Precursor defect to the vacancy-dioxygen center in Si

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In a recent paper [Phys. Rev. B **50**, 11 531 (1994)] we have tentatively attributed two new infrared bands at 914 cm $^{-1}$ and 1000 cm^{-1}, in neutron-irradiated Czochralski-grown silicon, to a [VO+O_i] structure that was considered to develop as an intermediate stage in the process of conversion of a VO center to a VO_2 complex upon heat treatment. As a continuation of this work, we further investigate [VO+O_i] structure and the formation of intermediate defects. In addition, we present semiempirical calculations of the localized vibrational mode frequencies of the [VO+O_i] defect. The results are consistent with the experimental observations.

VO is the dominant defect formed in Czochralski-grown (Cz) Si upon irradiation when a mobile vacancy is captured by an interstitial oxygen atom. In the VO structure, oxygen occupies an off-center substitutional site. In its neutral charge state the defect gives rise to a localized vibrational mode (LVM) at 827 cm^{-1}. Upon thermal treatment VO begins to disappear around 300 °C. The decay of the VO signal is accompanied by the emergence of another band at 885 cm^{-1} that is attributed to a VO_2 center where an oxygen pair shares a vacancy site.[1] The main formation mechanism of the VO_2 center involves the diffusion of the VO defect and its capture by an isolated oxygen interstitial atom. In a previous paper[2] we have considered the existence of intermediate defect stages in the process of VO transformation to the VO_2 complex and two LVM's at 914 and 1000 cm^{-1} were tentatively attributed to a [VO+O_i] structure. This paper details our previous publication. We further provide semiempirical calculations for the LVM frequencies to demonstrate our suggestions for the defect configuration. In particular, we estimate the frequency shifts of isolated O_i and VO defects when they come together in a [VO+O_i] structure. The analysis enables one to elucidate the effects of bond-length changes on the vibrational frequencies.

A set of samples cut from a wafer grown with the Czochralski technique with initial oxygen concentrations $\approx 9.4\times 10^{17}$ cm^{-3} and a float-zone (fz) sample ($[O_i]_0 < 10^{16}$ cm^{-3}) were irradiated at room temperature (RT) by fast neutrons at a dose of 1.5×10^{17} n/cm^2. The carbon content of all samples was beyond detection limit. The details of irradiation and the IR measurements procedure were reported elsewhere.[2] The IR spectra showing absorbance versus wave number after irradiation and after 15-min isochronal annealings of the Cz samples at various temperatures are similar to those presented in Fig. 1 of Ref. 2. It was shown there that the emergence of the two peaks at 914 and 1000 cm^{-1} occurs prior to the growth of the 885-cm^{-1} band of VO_2. The evolution with temperature of these two peaks together with those of 827- and 885-cm^{-1} lines is exhibited in Fig. 1. Peaks of 914 and 1000 cm^{-1} arise and disappear together in the spectra, indicating a common origin.

The fz sample was submitted to the same isochronal annealing sequence as the Cz samples but there was no indication of 914- and 1000-cm^{-1} bands. This demonstrates that the bands are probably related to an oxygen-defect complex. The whole behavior points to intermediate defects structures between VO and VO_2 centers. This interesting angle of consideration was first promoted for the VO $\rightarrow$ VO_2 conversion by Pomozov *et al.*,[3] although the idea of metastable precursor structures is not new in semiconductors. It has been considered previously for the cases of the vacancy-oxygen pair,[4] the carbon-interstitial–carbon-substitutional defect,[5] and the carbon-interstitial–oxygen-interstitial complex[6] in silicon.

Figure 2(a) illustrates the suggested geometry and band assignments of the [VO+O_i] structure. The center is composed of a VO and O_i defect in close proximity. In this picture the observed bands centered at 1000 cm^{-1} and 914 cm^{-1} are attributed to the vibrations of the oxygen atoms of the O_i and VO defect, respectively. This is very reasonable since, considering separate configurations, O_i and VO structures correspond to the less roomy and the more roomy arrangements of oxygen atoms in the Si lattice, respectively. When they come together, the bonds related with O_i tend to expand. As a consequence, oxygen bonds in the VO center tend to contract. This means that the force constant of O_i in the [VO+O_i] defect decreases, although the force constant of VO increases. Within these lines, we shall assume that though generally the observed frequencies are collective modes of the [VO+O_i] complex, they correspond to independent oscillations of each defect component. Consequently, in the analysis that follows the 1000-cm^{-1} band is considered as arisen from the antisymmetric stretching vibration of O_i in a modified crystal environment. Besides changes in bond lengths, other causes that affect local force constants, as, for example, angle bending, were not taken into account in this work. Due to the directional nature of the covalent bonds the interatomic forces cannot be represented by a simple potential. However, we shall approach the problem by assuming that the O_i atom oscillates near the minimum of a power-law potential:

$$U(r)=4\epsilon\{(\sigma/r)^m-(\sigma/r)^n\},$$

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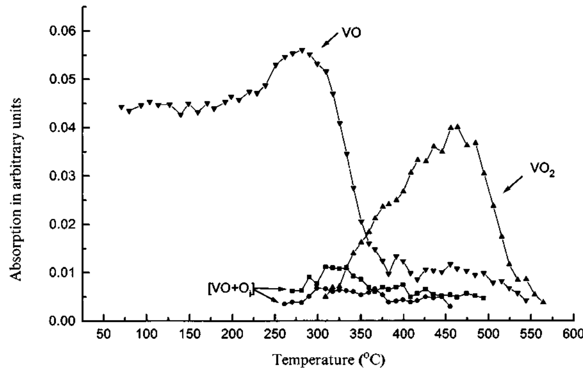

