885 cm$^{-1}$ band and/or they act as traps for each other leading to the formation of the $V_2 O_2$ defect. The latter defect, due to its structure, is expected to have a LVM frequency close to that of the A center. Consequently, it seems reasonable to pursue the correlation of the $V_2 O_2$ defect with the 824 cm$^{-1}$ band.

To estimate the vibrational frequencies of the $V_2 O_2$ structure (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:

$$H = \frac{1}{2}M_O q_{10}^2 + \frac{1}{2}k_{0}q_{10}^2. \quad (6)$$

where $M_O=16$ amu is the mass of the oxygen and $k_{0}=40.4$ eV/Å$^2$ is the force constant. In the case of the $V_2 O_2$ defect, the two oxygen atoms oscillate along the same direction. Modification of the frequencies of the oxygen atoms in $V_2 O_2$ 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 $V_2 O_2$ structure are given by the formula

$$p_1 = Z^*(r\hat{k} + q_1\hat{q}), \quad p_2 = Z^*(r\hat{k} + q_2\hat{q}). \quad (7)$$

where $\hat{k}, \hat{q}$ are the unit vectors along the (001) and (110) 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 $\theta$ of about 18° (this is the mean value of $\theta = 15.5^\circ$ from Ref. 12 and $\theta = 21^\circ$ from Ref. 13), is found to be $Z^* = 1.1e$, where $e$ is the electron charge. The mutual potential energy of these two dipoles is given by

$$U = \frac{1}{2}Z^2 e^2 \left( \frac{1}{r^3} + \frac{1}{r^5} \right). \quad (8)$$

where $r$ is the distance between the two dipoles. The potential energy of the system is then given by

$$U_{total} = \sum_{i<j} U_{ij}, \quad (9)$$

where $U_{ij}$ is the energy between dipoles $i$ and $j$. The total energy of the system is then

$$E_{total} = E_{atom} + E_{trans} + E_{int}, \quad (10)$$

where $E_{atom}$ is the energy of the atoms, $E_{trans}$ is the energy of the transients, and $E_{int}$ is the energy of the interactions. The total energy is then

$$E_{total} = E_{atom} + E_{trans} + E_{int}.$$
where $\hat{n}$ 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 $d = 3.9\,\text{Å}$. The $q$-dependent part of the dipole-dipole interaction is found by combining Eqs. (7) and (8) to be equal to 

$$[(Z^{*})^2/d^3]q_1q_2.$$ 

This interaction introduces a coupling between the two oscillating oxygen atoms in the effective Hamiltonian that describes their motion

$$H = \frac{1}{2} M O q_1^2 + \frac{1}{2} k_O q_1^2 + \frac{1}{2} M_O q_2^2 + \frac{1}{2} k_O q_2^2 + \lambda q_1 q_2,$$

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

In the dipole approximation, the coupling energy $U$ of the $\text{V}_2\text{O}_2$ defect with a plane electromagnetic wave $E(r,t) = E_0 e^{i(k \cdot r - \omega t)}$ is given by

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

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

$$H_1 = -Z^* E_0 \mathbf{k} \cdot \mathbf{r}_1 \cdot \mathbf{r}_2 \cdot \mathbf{d}/2(q_1 + q_2) + i \sin(k \cdot \mathbf{d}/2)(q_1 - q_2),$$

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($k \cdot \mathbf{d}/2$). For electromagnetic waves in the region of the IR ($\approx 10\,\text{µm}$), tan($k \mathbf{d}/2$) is smaller than $1.3 \times 10^{-4}$. Therefore the antisymmetric mode of the $\text{V}_2\text{O}_2$ defect is expected to be much weaker than the symmetric one. Thus our semiempirical calculations agree well with the correlation of the $824\,\text{cm}^{-1}$ infrared band to the $\text{V}_2\text{O}_2$ defect.

It is worth noting that the emergence in the spectra of $824\,\text{cm}^{-1}$ occurs at about the same temperature as that of the $887\,\text{cm}^{-1}$ band of the $\text{VO}_2$ defect. This is consistent with the assignment of the $824\,\text{cm}^{-1}$ band to the $\text{V}_2\text{O}_2$ defect considering that in both cases the moving agent is the same defect i.e., the VO center which in the case of $887\,\text{cm}^{-1}$ band is trapped by an isolated oxygen interstitial atom to form the $\text{VO}_2$ defect$^2$ ($\text{VO} + \text{O} - \text{VO}_2$), whereas in the case of the $824\,\text{cm}^{-1}$ band it is paired with another VO center to form the $\text{V}_2\text{O}_2$ defect.

In principle, one would also expect in this temperature range signals arising from the $\text{V}_3\text{O}_2$ defect. 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 oxygen atoms of the $\text{V}_3\text{O}_2$ defect oscillate along the $(110)$ axis with a frequency of $833.5\,\text{cm}^{-1}$. This frequency is the average $(828+839)/2\,\text{cm}^{-1}$ of the VO and $\text{V}_2\text{O}$ 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 $\text{V}_3\text{O}_2$ 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 $\text{V}_2\text{O}_2$ defect, and the distance between the two oxygen atoms is found to be $d = 3.8\,\text{Å}$ leading to a value for $\lambda$ equal to $0.3\,\text{eV/Å}^2$. The corresponding effective Hamiltonian now has the form

$$H' = \frac{1}{2} M O q_1^2 + \frac{1}{2} k_0' q_1^2 + \frac{1}{2} M_O q_2^2 + \frac{1}{2} k_O q_2^2 + \lambda q_1 q_2,$$

where $k_0' = 40.9\,\text{eV/Å}^2$ is the force constant corresponding to the $833.5\,\text{cm}^{-1}$ frequency. This Hamiltonian has a symmetric $(q_1 + q_2)/2$ mode with a LVM frequency at $831\,\text{cm}^{-1}$ and an antisymmetric mode $(q_1 - q_2)$ with a LVM frequency at $837\,\text{cm}^{-1}$. 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 $833\,\text{cm}^{-1}$ satellite band to the $\text{V}_3\text{O}_2$ structure.

In summing up, we have tried to calculate the LVM frequencies of $\text{V}_2\text{O}$, $\text{V}_3\text{O}_2$ and $\text{V}_2\text{O}_2$ defects. First, for the $\text{V}_2\text{O}$ 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 $\text{V}_2\text{O}_2$ 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 $\text{V}_2\text{O}$ defect can only give qualitative indications. In the next step, for the $\text{V}_2\text{O}_2$ and $\text{V}_3\text{O}_2$ 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 $\text{V}_3\text{O}_2$ 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 $839\,\text{cm}^{-1}$ line with the $\text{V}_3\text{O}_2$ defect, the $833\,\text{cm}^{-1}$ line with the $\text{V}_3\text{O}_2$ defect and the $824\,\text{cm}^{-1}$ line with the $\text{V}_2\text{O}_2$ 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 $839\,\text{cm}^{-1}$ were obtained by fitting data to Lorentzian functions. The bands were correlated with the $\text{V}_2\text{O}_2$, $\text{V}_3\text{O}_2$ and $\text{V}_2\text{O}$ 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.
ACKNOWLEDGMENTS

One author (N.V.S.) was supported by a grant of the National Scholarship Foundation of Greece, IKY. The authors thank L. Spiliopoulos for preparation of the three-dimensional images of the defects.