

Investigation of two infrared bands at 1032 and 1043 cm^{-1} in neutron irradiated silicon

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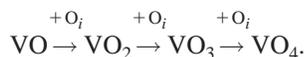
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We report on infrared (IR) studies of defects in Czochralski-grown silicon (Cz-Si) subjected to fast neutron irradiation and subsequent thermal anneals. We focus mainly on the investigation of the VO_4 defect which, in the literature, has been correlated with the pair of bands (1032 and 1043 cm^{-1}) in neutron-irradiated Si and another pair of bands (983 and 1004 cm^{-1}) in oxygen-implanted Si. Semiempirical calculations of the localized vibrational mode frequencies of the VO_4 structure support its correlation with the second pair of bands. This correlation is consistent with the ascertainment that the zero point energy of each VO_n ($n=1,2,3,4$) defect is smaller than the zero point energy of the constituent defects VO_{n-1} , O_i , that is: $E_{\text{VO}_n} < E_{\text{VO}_{n-1}} + E_{\text{O}_i}$.

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I. INTRODUCTION

Upon irradiation of oxygen rich silicon at room temperature, the main defect formed (besides the divacancy) is the vacancy–oxygen (VO) center,¹ which in the neutral charge state gives rise to a localized vibrational mode (LVM) band at $\sim 827 \text{ cm}^{-1}$ in our spectra.² Upon thermal treatment, the main reaction process is that of the formation of VO_n defects by successive addition of oxygen atoms in the initially formed VO defect; i.e.,



When the VO pair anneals out at about 300 °C a LVM band at $\sim 885 \text{ cm}^{-1}$ emerges in our spectra.² This band is generally attributed¹ to the VO_2 defect formed by the diffusion of the VO center and its trapping by an oxygen interstitial atom. In this dioxygen vacancy structure, the two oxygen atoms share a vacancy site. Upon further annealing, the 885 cm^{-1} band begins to decay (at $\sim 450 \text{ °C}$) accompanied by the emergence in the spectra³ of three bands at 899, 962, and 993 cm^{-1} . These bands have been attributed¹ to the VO_3 defect formed by the diffusion of the VO_2 defect and its capture by an O_i atom. At a slightly higher temperature another peak at 978 cm^{-1} appears in the spectra.³ This peak has been tentatively correlated⁴ with a modified VO_3 defect.

Annealing studies based on electron-irradiated Si data show that the decay of the VO_3 peaks (at $\sim 520 \text{ °C}$) follow first order kinetics,⁴ indicating further addition of another oxygen atom, leading to the formation of the VO_4 defect. Due to its structure, this defect is expected to produce two infrared (IR)-active LVM frequencies. Actually, two bands at 983 and 1004 cm^{-1} in oxygen-implanted silicon have been correlated⁵ with this center. Nevertheless, more recent IR studies of defects in neutron-irradiated silicon have

correlated³ another two bands at 1032 and 1043 cm^{-1} with the VO_4 defect.

The main objective of the present work is to find the correct band assignment of the VO_4 defect. Calculations and a simple thermodynamic analysis favor the correlation of the (983 and 1004 cm^{-1}) pair of bands with the VO_4 defect. Subsequently, based on the fact that the evolution of defects in oxygen-implanted and neutron-irradiated silicon is expected to be different due to the different damages that the two types of irradiation induce in the lattice, we generally suggest that the (1032 and 1043 cm^{-1}) pair of bands may be attributed to an oxygen aggregate associated with a multivacancy complex.

