

# Shoulder at the $887\text{ cm}^{-1}$ infrared band in neutron irradiated Si

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Infrared spectroscopy was used to study the  $887\text{ cm}^{-1}$  band in neutron irradiated Czochralski-grown silicon arising in the spectra upon annealing of the  $830\text{ cm}^{-1}$  band of the VO defect. Our analysis showed the presence of a  $884\text{ cm}^{-1}$  shoulder in the region of the  $887\text{ cm}^{-1}$  infrared band. The  $887\text{ cm}^{-1}$  band is generally attributed to the  $\text{VO}_2$  defect formed by the capture of a mobile VO center by an oxygen interstitial impurity. In our study the shoulder at  $884\text{ cm}^{-1}$  is tentatively correlated with the  $\text{V}_3\text{O}$  defect. Semiempirical calculations carried out for the vibrational frequency of  $\text{V}_3\text{O}$  structure gave a value at  $883\text{ cm}^{-1}$  thus corroborating the latter assignment. This new picture of the spectra in the range of the  $887\text{ cm}^{-1}$  band could explain some so far unaccounted for experimental findings previously reported in literature. © 1999 American Institute of Physics.

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## I. INTRODUCTION

Oxygen is considered to be the major in-grown impurity in Czochralski (Cz)-grown Si interstitially incorporated into the crystal matrix. Upon irradiation, vacancies are captured by oxygen interstitial atoms to form VO pairs, the so-called A centers with a well established<sup>1</sup> infrared (IR) signal  $\approx 830\text{ cm}^{-1}$  for the neutral charge state. Upon annealing, the  $830\text{ cm}^{-1}$  band decays and another band emerges at  $\approx 887\text{ cm}^{-1}$ . This band is generally attributed<sup>2</sup> to  $\text{VO}_2$  defects formed as a result of the reaction  $\text{VO} + \text{O}_i \rightarrow \text{VO}_2$  that describes<sup>3</sup> the migration of VO centers and their capture by  $\text{O}_i$  atoms. Experimentally this assignment was supported<sup>3,4</sup> by the fact that the amplitude of the  $887\text{ cm}^{-1}$  band is approximately proportional to the square of the initial oxygen concentration of the material. In addition, the correlation of the  $887\text{ cm}^{-1}$  band with the  $\text{VO}_2$  defect facilitates the assignments to three localized vibrational mode (LVM) bands at 904, 969 and  $1004\text{ cm}^{-1}$  emerging in the spectra when the  $887\text{ cm}^{-1}$  band anneals out. These three bands were attributed<sup>2</sup> to a  $\text{VO}_3 = [\text{VO}_2 + \text{O}_i]$  structure formed as a result of the reaction  $\text{VO}_2 + \text{O}_i \rightarrow \text{VO}_3$  when a  $\text{VO}_2$  defect traps<sup>3</sup> an  $\text{O}_i$  impurity.

However, scientists have found difficulty in reconciling, with the model of a  $\text{VO}_2$  structure, some experimental findings concerning the behavior of the  $887\text{ cm}^{-1}$  band. Moreover, these findings seem, at first sight, to militate against such a correlation. Thus, in the  $\text{VO}_2$  geometry the two oxygen atoms share a vacancy site, each of them centered on a pair of silicon bonds, and the structure exhibits  $\text{D}_{2d}$  symmetry. Uniaxial stress studies,<sup>5</sup> however, have indicated that the defect symmetry should be less than  $\text{D}_{2d}$ . In addition, isotopic splitting studies<sup>6</sup> for the LVMs, corresponding to the dioxygen-vacancy defect, gave results which are generally inconsistent with the presence of two oxygen atoms in the  $\text{VO}_2$  structure, unless they are totally decoupled in their vibrations. Finally, during the growth, in the spectra, of the

$887\text{ cm}^{-1}$  band, no loss of  $\text{O}_i$  from the solution was detected,<sup>3,4</sup> as one would expect for a  $\text{VO}_2$  center formed by the reaction  $\text{VO} + \text{O}_i \rightarrow \text{VO}_2$ . It is worth noting at this point that early electron paramagnetic resonance (EPR) studies on  $\text{V}_n\text{O}_m$  defects in irradiated Si have tentatively correlated<sup>7</sup> a band at  $887\text{ cm}^{-1}$  with the  $\text{V}_3\text{O}$  structure. These data have recently led to the possible relation<sup>8</sup> of the  $887\text{ cm}^{-1}$  band to a  $\text{V}_3\text{O}$  defect. The  $\text{V}_3\text{O}$  structure has one oxygen atom, which could account for the isotopic splitting results, and exhibits  $\text{C}_{1h}$  symmetry which is less than the  $\text{D}_{2d}$  one, in accordance with the uniaxial stress results.

