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# Infrared bands association with multivacancy-oxygen defects in Silicon

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## Summary

Localized Vibrational Mode (LVM) studies, in neutron irradiated oxygen-rich Silicon, has been carried out in order to investigate the origin of certain bands appearing in the spectra after heat treatment. The investigation was mainly focused on two satellite lines at 840cm$^{-1}$ and 825 cm$^{-1}$ observed on either side of the 829cm$^{-1}$ band of VO above 250$^0$C and 350$^0$C respectively upon 15min isochronal annealings. Theoretical analysis supports the identification of the two satellites with $V_2O$ and $V_2O_2$ defects respectively.

## 1 Introduction

A significant aspect of the oxygen issue in Si is its tendency to associate with impurities and lattice defects creating numerous complexes. The full knowledge of the structure and properties of these complexes would help in improving the performance of silicon-based devices. Addmitably, the association of oxygen with lattice vacancies is mainly studied in irradiated Si material. The dominant defects formed upon irradiation, at room temperature, are $V_2$ and VO defects. The latter defect in its neutral charge state dominates in the IR spectra giving rise to a Localized Vibrational Mode (LVM) peak at about 830cm$^{-1}$. Upon annealing at elevating temperatures two main reaction sequencies involving oxygen and vacancies could take place[1, 2, 3, 4] leading to the formation of $VO_n$ and $V_nO$ complexes. Branching reaction channels also occur at higher temperatures and the formation of multivacancy-oxygen complexes as for example $V_2O_2$, $V_3O_2$, $V_3O$ e. t. c. has also been discussed in the literature[4, 5].

On examination of the IR spectra of neutron irradiated Si material subjected to heat treatment two small lines in the region of A-center band could be observed at 840cm$^{-1}$ and 825cm$^{-1}$. These lines, designated as satellites[4], have been discussed previously in terms of their origin and correlated with multivacancy oxygen complexes. The argument was that the vibrating units that give rise to the satellites should have a structure similar to that of VO center. We have attached to this view. The purpose of this paper is to find out the particular defects that generate these satellite lines, by means of Localized Vibrational Mode spectroscopy.

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## 2 Experimental Details

Cz-grown Si samples with initial oxygen concentration $[O_i]_0 \approx 10^{18}$ cm$^{-3}$ were irradiated by fast neutrons at $\approx 40^0$C, with a dose of $\approx 10^{17}$n.cm$^{-2}$. 15-min isochronal anneals up to 650$^0$C were performed with the samples in air. Measurements were carried out in room temperature, with a JASCO-IR 700 double beam dispersive spectrometer.

## 3 Experimental Results and Discussion

Upon annealing at $\approx 250^0$C a weak band ($\approx 840$cm$^{-1}$ ) at the high frequency side of the 829cm$^{-1}$ band of VO defect begins to emerge. Subsequently, at about 350$^0$C, a second weak band ($\approx 825$cm$^{-1}$ ) at the low frequency side of 829cm$^{-1}$ appears. In order to recover their individual contributions we have made computer decomposition using Lorentzian profiles. Figure 1 presents the annealing behavior of the two satellite bands at 840 and 825 cm$^{-1}$ together with the evolution of the VO, $VO_2$(885cm$^{-1}$ )[2] and $O_i$ (1106cm$^{-1}$ ) bands. In general lines, the appearence in the spectra of 840cm$^{-1}$ band coincides

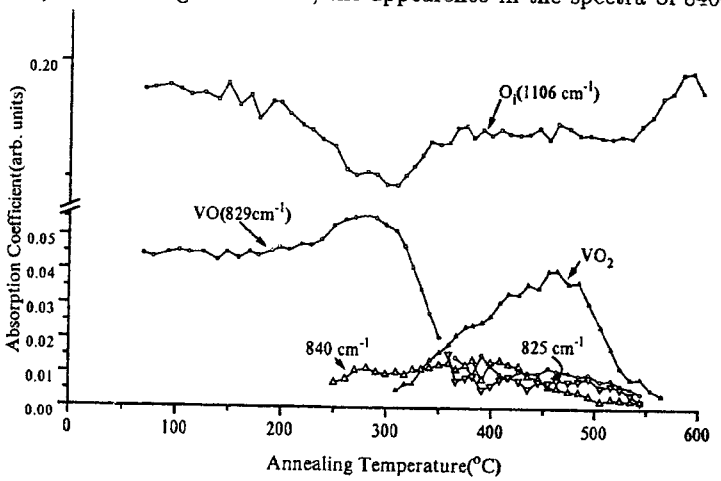


Figure 1: The evolution curves of VO, $O_i$, $VO_2$ , 825cm$^{-1}$ and 840cm$^{-1}$ bands as a function of the isochronal annealing temperature.