II. EXPERIMENT

Czochralski-grown samples of typical dimensions of $10 \times 20 \times 2 \text{ mm}$ with initial oxygen concentration of $\sim 10^{18} \text{ cm}^{-3}$ (and carbon content below detection limit) were irradiated with fast neutrons at $\sim 40 \text{ °C}$. We used three fluences of irradiation: $D_1 = 1 \times 10^{16}$, $D_2 = 5 \times 10^{16}$, and $D_3 = 1 \times 10^{17} \text{ n cm}^{-2}$. 15 min isochronal anneals of $\sim 10 \text{ °C}$ steps were conducted from 50 to 700 °C. Infrared measurements were made with a JASCO IR-700 double beam dispersive spectrometer.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 exhibits the evolution of the peaks correlated with the VO_2 (885 cm^{-1}), VO_3 (899, 962, and 993 cm^{-1}), VO_3 -modified (978 cm^{-1}) defects and the pair of (1032 and 1043 cm^{-1}) bands, as they appeared in our IR spectra of neutron-irradiated silicon during the isochronal annealing sequence. Original infrared spectra have been published elsewhere.³ In what follows, we concentrate on the study of the origin of the 1032 and 1043 cm^{-1} bands emerging in our spectra after the decay of the peaks of the VO_3 defect. In doing so, it is reasonable to calculate first the LVM frequencies of the VO_4 defect, since the latter defect is expected to

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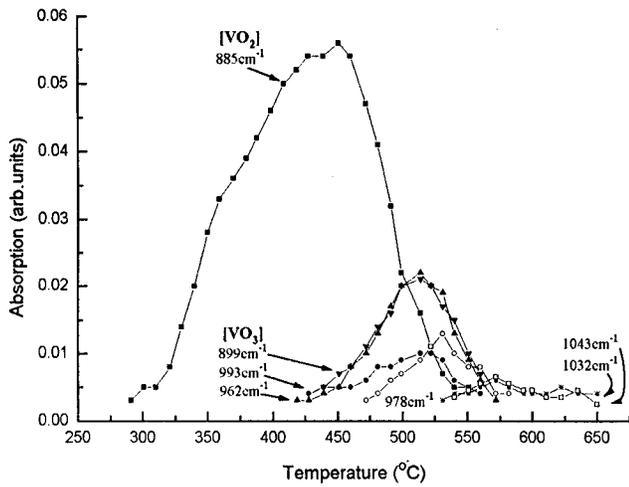


FIG. 1. The annealing behavior of VO₂ and VO₃ defects, the 978 cm⁻¹ band, and the 1032 and 1043 cm⁻¹ pair.

form when the VO₃ defect anneals out. To this end, we have performed semiempirical calculations in order to estimate the vibrational frequencies of the VO₄ defect.

In the following, the VO₄ defect would be considered equivalently as a [VO₂+2O_i] structure. In order to estimate the vibration frequency of the two equivalent oxygen atoms of the VO₄ defect which share the same vacant site, it appears more instructive to begin from the study of the geometry of Si–O–Si bond, and then to evaluate the changes that occur to this bond when an additional oxygen atom is introduced at the same vacant site. To this end, we shall proceed by estimating the changes occurring when an oxygen atom is introduced in the VO configuration leading to the VO₂ structure, and then we shall extend these results in the case of the VO₄ defect.

The geometry of Si–O–Si is depicted in Fig. 2. According to the theory of the covalent bond,⁶ we assume that the oxygen atom is subjected to a power law potential

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

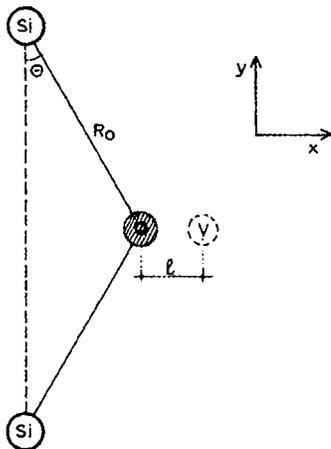


FIG. 2. The VO center geometry projected in the <110> plane.

