



# An infrared investigation of the $887\text{ cm}^{-1}$ band in Cz-Si

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## Abstract

We report on infrared studies of the  $887\text{ cm}^{-1}$  band arising in silicon, subjected to neutron irradiation with subsequent thermal anneals. Deconvolution of this band indicates the presence of two peaks: a strong one at  $887\text{ cm}^{-1}$  and a weak one at  $884\text{ cm}^{-1}$ . The  $887\text{ cm}^{-1}$  peak is, generally, attributed to the  $\text{VO}_2$  defect. We have tentatively correlated the  $884\text{ cm}^{-1}$  peak to a  $[\text{VO}_2 + \text{V}]$  defect structure. Theoretical calculations of the vibrational frequencies of the two defects support the above hypothesis. The new picture for the  $887\text{ cm}^{-1}$  band, could account for the exhibited uniaxial-stress behaviour. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Silicon; Oxygen; Infrared; Neutron irradiation

## 1. Introduction

Upon irradiation of Czochralski-grown (Cz-grown) silicon, the VO pair is formed. Its presence in the IR spectra is verified by an LVM band at  $830\text{ cm}^{-1}$  [1]. Upon annealing at temperatures of  $\approx 300^\circ\text{C}$  this band begins to disappear and another band arises with a frequency at  $\approx 887\text{ cm}^{-1}$ . In general, this band is correlated with the  $\text{VO}_2$  defect [2]. However, some aspects in the behaviour of the  $887\text{ cm}^{-1}$  band cannot be explained if one correlates it only with the  $\text{VO}_2$  defect. Thus, the  $\text{VO}_2$  structure has a  $D_{2d}$  symmetry, although uniaxial stress studies [3] indicate a lower symmetry for the defect correlated with the  $887\text{ cm}^{-1}$  band.

In this work we used IR spectroscopy to investigate the  $887\text{ cm}^{-1}$  band in Si. Our results indicate the presence of two peaks in the band. We propose that the second peak originates from a  $[\text{VO}_2 + \text{V}]$  defect. Semiempirical cal-

culations of the LVM frequency of this defect support such a correlation.

## 2. Experimental results and discussion

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 were irradiated by fast neutrons at a dose of  $\approx 1 \times 10^{17}\text{ n cm}^{-2}$ , at room temperature. The IR spectra were obtained at room temperature.

Fig. 1 presents the region in the spectra around the  $887\text{ cm}^{-1}$  frequency. Deconvolution of the band using Lorentzian profiles indicates the presence of two peaks. As is well established in the literature [2],  $\text{VO}_2$  has an LVM frequency at  $887\text{ cm}^{-1}$ , and therefore, one of the peaks is attributed to this defect. We have tentatively correlated the second peak at  $884\text{ cm}^{-1}$  with a  $[\text{VO}_2 + \text{V}]$  structure, where a vacancy is trapped near a  $\text{VO}_2$  defect. This is not unreasonable, since in the neutron-irradiated Si there are potential sources for vacancies. Thus, multivacancy clusters, like  $\text{V}_3, \text{V}_4, \text{V}_5$ , exist, and some of them, i.e.  $\text{V}_4$ , anneal out [4] at the

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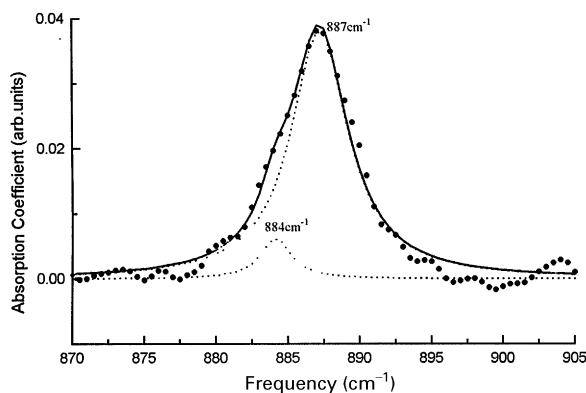


Fig. 1. Deconvolution of the  $887\text{ cm}^{-1}$  region infrared band.

temperature range where this band arises, liberating the necessary vacancies. In principle, these vacancies could be trapped by  $\text{VO}_2$  defects to form a  $[\text{VO}_2 + \text{V}]$  structure.

In what follows, we shall perform theoretical calculations, using semiempirical methods, of the LVM frequencies of the  $\text{VO}_2$  and  $[\text{VO}_2 + \text{V}]$  defects. The results support the above assignments.