with the region where divacancies are expected to become mobile[6]. The concomitant decrease of oxygen concentration leads to the conclusion that a possible reaction to occur, correlated with the above observations, is the following : $V_2 + O_i \rightarrow V_2O$. The $V_2O$ defect, due to its suggested structure[7] is expected to give rise to a LVM frequency close to that of VO center. A picture therefore emerges correlating 840cm$^{-1}$ line with the $V_2O$ defect. The appearence of 825cm$^{-1}$ line at $\approx 350^0$C may be correlated to reaction processes related with the decay of VO signal. At the initial stages, the decrease of VO signal in neutron irradiated material is probably dominated by its destruction from 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.1). Other reaction channels are related to the migration of VO pairs as entities where either they are captured by $O_i$ to form $VO_2$ center[2] giving rise to the 885cm$^{-1}$ band or/and they act as traps for each other leading to the formation of $V_2O_2$ defect. The latter defect, due to its structure[7], is expected to have a LVM frequency close to that of A-center and therefore it is a potential candidate for the 825cm$^{-1}$ band.

As a next step we have performed semiempirical calculations for the LVM frequencies of $V_2O$ and $V_2O_2$ defects, in order to support the above assignments and assist the overall interpretation.

## 3.1 Calculations of the LVM frequencies of $V_2O$ and $V_2O_2$ defects

Figures 2(a) and 2(b) exhibit the atomic configurations of $V_2O$ and $V_2O_2$ defects as suggested by Lee and Corbett[7] from EPR investigations. In the following, we shall try to calculate the LVM frequencies

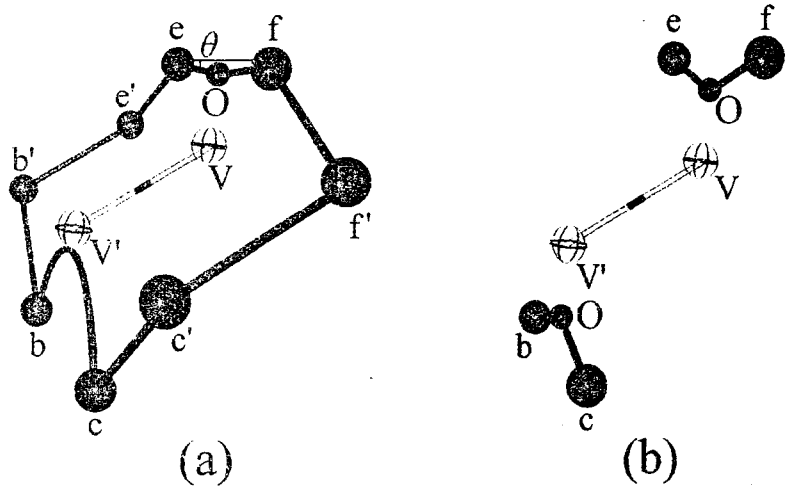


Figure 2: The structure models for $V_2O$ and $V_2O_2$ centers.

of both defects.

**The $V_2O$ defect:**The LVM frequency of $V_2O$ defect will be determined from that of the VO defect by calculating the modification of the Si-O-Si bond in the $V_2O$ structure as a result of the attachment of an extra vacancy next to the Si-O-Si bridge. According to the theory of the covalent bond[8], the oxygen atom, in the Si-O-Si unit, interacts with the two Si atoms by a power law potential of the form

$$U = \epsilon \left[ \left( \frac{\sigma}{R_0 + q\cos\theta} \right)^4 - \left( \frac{\sigma}{R_0 + q\cos\theta} \right)^2 + \left( \frac{\sigma}{R_0 - q\cos\theta} \right)^4 - \left( \frac{\sigma}{R_0 - q\cos\theta} \right)^2 \right], \qquad (1)$$