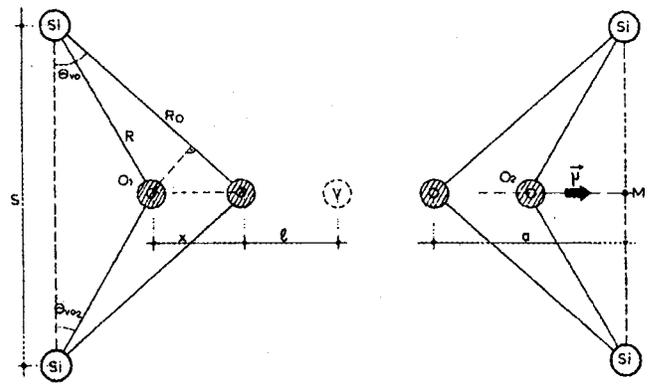


FIG. 3. The VO geometry with an additional oxygen atom attached at the same vacant site.

where ϵ and σ are empirical constants and R is the length of the Si–O bond. The vibrational frequency of 827 cm⁻¹ of the VO structure arises from the stretching mode of the oxygen atom in the y direction. Since the oxygen atom is bonded with two Si atoms the total potential, for small displacements around the equilibrium site, is given by the expression

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

Upon expanding this relation in a Taylor series and keeping only second order terms we find

$$U_{\text{tot}} = \epsilon \frac{\sigma^2}{R^4} \left(20 \left(\frac{\sigma}{R} \right)^2 - 6 \right) y^2 \cos^2 \theta. \quad (3)$$

Given the validity of the Hook law, the potential energy has the general expression

$$U_{\text{tot}} = \frac{1}{2} K y^2, \quad (4)$$

where K is the force constant of the Si–O bond in the y axis. On combining Eqs. (2) and (4) we have

$$K = 2\epsilon \frac{\sigma^2}{R^4} \left(20 \left(\frac{\sigma}{R} \right)^2 - 6 \right) \cos^2 \theta. \quad (5)$$

Minimizing the potential energy given by the relation Eq. (1), the length R_0 of the Si–O bond at the equilibrium position is found to be $R_0 = \sqrt{2}\sigma$. The corresponding value of the force constant is then

$$K = 8\epsilon \frac{\sigma^2}{R_0^4} \cos^2 \theta. \quad (6)$$

Upon introducing the second oxygen atom, a new situation is established. In order to study the new structure, we shall consider the initial oxygen atom under the influence of the dipole field of the added oxygen atom (Fig. 3). The effective charge of the added atom has a value⁷ $n = 1.02|e|$ leading to a dipole moment

$$\mu = -\eta(a-x)\hat{r} \quad (7)$$

where \hat{r} is the unit vector from O₂ towards O₁ which, because of the two equivalent Si–O bonds, lies on the x axis as

depicted in Fig. 2. We assume that this dipole moment lies in the middle of the O₂M segment. The corresponding electrical field is given by the familiar expression for dipoles

$$\mathbf{E} = \frac{1}{4\pi\epsilon_0} \frac{3\hat{r}(\boldsymbol{\mu}\hat{r}) - \boldsymbol{\mu}}{r^3}. \quad (8)$$

Under the influence of this field, the initial oxygen atom is pushed towards the Si atoms to which it is bonded, and its new equilibrium position is characterized by the new relation

$$E\eta = K'x, \quad (9)$$

where K' is the force constant of the Si–O bond in the x axis for the Si–O–Si chain and x is the displacement of the initial oxygen atom due to the addition of the second oxygen atom. Combining relations (7), (8), and (9) we finally get

$$K'x = \frac{2\eta(a-x)}{4\pi\epsilon_0(a+2l+x)^3} \eta. \quad (10)$$

The K' has a value⁸ of 92.46 K gr/sec². Taking into account that $R_0 = 1.66 \text{ \AA}$ and $\theta = 18^\circ$,⁹ we easily evaluate $\alpha = R_0 \sin \theta = 0.5129 \text{ \AA}$.