### 2.1. Calculation of the LVM frequency of the $\text{VO}_2$ defect

It is known [5] that VO is characterised by a  $\langle 100 \rangle$  off-center configuration where the oxygen atom is displaced by  $1.22\text{ \AA}$  towards the two Si atoms to which it is bonded. The defect has a LVM frequency at about  $830\text{ cm}^{-1}$ , which reflects the oscillation of the O(1) oxygen atom along the  $y$ -direction (Fig. 2).

We shall now try to calculate the frequency of the  $\text{VO}_2$  defect, knowing the frequency of the VO defect. A reasonable approximation is to assume, according to the theory of the covalent bond Ref. [6], that the oxygen atom interacts with the two Si atoms to which it is bonded by a power-law potential which for the case of the O(1) oxygen atom (Fig. 2) has the form

$$U_{\text{tot}} = \varepsilon \left[ \left( \frac{\sigma}{R + y \cos \theta} \right)^4 - \left( \frac{\sigma}{R - y \cos \theta} \right)^2 + \left( \frac{\sigma}{R - y \cos \theta} \right)^4 - \left( \frac{\sigma}{R + y \cos \theta} \right)^2 \right], \quad (1)$$

where  $\varepsilon$ ,  $\sigma$  are empirical parameters determined from independent measurements and  $R$  is the length of the Si–O bond. By making a Taylor expansion around the equilibrium position  $y = 0$  we easily obtain

$$U_{\text{tot}} = \varepsilon \frac{\sigma^2}{R^4} \left[ 20 \left( \frac{\sigma}{R} \right)^2 - 6 \right] y^2 \cos^2 \theta + \text{O}(y^4), \quad (2)$$

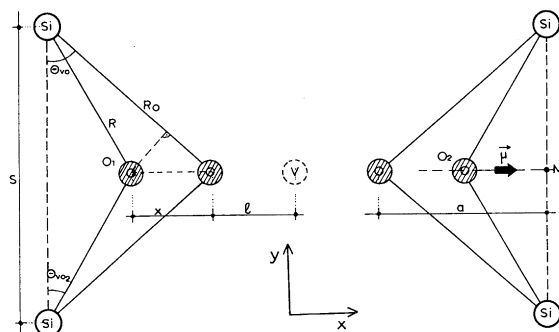


Fig. 2. The geometry of the  $\text{VO}_2$  defect.

where  $\text{O}(y^4)$  refers to higher-order terms. Thus, the force constant  $K_y$  in the  $y$ -direction would be

$$K_y = 2\varepsilon \frac{\sigma^2}{R^4} \left[ 20 \left( \frac{\sigma}{R} \right)^2 - 6 \right] \cos^2 \theta, \quad (3)$$

We consider that the  $\text{VO}_2$  defect forms from VO by the addition of a second oxygen atom, labelled O(2), at the same vacant site as that of O(1) atom. Upon introducing this oxygen atom, a new situation is established (Fig. 2). The effective charge “ $\eta$ ” of the added atom O(2) has a value  $\eta = 1.02|e|$  [7] leading to a dipole moment,  $\mu = -\eta(a-x)\hat{r}$ , where  $\hat{r}$  is the unit vector from the O(2) to the O(1) atom, which due to the two equivalent Si–O bonds lies on the  $x$ -axis, as depicted in Fig. 2. Assuming that this dipole moment lies in the middle of the  $\text{O}_2\text{M}$  segment its corresponding electric field will be given by the well-known expression:  $E = (1/4\pi\epsilon_0)(3\hat{r}(\mu\hat{r}) - \mu)/r^3$ . Under the influence of this field the initial atom O(1) is pushed towards the Si atoms to which it is bonded. For the new equilibrium position the following relation holds:  $E\eta = K_x x$ , where  $K_x$  is the force constant in the  $x$ -axis direction and  $x$  is the displacement of the initial oxygen atom due to the addition of the second oxygen atom. Considering the geometry of  $\text{VO}_2$  defect (Fig. 2), the last relation  $E\eta = K_x x$  finally gives