It is obvious that the whole picture concerning the origin of the  $887\text{ cm}^{-1}$  band and its general behavior is not clear. A completely satisfactory explanation with all the loose ends tied up in a composite whole has not been suggested so far. This prompted the idea of studying the  $887\text{ cm}^{-1}$  IR band in detail with the aim to elucidate some of the remaining obscure points. Another peak at  $884\text{ cm}^{-1}$  in the form of a shoulder in the region of the  $887\text{ cm}^{-1}$  band was observed. The latter is generally attributed to the  $\text{VO}_2$  defect. We have tentatively correlated the former to the  $\text{V}_3\text{O}$  defect.

## II. EXPERIMENTAL DETAILS

The material used was Cz-grown silicon crystals with an initial oxygen concentration of  $[\text{O}_i]_0 \approx 10^{18}\text{ cm}^{-3}$  and undetectable levels of the carbon impurity (i.e.,  $[\text{C}] < 10^{16}\text{ cm}^{-3}$ ). The samples, which had been polished on both sides, were cut in the form of rectangular plates of  $\approx (12 \times 20 \times 1.8)\text{ mm}$  suitable for IR measurements. Fast neutron irradiations were carried out inside a water cooled tank at a dose of  $\approx 1 \times 10^{17}\text{ n cm}^{-2}$  ( $T_{\text{irr}} \approx 40^\circ\text{C}$ ). In order to reduce the effect of thermal neutrons, the samples were wrapped in cadmium. Fifteen minute isochronal anneals were carried out up to  $700^\circ\text{C}$  in air. The IR spectra were obtained at room temperature with a JASCO-IR 700 dispersive spectrometer. The two phonon background absorption was subtracted by using floating-zone samples of equal thickness.

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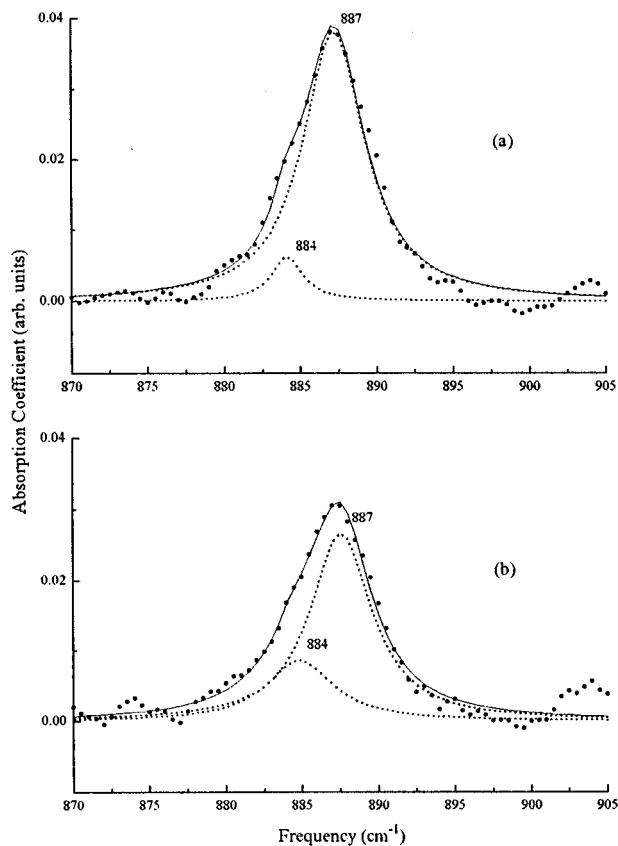


FIG. 1. IR absorption spectra and their fitted curves for the  $887\text{ cm}^{-1}$  band of neutron irradiated (a) and reirradiated (b) silicon, at a characteristic temperature ( $\approx 460\text{ }^{\circ}\text{C}$ ) of the 15 min isochronal annealing procedure. Dotted lines represent experimental results; solid lines the best fitting curves; dashed lines the Lorentzian profiles of the contributed peaks.