where the first two terms refer to the one Si-O bond and the second two terms to the other. $R_0$ is the length of the Si-O bond, $q$ the displacement of the oxygen atom measured from equilibrium along the $\langle 110 \rangle$ direction and $\theta$ the angle between the Si-O bond and the $\langle 110 \rangle$ direction; $\epsilon$ and $\sigma$ are empirical parameters. Making a Taylor expansion with respect to $q$ around the equilibruim position, we find that the coefficient of $q^2$, which is proportional to the force constant for the oscillation of the oxygen atom, is proportional to $\cos^2\theta$. Thus, the angular dependence of the frequency has the form:

$$\omega \propto |\cos\theta|. \qquad (2)$$

Notice that a decrease of the angle $\theta$, with respect to its value in VO, will lead to an increase for the LVM frequency in the $V_2O$ structure. The reason for the decrease of the angle $\theta$ in the case of $V_2O$ is that the atoms e and f are displaced as a result of the attachment of the second vacancy V'. The attachment of this vacancy results in a displacement of the atoms b and c which causes, through the bonds b-b'-e'-e and c-c'-f'-f (Fig.2(a)), a displacement of the Si atoms that bond with the oxygen atom. The maximum displacement of atoms e and f occurs when the bonds b-b'-e'-e and c-c'-f'-f do not expand. In this case due to the symmetry of the structure the atoms e and f are displaced as much as the atoms c and b respectively. Using data[9] for the free vacancy, the angle $\theta$ (Fig.2(a)) of the Si-O-Si unit in $V_2O$ is found to be $6^0$. This leads, according to Eq.(2), to a relative frequency shift for the $V_2O$ defect

$$\frac{\delta\omega}{\omega} = \frac{|\cos\theta'| - |\cos\theta|}{|\cos\theta|} = 3\%, \qquad (3)$$

giving rise to a LVM frequency of 855cm$^{-1}$ . This frequency shift as we mentioned previously is an estimation of the maximum frequency for $V_2O$ since the displacements of atoms e and f will be certainly smaller than those of atoms c and b. Notably, the main point of our 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 in the corresponding LVM frequency. Thus, experimental data and theoretical analysis give support to the association of 840cm$^{-1}$ band with the $V_2O$ defect.

**The $V_2O_2$ defect:** To estimate the LVM frequencies of $V_2O_2$ structure[7] (Fig.2(b)), we shall assume that the two oxygen atoms are also sited 1.03Å off-center[10] from their respective vacancies. The motion of the oxygen atom of the VO defect is described by an effective hamiltonian, $H = \frac{1}{2}M_O\dot{q}^2 + \frac{1}{2}k_Oq^2$, where $M_O$ is the mass of the oxygen, 16 amu, and $k_O$ the force constant, 40.4 eV/Å$^2$, corresponding to the 829cm$^{-1}$ frequency. The modification of the frequencies of the oxygen atoms in $V_2O_2$ is related to the polarity of the Si-O-Si bond which leads to a dipole-dipole interaction. This interaction introduces a coupling between the two oscillating oxygen atoms in the effective Hamiltonian that describes their motion,

$$H = \frac{1}{2}M_O\dot{q}_1^2 + \frac{1}{2}k_Oq_1^2 + \frac{1}{2}M_O\dot{q}_2^2 + \frac{1}{2}k_Oq_2^2 + \lambda q_1q_2, \tag{4}$$

where $\lambda = (Z^*)^2/d^3 = 0.3$ eV/Å$^2$; $Z^* = 1.1e$ is the effective charge[11]. Only the symmetric mode of this Hamiltonian with $\omega_{sym} = \sqrt{(k_0 - \lambda)/M_0}$=826cm$^{-1}$ is expected to be IR-active. The estimated value is very close to the experimental one, justifing the attribution of the 825cm$^{-1}$ infrared band to the $V_2O_2$ defect.

## 4 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 two satellite bands of A-center at 825 and 840 cm$^{-1}$ were obtained by fitting data to Lorentzian functions. The two bands were correlated with the $V_2O$ and $V_2O_2$ defects respectively. These assignments are corroborated by semiempirical calculations of the LVM frequencies of the above structures.

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