$$K_x x = \frac{2\eta(a-x)}{4\pi\epsilon_0(a+2l+x)^3} \eta, \quad (4)$$

where  $l = 1.22\text{ \AA}$  is the distance between the vacancy and the oxygen atom in the VO configuration.  $K_x$  has a value  $92.16\text{ Kgr/s}^2$  [8]. Taking into account [5], that  $R_0 = 1.66\text{ \AA}$  and  $\theta = 18^\circ$  we easily find:  $\alpha = R_0 \sin \theta = 0.5129\text{ \AA}$ , and substituting into Eq. (4) we obtain  $x = 0.08061\text{ \AA}$ . Note that the oxygen atoms in both VO and  $\text{VO}_2$  structures vibrate along the  $y$ -axis. Thus, from Eq. (3), the ratio of the force constants  $K_{y,\text{VO}}$  and  $K_{y,\text{VO}_2}$  of the VO and  $\text{VO}_2$  structures, is given by

the relation:  $K_{y,VO} : K_{y,VO_2} = (8\varepsilon(\sigma^2/R_0^4) \cos^2 \theta_{VO}) : (2\varepsilon\sigma^2/R^4(20(\sigma/R)^2 - 6) \cos^2 \theta_{VO_2})$ , where the relation for  $K_{y,VO}$  was obtained by setting  $R = R_0 = \sqrt{2}\sigma$  in Eq. (3) where  $R_0$  is the length of the Si–O bond at the equilibrium position. Since, in general,  $K = m\omega^2$  and taking into account that  $\cos \theta_{VO} = (s/2)/R_0$  and  $\cos \theta_{VO_2} = (s/2)/R$  (Fig. 2) we finally obtain

$$\omega_{VO_2} = \omega_{VO} \left( \frac{R_0}{R} \right)^3 \frac{1}{2} \left[ 20 \left( \frac{\sigma}{R} \right)^2 - 6 \right]^{1/2}. \quad (5)$$

Assuming now that the displacement of the silicon atoms that are bonded to the oxygen impurity is negligible, we can write:  $R = R_0 - x \sin \theta$  whereupon we get  $R = 1.6351 \text{ \AA}$ . Since  $\sigma = R_0/\sqrt{2} = 1.1738 \text{ \AA}$ , by substituting into Eq. (5) we finally have:  $\omega_{VO_2} = 901 \text{ cm}^{-1}$ , which is very close to the experimentally observed frequency of  $887 \text{ cm}^{-1}$ , for the  $VO_2$  defect.

## 2.2. Calculation of the LVM frequency of the $[VO_2 + V]$ defect

In this section we shall try to calculate the frequency of the  $[VO_2 + V]$  defect, given the frequency of the  $VO_2$  defect, by using the dipole–dipole interaction. We consider that due to the dipole moment  $\mu$  of the Si–O–Si chain, the neighbouring Si atoms are subjected to a corresponding electric field  $E$  which polarizes their bonds. The polarization  $P_{Si}$  of each Si atom is given by the relation Ref. [9]:  $P_{Si} = \alpha_{Si} \varepsilon_0 E$ , where  $\alpha_{Si}$  is the polarisability of each silicon atom, due to the four bonds in which it participates. Due to the high-order symmetry of the silicon crystal, we assume that the polarizability is given by the Mossotti relation Ref. [9]:  $\alpha_{Si} = 3(\varepsilon - 1)/N(2 + \varepsilon)$ , where  $\varepsilon = 11.7$  [10] is the relative dielectric constant of silicon, and  $N = 0.04969 \times 10^{-30} \text{ at/m}^3$  is the concentration of the silicon atoms per unit cell. Upon substituting these values we get:  $\alpha_{Si} = 4.68988 \times 10^{-29} \text{ m}^3$ . Since there are two Si–O–Si chains in the  $VO_2$  configuration, two permanent dipole moments  $\mu_1$  and  $\mu_2$  exist, where  $\mu_1$  is associated with the O(1) oxygen atom and  $\mu_2$  with the O(2) oxygen atom, as seen in Fig. 3. Due to these dipole moments, the Si atom, which will be removed from its lattice site, so that the remaining vacancy participates in the formation of the  $[VO_2 + V]$  defect, is subjected to an electric field  $E_{tot} = E_1 + E_2$ , where  $E_1$  and  $E_2$  are related to  $\mu_1$  and  $\mu_2$  moments as follows:

$$E_{tot} = E_1 + E_2 = \frac{1}{4\pi\varepsilon_0} \left( \frac{3(\hat{r}_1 \mu_1) \hat{r}_1 - \mu_1}{d_1^3} + \frac{3(\hat{r}_2 \mu_2) \hat{r}_2 - \mu_2}{d_2^3} \right), \quad (6)$$

where  $d_1 = 2.9842 \text{ \AA}$  is the distance between the points where the dipole moment  $\mu_1$  is situated and the silicon