### III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1(a) shows the  $887\text{ cm}^{-1}$  band in the spectra. A fitting procedure using Lorentzians was used to analyze the data. The major feature immediately noted in this analysis is that on the left side of the  $887\text{ cm}^{-1}$  band there is a small shoulder at  $884\text{ cm}^{-1}$ , which appears from the beginning of the growth of the  $887\text{ cm}^{-1}$  band. At the end of the isochronal annealing sequence, the samples were submitted to a new irradiation under the same conditions. Figure 1(b), again, shows the  $887\text{ cm}^{-1}$  band in the spectra. The shoulder at  $884\text{ cm}^{-1}$  is now more profound. The evolution with temperature of the two peaks in the reirradiated material is shown in Fig. 2. Admittedly, due to the low intensity of the shoulder, and the fact that its existence is mainly verified through Lorentzian profiles fittings, its reliability may be considered as poor. However, it must be noted that four silicon samples have been used in this experiment, with an initial oxygen concentration in the range of  $\approx 10^{18}\text{ cm}^{-3}$ , and the following systematic behavior was observed in the shoulder: (i) it appeared in all the samples and it was stronger in the reirradiated material, (ii) its position in the infrared spectra was always at  $\approx 884\text{ cm}^{-1}$ , (iii) its evolution with temperature was always the same as exhibited in Fig. 2. We take all these as suggestive, but adequate, evidence indicating the presence of another center in the spectra, with a LVM signature at  $884\text{ cm}^{-1}$ .

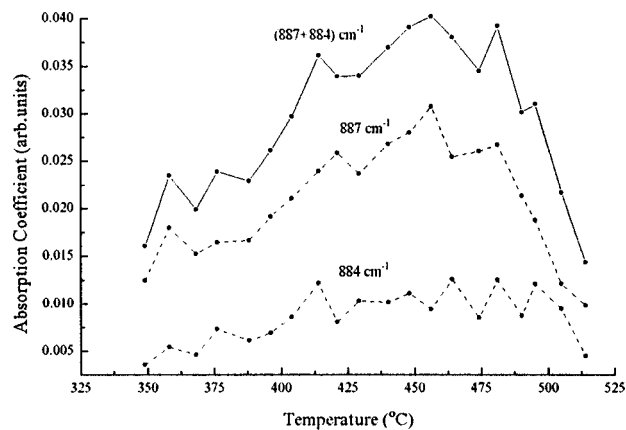
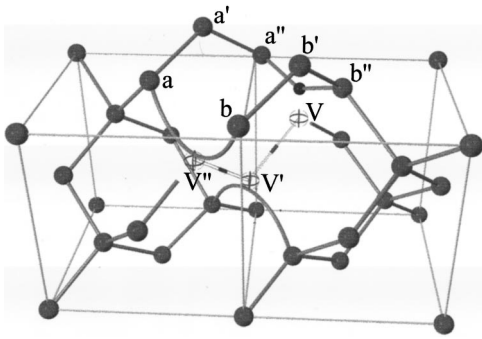


FIG. 2. Absorbance of the  $887\text{ cm}^{-1}$  band (solid lines) and its two contributing peaks (dashed lines) as a function of the isochronal annealing temperature.

At first sight, it might be argued that since the two constituent bands evolve in the same temperature range they may arise from the same center, i.e., the  $\text{VO}_2$  defect. This is not the case, however, since for the  $\text{VO}_2$  structure we expect the two bands to have similar amplitudes, given that the two oxygen atoms are almost equivalent.