It is worth noting that the oxygen atoms in both VO and VO₂ structures vibrate in the y axis. Thus, from relation (5), the ratio of the force constant K_{VO} and K_{VO_2} of the VO and VO₂ structures is given by the relation

$$\frac{K_{VO}}{K_{VO_2}} = \frac{8\epsilon \frac{\sigma^2}{R_0^4} \cos^2 \theta_{VO}}{2\epsilon \frac{\sigma^2}{R^4} \left(20\left(\frac{\sigma}{R}\right)^2 - 6\right) \cos^2 \theta_{VO_2}}, \quad (11)$$

where R is the distance between the Si and O atoms in the VO₂ configuration. Assuming that the displacement of the silicon atoms that are bonded to the oxygen impurity are negligible, we can write

$$R = R_0 - x \sin \theta. \quad (12)$$

Since, in general, $K = m\omega^2$ one has

$$\omega_{VO_2} = \omega_{VO} \left(\frac{R_0}{R}\right)^2 \frac{\cos \theta_{VO_2}}{\cos \theta_{VO}} \frac{1}{2} \left(20\left(\frac{\sigma}{R}\right)^2 - 6\right)^{1/2}. \quad (13)$$

As is easily seen from Fig. 2

$$\cos \theta_{VO} = \frac{s/2}{R_0}$$

and

$$\cos \theta_{VO_2} = \frac{s/2}{R}. \quad (14)$$

In view of relations (13) and (14) we obtain

$$\omega_{VO_2} = \omega_{VO} \left(\frac{R_0}{R}\right)^3 \frac{1}{2} \left(20\left(\frac{\sigma}{R}\right)^2 - 6\right)^{1/2}. \quad (15)$$

Since the VO₄ structure contains a VO₂ core, as is easily seen from Fig. 4, it is reasonable to apply the reasoning of the above analysis in the case of the VO₄ defect. Using again Eq. (10) now for the VO₄ defect we have

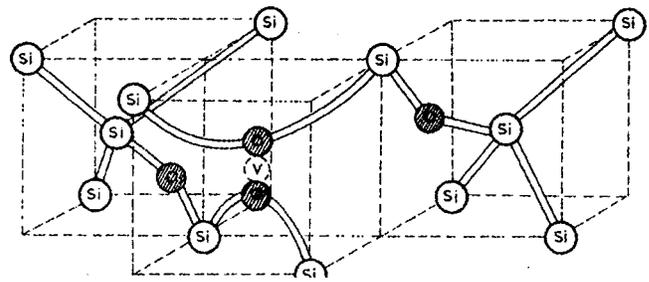


FIG. 4. The VO₄ structure.

$$K''x = \frac{2\eta(a-x)}{4\pi\epsilon_0(a+2l+x)^3} \eta, \quad (16)$$

where K'' is the force constant of the Si–O bond in the x axis for the chain Si–O_i–Si–O–Si, which corresponds to a [VO+O_i] structure.² Due to the general formula $K = m\omega^2$, the following relation between K' and K'' holds:

$$\frac{K''}{K'} = \left(\frac{\omega_{VO+O_i}}{\omega_{VO}}\right)^2. \quad (17)$$

Since $\omega_{VO} = 827 \text{ cm}^{-1}$ and $\omega_{VO+O_i} = 914 \text{ cm}^{-1}$, we finally get $K'' = 112.57 \text{ K gr/s}^2$. Upon solving Eq. (16), we get for the displacement x the value $x = 0.06868 \text{ \AA}$. Therefore, ω_{1,VO_4} is given, respectively, to the relation Eq. (15) by the expression

$$\omega_{1,VO_4} = \omega_{VO+O_i} \left(\frac{R_0}{R_{VO+O_i}}\right)^3 \frac{1}{2} \left(20\left(\frac{\sigma}{R_{VO+O_i}}\right)^2 - 6\right)^{1/2}, \quad (18)$$

where $R_{VO+O_i} = 1.6396 \text{ \AA}$ is the corresponding length of the Si–O bond in the [VO+O_i] configuration, estimated according to Eq. (12). Taking into account Eqs. (12) and (18) for the case of VO₄, we finally get

$$\omega_{1,VO_4} = 980 \text{ cm}^{-1}. \quad (19)$$

The frequencies ω_{2,VO_4} of the other two equivalent interstitial oxygen atoms are considered almost the same as the frequencies of the [VO+O_i] center that is 1000 cm^{-1} , since the changes induced by the addition of the O₂ atom are negligible for those atoms. Obviously, these values are closer to the values reported by Stein.⁵