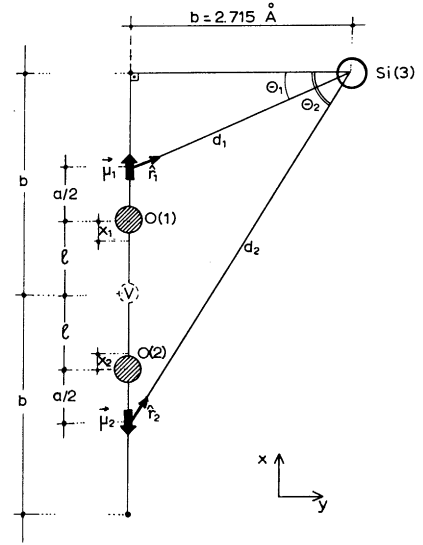


Fig. 3. The geometry of the  $[VO_2 + V]$  defect in the plane where the dipole moments  $\mu_1, \mu_2$  and Si(3) atom lie.

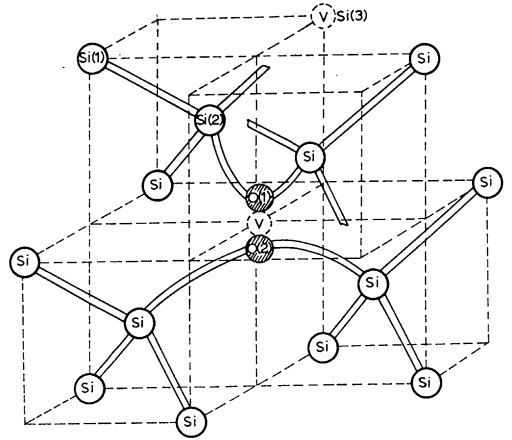


Fig. 4. The structure of the  $[VO_2 + V]$  defect.

atom Si(3) (Fig. 3), and  $d_2 = 4.9939 \text{ \AA}$  is the distance between the points where the dipole moment  $\mu_2$  is situated and the silicon atom Si(3).  $\hat{r}_1 = (0.9098\hat{x} + 0.4151\hat{y})$  and  $\hat{r}_2 = (0.5436\hat{x} + 0.8393\hat{y})$  are unit vectors on the  $d_1$  and  $d_2$  direction, respectively.

As stated above, in order to form a  $[VO_2 + V]$  defect, a Si atom near a  $VO_2$  defect must be removed. There are two possibilities for the formation of  $[VO_2 + V]$ : (i) to remove the Si(1) atom, (ii) to remove the Si(3) atom, Fig. 4. Only the second case is considered here. When the Si(3) atom is removed the displacement of the Si(2) atom is expected to be perpendicular to the Si–O(1)–Si plane and

therefore the bond length will remain almost the same. As a result, the vibration frequency of the O(1) atom will be affected slightly. The O(1) atom will move downwards and the Si–O(1) bond will expand. The vibrational frequency of the O(1) atom will be smaller than the corresponding frequency of this atom in the VO<sub>2</sub> structure. In contrast, the O(2) atom will move upwards and the Si–O(2) bond will contract. As a result, the vibration frequency of the O(2) atom will become larger than it is inside the VO<sub>2</sub> structure.

The interaction energy between the electric field and the neutral Si(3) atom is:  $W = -\frac{1}{2}(\mathbf{P}_{\text{Si}} \mathbf{E}_{\text{tot}})$ . However, when the Si(3) atom is removed, the four initial bonds in which it participates will be reduced to two. Therefore, assuming that the polarizability is slightly affected by the changes of the bond lengths, its value may be taken approximately equal to one-half of the initial value. Consequently, we obtain  $W = -\frac{1}{2}(\alpha_{\text{Si}}/2)\epsilon_0 E_{\text{tot}}^2$ .

Assuming that the displacements  $x_1$  and  $x_2$  of the two oxygen atoms, respectively, are quite small so that,  $x_i \ll d_i$  ( $i = 1, 2$ ) and  $x_1, x_2 \ll a$  (Fig. 3), we finally get that