Thus, in the vicinity of the  $887\text{ cm}^{-1}$  frequency, two defect structures appear to give rise to LVM signals in the spectra. This is important new information. The existence of a second defect has a significant physical role and certainly helps to understand a number of, so far, unreconciled data cited in the literature, thus allowing us to develop a clearer and more acceptable picture. Theoretical calculations<sup>9,10</sup> of the LVM frequency of the  $\text{VO}_2$  defect are in accordance with the assignment of the  $887\text{ cm}^{-1}$  band to this defect. Given the information presented in the introduction, it would be logical to try to correlate the  $884\text{ cm}^{-1}$  shoulder with the  $\text{V}_3\text{O}$  defect. For any further consideration of the  $\text{V}_3\text{O}$  structure, as the second defect giving rise to the shoulder at  $884\text{ cm}^{-1}$ , we have first to estimate the LVM frequency of the latter defect.

To this end, we have endeavored to perform a semi-empirical calculation of the vibrational frequency of the  $\text{V}_3\text{O}$  defect, based on the results reported in the literature. In a previous article,<sup>11</sup> we investigated the origin of the satellites in the A-center band and correlated an IR band at  $\approx 839\text{ cm}^{-1}$  with the  $\text{V}_2\text{O}$  defect. It was noted that the LVM frequency of the  $\text{V}_3\text{O}$  defect is expected to be higher than that of  $\text{V}_2\text{O}$ . The structure of the  $\text{V}_3\text{O}$  defect, where an oxygen atom is sited at the end of a three vacancy chain, was examined by EPR measurements<sup>12</sup> and is shown in Fig. 3. For the purpose of this calculation, we consider the  $\text{V}_3\text{O}$  defect to have come from the  $\text{V}_2\text{O}$  defect after the removal of a Si atom, thus adding an extra vacancy to the structure. Apparently, the presence of this additional vacancy  $V''$ , in Fig. 3, is accompanied by a Jahn-Teller distortion that displaces its nearest neighbors<sup>13-15</sup> in relation to their position for the  $\text{V}_2\text{O}$  structure. This displacement, which can be resolved<sup>13</sup> into a breathing  $Q_b$  and a tetragonal  $Q_E$  distortion, compels the Si atoms, named  $a$  and  $b$ , to approach each other. A measure of this approach can be found using the existing

FIG. 3. The structural model for V<sub>3</sub>O.

results in literature for the neutral vacancy in silicon. Specifically, let us suppose the lattice vacancy is sited at the origin and its four nearest neighbors (NN) initially positioned at the sites  $\mathbf{r}_i, i=1,2,3,4$  of Table I, as shown in Fig. 4(a). The unit vectors  $\hat{\mathbf{n}}_{bi}$  describing<sup>16</sup> the breathing distortion  $Q_b$  at each neighbor  $i$ , respectively, are given in Table I. The respective unit vectors that describe the tetragonal distortion  $Q_E$ , which turns<sup>13,16</sup> the initial tetrahedral  $T_d$  symmetry into a tetragonal  $D_{2d}$  symmetry are denoted by  $\hat{\mathbf{n}}_{Ei}$  and are also given in Table I. According to published results,<sup>13</sup> the magnitude of the displacement of each neighbor for each mode is, respectively,  $Q_b=0.1$  and  $Q_E=0.3$  Å; the new positions, shown in Fig. 4(b), of the four NNs are expressed in the relation  $\mathbf{r}'_i = \mathbf{r}_i + Q_b \hat{\mathbf{n}}_{bi} + Q_E \hat{\mathbf{n}}_{Ei}$ . Initially, in the ordinary silicon lattice the four NN atoms are<sup>15</sup>  $d_0 = |\mathbf{r}_i - \mathbf{r}_{j \neq i}| = 3.84$  Å apart. The new positions  $\mathbf{r}'_i$  imply that the four NN atoms must approach each other in pairs, i.e., atom labeled 1 approaches atom 4 and the same occurs for the atoms 2 and 3. The new calculated distances are then  $d = |\mathbf{r}'_1 - \mathbf{r}'_4| = |\mathbf{r}'_2 - \mathbf{r}'_3| = 3.66$  Å. Undoubtedly, the atoms that approach each other share<sup>13</sup> a pair of the electrons that remained in the dangling bonds when a Si atom was removed from a lattice site (see Fig. 4). Noticeably, the presence of the additional vacancy causes a contraction in the distance between NNs that are bonded to each other. This contraction, denoted by  $\mu = d/d_0$ , is approximately 95%. Upon considering the atoms  $a$  and  $b$  in Fig. 3, a similar contraction  $\mu_{a-b}$ , with respect to