One other very important point must be mentioned. Tables I and II give the zero point energies, E_f of the suc-

TABLE I. E_f and E_i according to Stein.^a

Defect	Frequency	E_f	E_i	Remark
O _i	1106			
VO	830			
VO ₂	889, 889	1778		
VO+O _i			1106+830=1836	$E_f^{VO_2} < E_i^{VO+O_i}$
VO ₃	905, 968, 998	2871		
VO ₂ +O _i			1778+1106=2884	$E_f^{VO_3} < E_i^{VO_2+O_i}$
VO ₄	983, 983, 1004, 1004	3974		
VO ₃ +O _i			2871+1106=3977	$E_f^{VO_4} < E_i^{VO_3+O_i}$

^aSee Ref. 5.

TABLE II. E_f and E_i according to Londos *et al.*^a

Defect	Frequency	E_f	E_i	Remark
O_i	1106			
VO	827			
VO_2	885, 885	1770		
$VO+O_i$			1106+827=1833	$E_f^{VO_2} < E_i^{VO+O_i}$
VO_3	899, 962, 993	2854		
VO_2+O_i			1770+1106=2876	$E_f^{VO_3} < E_i^{VO_2+O_i}$
VO_4	1032, 1032, 1043, 1043	4150		
VO_3+O_i			2854+1106=3960	$E_f^{VO_4} > E_i^{VO_3+O_i}$

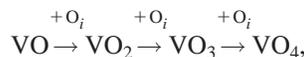
^aSee Ref. 3.

cessive VO_n defects and the sum E_i of the respective energies of the defects VO_{n-1} , O_i from which they are formed according to the experimental values presented by Stein⁵ and Londos *et al.*,³ respectively. To simplify matters, we have taken $\hbar = 1$. According to Table I, the zero point energies E_f of all the VO_n defects are always smaller than the respective energies E_i , i.e., $E_f < E_i$. A similar trend is also shown for the results in Table II up to the VO_3 defect. This trend, however, is not verified for the 1032 and 1043 cm^{-1} bands, as we can easily see, since for this case $E_f > E_i$. This may be taken as an indication that, in neutron-irradiated materials, the oxygen agglomeration process for the formation of the VO_4 defects is modified after the annealing out of the VO_3 defects and, therefore, that the (1032 and 1043 cm^{-1}) pair is related to some other structures.

It is well known that the Gibbs free energy $G = U + TS$ is the physical parameter, the minimum of which characterizes the equilibrium situation of a structure. Thus, in the case of the VO_n defects, where each structure VO_n is formed from the previous one, $VO_{(n-1)}$, by the addition of an O_i atom, it is expected that their formation process would comply with the relation $G_{VO_{n-1}} + G_{O_i} < G_{VO_n}$. Only in the case of $T = 0$ K does this relation become $U_{VO_{n-1}} + U_{O_i} < U_{VO_n}$, which reflects an analogous relation for the zero point energies we used above. As the temperature increases other terms, for example of kinetic origin, are added to the internal energy U . However, it appears that the changes occurring in ΔU and $T\Delta S$ for the VO_n defects' family have magnitudes that always comply with the fundamental relation $G_{VO_{n-1}} + G_{O_i} < G_{VO_n}$. Evidently, the fact that the criterion we used regarding zero point energies holds for the family of VO_n defects does not mean that it can be unquestionably extended to any defects' family. In any case, it cannot be generalized and its validity should always be carefully verified by experimental results.