$$W = -\frac{1}{2} \frac{a_{\text{Si}}}{2} \frac{q^2}{(4\pi)^2 \epsilon_0} \left[ \frac{(a+x_1)^2(1+3\sin^2\theta_1)}{d_1^6} + \frac{(a-x_2)^2(1+3\sin^2\theta_2)}{d_2^6} \right. \\ \left. + 2 \frac{9(a+x_1)\sin\theta_1(a-x_2)(-\sin\theta_2)\hat{r}_1\hat{r}_2 - (a+x_1)(a-x_2)}{d_1^3 d_2^3} \right. \\ \left. - 2 \frac{3(a+x_1)\sin\theta_1(a-x_2)(-\sin\theta_1) + 3(a+x_1)\sin\theta_2(a-x_2)(-\sin\theta_2)}{d_1^3 d_2^3} \right], \quad (7)$$

where  $\theta_1 = 24.5^\circ$  and  $\theta_2 = 57.1^\circ$ , as is shown in Fig. 3. Thus, the forces on the atoms O(1) and O(2) are given by the relations  $F_1 = -\partial W/\partial x_1$ ,  $F_2 = -\partial W/\partial x_2$ , respectively, which for harmonic oscillators have the form,

$$F_1 = -\frac{\partial W}{\partial x_1} = -K_{x,\text{VO}_2} x_1, \\ F_2 = -\frac{\partial W}{\partial x_2} = -K_{x,\text{VO}_2} x_2, \quad (8)$$

where  $K_{x,\text{VO}_2}$  is the force constant along the  $x$ -axis direction of the VO<sub>2</sub> defect. Assuming that  $K_{x,\text{VO}_2}/K_{x,\text{VO}} = K_{y,\text{VO}_2}/K_{y,\text{VO}} = (\omega_{\text{VO}_2}/\omega_{\text{VO}})^2$  and  $K_{x,\text{VO}} = 92.16 \text{ Kgr/s}^2$  we get  $K_{x,\text{VO}_2} = 105.25 \text{ Kgr/s}^2$ . We have assumed that the angles  $\theta_1$  and  $\theta_2$  remain almost constant during the formation of [VO<sub>2</sub> + V], considering that the displacements of the oxygen atoms are very small.

From Eq. (8) we get that the displacement of the O(1) atom is  $x_1 = 0.00402 \text{ \AA}$  and the corresponding one of the O(2) atom is  $x_2 = 0.00023 \text{ \AA}$ . Then, the vibrational fre-

quencies of the two oxygen atoms of the [VO<sub>2</sub> + V] structure are calculated from Eq. (5) by writing it down for [VO<sub>2</sub> + V] and VO<sub>2</sub> defects, and their values are, respectively, found to be:  $\omega_1 = 883.4 \text{ cm}^{-1}$  and  $\omega_2 = 887.2 \text{ cm}^{-1}$ . We therefore tentatively attribute the second peak in the spectra to  $\omega_1$  LVM of the [VO<sub>2</sub> + V] structure. The peak with  $\omega_2$  frequency coincides with the  $887 \text{ cm}^{-1}$  band of VO<sub>2</sub>.

This new correlation of the  $887 \text{ cm}^{-1}$  band with two defects, VO<sub>2</sub> and [VO<sub>2</sub> + V] could explain its uniaxial-stress behaviour previously reported [3] in the literature. This behaviour is consistent with a defect structure having a symmetry lower than orthorhombic [3]. Actually, the VO<sub>2</sub> defect has D<sub>2d</sub> symmetry, although the [VO<sub>2</sub> + V] structure has apparently a symmetry lower than orthorhombic. The presence of two defects at this band could explain rather well this behaviour, since the measured piezospectroscopic tensor is related to both defects, and it is particularly affected by the piezospectroscopic tensor of the defect with the lower symmetry. This means that due to the presence of the [VO<sub>2</sub> + V] defect

the apparent symmetry of  $887 \text{ cm}^{-1}$  is expected to become lower than D<sub>2d</sub>, in agreement with the experimentally observed behaviour [3].

We should report here that the  $887 \text{ cm}^{-1}$  band has been correlated also with the V<sub>3</sub>O defect [11,12]. However, the results of the above analysis are more in line with a correlation with a [VO<sub>2</sub> + V] defect.

### 3. Conclusions

We have performed a study of the  $887 \text{ cm}^{-1}$  band in neutron irradiated silicon. Using computer deconvolution by employing Lorentzian functions, we found that this band consists of two peaks at  $884$  and  $887 \text{ cm}^{-1}$ . The  $887 \text{ cm}^{-1}$  is generally attributed to the VO<sub>2</sub> defect. The  $884 \text{ cm}^{-1}$  is tentatively attributed to a [VO<sub>2</sub> + V] defect structure. These correlations are supported by theoretical calculations of their LVM frequencies. Our results could account for the behaviour of the band under uniaxial stresses.

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