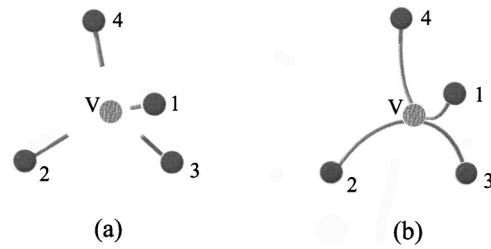


FIG. 4. A neutral vacancy in silicon: (a) before and (b) after the Jahn-Teller distortion. The coordinates of the atoms were calculated according to Ref. 13.

their positions in the V<sub>2</sub>O defect, could be attributed to the presence of the extra vacancy V''.

Let us now return to the vibrating Si-O-Si chain. According to the theory of the covalent bond,<sup>17,18</sup> the oxygen atom interacts with its neighbors through a power law potential in the form

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

where  $\epsilon, \sigma$  are empirical parameters and  $R$  is the length of the Si-O bond. Using this power law, it can easily be seen that the force constant for small oscillations around the equilibrium length  $R_0$  is

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

and since  $\kappa \propto \omega^2$ , the dependence of the frequency on the bond length is

$$\omega \propto 1/R_0. \quad (3)$$

Consider the chain of the  $a-a'-a''$  Si atoms. Any displacement of the  $a$  atom of the  $a-a'$  bond should be accompanied by a similar displacement of the  $a''$  atom of the  $a'-a''$  bond, so that the coupling of the  $sp^3$  orbitals of the bonds  $a'-a$  and  $a'-a''$  remains minimal in accordance with the *bond orbital approximation*.<sup>17,19</sup> Note, that the so-called metallic energy, which exactly involves the above coupling, should remain minimal. A similar argument can

TABLE I. The initial positions  $\mathbf{r}_i$  of vacancy nearest neighbors (NN) and the unit displacement vectors  $\hat{\mathbf{n}}_{bi}$  and  $\hat{\mathbf{n}}_{Ei}$ , corresponding to the breathing and the tetragonal modes for the Jahn-Teller distortion of the neutral vacancy in Si according to Ref. 16; for Si  $a_0=5.43$  Å.

NN index $i$	$\mathbf{r}_i$	$\hat{\mathbf{n}}_{bi}$	$\hat{\mathbf{n}}_{Ei}$
1	$\left( \frac{a_0}{4}, \frac{a_0}{4}, \frac{a_0}{4} \right)$	$\left( \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}} \right)$	$\left( -\frac{1}{\sqrt{6}}, -\frac{1}{\sqrt{6}}, \frac{2}{\sqrt{6}} \right)$
2	$\left( \frac{a_0}{4}, -\frac{a_0}{4}, -\frac{a_0}{4} \right)$	$\left( \frac{1}{\sqrt{3}}, -\frac{1}{\sqrt{3}}, -\frac{1}{\sqrt{3}} \right)$	$\left( -\frac{1}{\sqrt{6}}, \frac{1}{\sqrt{6}}, -\frac{2}{\sqrt{6}} \right)$
3	$\left( -\frac{a_0}{4}, \frac{a_0}{4}, -\frac{a_0}{4} \right)$	$\left( -\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, -\frac{1}{\sqrt{3}} \right)$	$\left( \frac{1}{\sqrt{6}}, -\frac{1}{\sqrt{6}}, -\frac{2}{\sqrt{6}} \right)$
4	$\left( -\frac{a_0}{4}, -\frac{a_0}{4}, \frac{a_0}{4} \right)$	$\left( -\frac{1}{\sqrt{3}}, -\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}} \right)$	$\left( \frac{1}{\sqrt{6}}, \frac{1}{\sqrt{6}}, \frac{2}{\sqrt{6}} \right)$

also be applied to the chain of  $b-b'-b''$  Si atoms. Therefore, it is reasonable to assume that the contraction in the distance between atoms  $a$  and  $b$  is approximately equal to that of the atoms  $a''$  and  $b''$  of the Si-O-Si chain. Upon applying Eq. (3), we obtain the following equation for the LVM frequency  $\omega'$  of  $V_3O$ :

$$\omega' = \omega_0 \frac{R'}{R_0} \approx \frac{\omega_0}{\mu_{a-b}} \approx \frac{\omega_0}{\mu}, \quad (4)$$

where  $\omega_0 = 839 \text{ cm}^{-1}$  is the LVM frequency of  $V_2O$  observed<sup>11</sup> in the experiment. Equation (4) for  $\mu = 0.95$  leads to a value  $\omega' = 883 \text{ cm}^{-1}$ , which is very close to the observed frequency of the peak under discussion.