Coming now to the VO_4 defect, this outcome is apparently consistent only with the data reported by Stein,⁵ and his attribution of the 984 and 1000 cm^{-1} bands to this structure is therefore more acceptable. Motivated by the results of the above analysis, we have repeated our experiments in a number of silicon samples with initial oxygen concentrations of $\sim 10^{18} cm^{-1}$ submitted to neutron fluences in the range of $10^{16} - 10^{17} n cm^{-2}$. However, the two bands reported by Stein⁵ for the VO_4 defect were never detected in our neutron-

irradiated samples, whereas the 1032 and 1043 cm^{-1} bands were always present. In the following, we shall briefly discuss the differences in the evolution of defects occurring between the two kinds of irradiation. We note at first that the damage caused by neutron irradiation in the silicon matrix is different than that caused by light ion implantation (for example, oxygen ions). This eventually leads to different reaction processes between intrinsic defects and the oxygen impurity, especially at high temperatures where oxygen interstitial atoms become mobile. Thus, light ion implantation produces mostly divacancies. Upon annealing, these divacancies do not affect the reaction channel



which unperturbably takes place with increasing temperature, leading to the formation of the VO_4 defect. In contrast to oxygen implantation, neutron irradiation is more effective for the production of multivacancy complexes. Fast neutron irradiation also produces disordered regions, which are essentially regions rich in multivacancy complexes. These multivacancy complexes serve as nucleation sites for oxygen aggregates, especially at temperatures around 600 °C (where the two bands at 1032 and 1043 cm^{-1} occur in the spectra). Note that at these temperatures, the diffusion coefficient of oxygen is sufficient for oxygen aggregation even during the course of the 15 min isochronal anneal intervals. Thus, in the case of neutrons, the formation efficiency of the VO_n defects at high temperatures is reduced, and the new situation inside the silicon matrix favors the prevalence of other processes which subsequently lead to the activation of alternative reaction channels. An enhancement of the oxygen aggregation due to the presence of multivacancies is reasonably expected. Thus, the reaction channel $VO_{n-1} + O_i \rightarrow VO_n$ occurring successively upon annealing in light ion-implanted material is modified at high temperatures, in the case of neutron irradiation, due to the increased tendency of the oxygen atoms to aggregate. In other words, at these temperatures, oxygen atoms prefer to participate in the formation of oxygen-related aggregates. If the existing multivacancies act as trapping sites, they can trap oxygen atoms and, because of the high temperatures, atomic displacements inside these (oxygen-vacancy) aggregates could occur.¹⁰ In our opinion, these large (oxygen-vacancy) complexes are potential candidate structures that give rise to the (1032 and 1043 cm^{-1}) pair of bands.

Our experimental data show that above 600 °C all the bands disappear except that of the oxygen interstitial, the concentration of which increases even higher than the original value. The increase of $[O_i]$ indicates that all defects dissociate, liberating the oxygen atoms which return to interstitial positions. The fact that the final oxygen concentration is found to be larger than the initial concentration prior to irradiation is attributed to the tendency of oxygen to participate in the structure¹¹ during crystal growth of other complexes besides its main interstitial incorporation in the Si lattice. These complexes dissociate at high temperatures providing the additional amount of oxygen, since the liberated oxygen returns to an interstitial site which is the main configuration

of oxygen in silicon and therefore is more preferable. It seems that a critical size that cannot be surpassed, exists beyond which the defect structure becomes unstable. This may reflect the critical number of oxygen atoms that can be incorporated in the structure. This would happen if the activation energy for the formation of the next defect is larger than the respective activation energy for its dissociation. In any case, the restoration of oxygen atoms at high temperatures to interstitial sites in the silicon matrix is a clear indication of annealing mechanisms dominated by oxygen cluster dissociation.

IV. CONCLUSIONS

In conclusion, we have investigated two bands at 1032 and 1043 cm^{-1} appearing in the spectra of neutron-irradiated silicon after annealing out of the VO_3 defect. We found that a previous assignment of these bands to a VO_4 center is incorrect. The VO_4 defect appears in oxygen-implanted silicon, and two bands at 983 and 1004 cm^{-1} are definitely correlated with this structure. In the case of neutron-irradiated material the evolution of defects at high temperatures is different from that in oxygen-implanted material, and

the two bands at 1032 and 1043 cm^{-1} may be correlated to an oxygen aggregate associated with a multivacancy cluster.

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