It should be noted that the  $V_3O$  defect is expected to form at high electron fluences or by irradiation with neutrons, since the latter causes greater damage. We note that in neutron irradiated Si, multivacancy clusters, for example,  $V_3, V_4, V_5$ , are formed. Some of them, for example, the  $V_4$  defect, anneal out<sup>20</sup> in the temperature range where  $V_3O$  is formed. It is evident, therefore, that in the case of neutrons more vacancy sources are available and therefore the possibility for  $V_3O$  formation is larger. In the case of electron irradiation the number of  $V_3O$  defects is expected to be found in small, though not insignificant, concentrations. Thus, we tentatively correlate the shoulder at  $884 \text{ cm}^{-1}$  with the  $V_3O$  defect. Such a suggestion is consistent with the above calculation. Furthermore, we notice that the appearance of the band in the temperature range  $300\text{--}450 \text{ }^\circ\text{C}$  is in accordance<sup>12</sup> with EPR data for the  $V_3O$  defect.

The fact that the shoulder at  $884 \text{ cm}^{-1}$  is stronger in the reirradiated material could be understood as follows: as we know, neutron irradiation produces disordered regions<sup>21</sup> with a core containing mainly vacancies and divacancies, and a surrounding shell of impurity complexes. Furthermore, investigations of the structure of defects in neutron-irradiated Si, after anneals at  $400\text{--}500 \text{ }^\circ\text{C}$ , have shown<sup>22</sup> the existence of dislocation loops, voids and rod-like defects. In our experiments in isochronal anneals up to  $700 \text{ }^\circ\text{C}$ , although all IR signals from multivacancy-multioxygen complexes ( $V_nO_m$ ) disappear,<sup>2</sup> the crystal does not remain unchanged, in the sense that all the damage caused by the combined effect of irradiation and annealing has not completely recovered. Upon reirradiation, additional damage is caused to the crystal matrix, in relation to the one of the initial irradiation. In general, the disordered regions would be expected to be larger. These regions are potential sources of vacancies. It would, therefore, be reasonable to expect that a larger number of vacancies would be available in the reirradiated material which, liberated at higher temperatures in the course of the anneals, would assist in the formation of a larger number of  $V_3O$  defects.

The correlation of the whole  $887 \text{ cm}^{-1}$  band with both the  $VO_2$  and  $V_3O$  defects gives additional evidence that could assist in the interpretation of previously reported uniaxial stress data,<sup>5</sup> which are inconsistent with the band being correlated only with the  $VO_2$  defect. The  $VO_2$  structure,<sup>2</sup> with two equivalent oxygen atoms sharing a vacancy site, has a  $D_{2d}$  symmetry, although uniaxial stress studies concluded that the defect symmetry should be lower

than orthorhombic, that is lower than  $D_{2d}$ . Nevertheless, the presence of two peaks in the  $887 \text{ cm}^{-1}$  signal alters the situation. Actually, the fact that the  $V_3O$  defect has a  $C_{1h}$  symmetry, which is lower than that of the  $VO_2$  defect, blurs the data and the symmetry properties of  $VO_2$  structure are missed. Let us express the piezospectroscopic tensor for a defect with  $D_{2d}$  symmetry as  $A_{D_{2d}}$ , and the corresponding tensor for a defect in  $C_{1h}$  symmetry as  $A_{C_{1h}}$ . When both centers are present, the application of a uniaxial stress  $P$  apparently provides information related to a new tensor  $A$ , which is expressed in the sum  $A = A_{D_{2d}} + A_{C_{1h}}$ . In the new tensor  $A$ , the symmetry  $D_{2d}$  is clearly missed due to the presence of the lower symmetry tensor  $A_{C_{1h}}$ . Thus, the experimentally measured piezospectroscopic tensor for the  $887 \text{ cm}^{-1}$  band has lower symmetry than that of  $D_{2d}$ . We should note at this point that uniaxial stress experiments would provide valuable information on this issue, since the application of uniaxial stresses in certain crystallographic directions is expected to produce changes in the relative intensities of the peaks at  $887$  and  $884 \text{ cm}^{-1}$ .

Oxygen-implanted silicon with equal doses of  $^{16}\text{O}$  and  $^{18}\text{O}$  isotopes, after annealing of the formed  $^{16}\text{OV}$  and  $^{18}\text{OV}$  centers, is expected to lead to three dioxygen-vacancy centers, that is,  $^{16}\text{O}_2\text{V}$ ,  $^{18}\text{O}_2\text{V}$  and  $^{16}\text{O}^{18}\text{OV}$ , giving rise to three LVMs peaks in the spectra. However, only two of them are detected.<sup>6</sup> This observation is consistent with the assignment of  $887 \text{ cm}^{-1}$  to the  $VO_2$  defect only if the two oxygen atoms in the structure are totally decoupled, which has been verified<sup>23</sup> from defect modeling studies. Our results, indicating that both  $VO_2$  and  $V_3O$  contribute to the emergence of the  $887 \text{ cm}^{-1}$  band, are not inconsistent with the above observation, considering that the isotopic shift of the two defects is expected to be the same. Actually, since in both defects the vibrating Si-O-Si chain is the same, although with different geometrical characteristics, we expect both frequencies to scale as  $\omega \propto 1/\sqrt{m_{\text{O}}}$ , giving rise to the same isotope effect. Thus, once they are at almost the same position in the spectra for  $^{16}\text{O}$ , their position for  $^{18}\text{O}$  will be almost the same.

The absence of oxygen loss during the growth of the  $VO_2$  band has been attributed<sup>3,24</sup> to a balance of processes where the number of liberated O atoms during VO destruction by  $\text{Si}_i$  ( $\text{VO} + \text{Si}_i \rightarrow \text{O}_i$ ) is equal to the number of oxygen atoms entering the formation of the  $VO_2$  defect ( $\text{VO} + \text{O}_i \rightarrow \text{VO}_2$ ). We know that oxygen clusters exist in the as-grown Czochralski Si. Upon annealing at elevated temperatures, these clusters also dissociate liberating oxygen atoms thus providing an additional oxygen source. Similar arguments could be put forward in the case of the  $V_3O$  defect which is predictably produced,<sup>8,25</sup> when thermally released vacancies from VO form stable divacancies which subsequently trap VO's.  $\text{O}_i$  atoms produced by the destruction of VO contribute to the simultaneous formation of the  $VO_2$  defect. This is also consistent with the fact that the  $887 \text{ cm}^{-1}$  peak, attributed to the  $VO_2$  defect, is much stronger than the  $884 \text{ cm}^{-1}$  peak of the  $V_3O$  defect.

#### IV. CONCLUSIONS

We have presented a study of the  $887\text{ cm}^{-1}$  band in neutron-irradiated Cz-grown Si by IR spectroscopy. A fitting procedure employing Lorentzian functions indicated that two defects with peaks at  $\approx 887$  and  $\approx 884\text{ cm}^{-1}$  contribute to this band. The latter appears as a shoulder to the former. The  $887\text{ cm}^{-1}$  peak is generally attributed to the  $\text{VO}_2$  defect. We have considered the  $\text{V}_3\text{O}$  defect as the dominant candidate for the origin of the  $884\text{ cm}^{-1}$  band. This correlation with the  $\text{V}_3\text{O}$  defect was further supported by semiempirical calculations which gave a LVM frequency at  $\approx 883\text{ cm}^{-1}$  in accordance with the experimental data. Accordingly, previous reports in the literature concerning the response of the band to uniaxial stresses fall into a rational pattern. In addition, the presence of the  $\text{V}_3\text{O}$  defect, besides that of the  $\text{VO}_2$ , is not inconsistent with the valid views about the isotopic splitting of the composite  $887\text{ cm}^{-1}$  band and the absence of oxygen loss during its growth.

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