FIG. 1. The annealing behavior of the 914- and 1000-cm^{-1} peaks of $[VO+O_i]$ together with that of VO and VO_2 defects.

where the positive part refers to the repulsive overlap interaction and the negative part to the attractive interaction due to the bonding. The physics of the covalent bond[7] entails $m=4$ for the overlap interaction and $n=2$ for the attraction, i.e.,

$$U(r)=4\epsilon\{(\sigma/r)^4-(\sigma/r)^2\}. \qquad (1)$$

Selecting the adjustable parameters ϵ,σ so as to fit the equilibrium position and vibrational frequency (1100 cm^{-1}) of the interstitial oxygen atom, we can have a suitable expression of the potential $U(r)$. It is therefore reasonable to enquire how this potential is modified in the case of the $[VO+O_i]$ defect. Geometrically, one of the six second-nearest silicon atoms has been substituted for an oxygen atom. Such a substitution leads to a modification in the attraction that O_i feels because of this second neighbor. The modification originates from the difference in the bonding of the intermediate Si atom, which is connected with both O_i and VO in the $[VO+O_i]$ structure. The whole geometry makes easier the expansion of the Si-O_i bond, a fact that could be represented in the potential form described in Eq. (1) by a smaller attractive part leading to the expression

$$U_-(r)=4\epsilon\{(\sigma/r)^4-(1-\lambda_-)(\sigma/r)^2\}. \qquad (2)$$

The λ_- parameter is a measure of the modification of the attractive interaction between the oxygen and its neighboring environment. The suggested geometry of the $[VO+O_i]$ center implies that the change in the attractive part of Eq. (1) is mainly related to the difference in the couplings of the hybrids of the intermediate Si atom before and after the $[VO+O_i]$ complex formation. In order to estimate λ_-, we have recourse to the study of the potential to which the intermediate Si atom is subjected. Generally, the coupling between two hybrids on the same atom but directed to different bonds is related to the metallic energy[8] V_1 that is used to correct the bond orbital approximation.[9] V_1 has the expression $V_1=\alpha_m V_2/2$, where V_2 is the covalent energy ($\propto 1/r^2$) and α_m the *metallicity*. Metallicity measures the metallic character of a covalent bond and its value for silicon is $\alpha_m=0.81$ (Table I of Ref. 8). However, when impurities are present in the lattice the situation is different since the metallicity of the Si atoms that bond with these impurities is expected to change. An average value $\langle\alpha_m\rangle$ should be considered. In the case of oxygen impurity in silicon, Si-O bonds are much less metallic than Si-Si bonds, as it is clear from the value of 9 eV energy gap of SiO_2.[10] In this sense, the contribution of the Si-O bond to the metallicity is almost negligible. Thus the initial metallicity of the Si atom $\langle\alpha_m\rangle_i=(3\times0.81+1\times0)/4\approx0.61$ (in the O_i configuration) becomes finally $\langle\alpha_m\rangle_f=(2\times0.81+2\times0)/4\approx0.40$ (in the $[VO+O_i]$ configuration). In order to relate these metallicities to the potential of the intermediate Si atom, we consider that the formula

$$E_{\rm bond}=V_2(1-\alpha_m) \qquad (3)$$

giving the bond energy as a function of metallicity[8] comes from a power potential,

$$U_\zeta(r)=4\epsilon\{(\sigma/r)^4-(1-\zeta)(\sigma/r)^2\}, \qquad (4)$$

where V_2 in Eq. (3) is the covalent energy and ζ in Eq. (4) is a parameter that measures the effect of metallicity. Calculating the bond energy with the help of Eq. (4) we get

$$E_{\rm bond}=\epsilon(1-\zeta)^2 \qquad (5)$$

Comparing Eqs. (3) and (5) we get $\epsilon=V_2$ and $\zeta=1-\sqrt{1-\alpha_m}$, from which we get

$$\zeta_f-\zeta_i=(1-\sqrt{1-0.40})-(1-\sqrt{1-0.61})\approx-0.15.$$

Apparently, $\zeta_f-\zeta_i$ is the change in the attractive part of the potential for the intermediate Si atom. Considering bond forces as classical two-body forces that obey the law of action and reaction, we shall assume that the relative change of

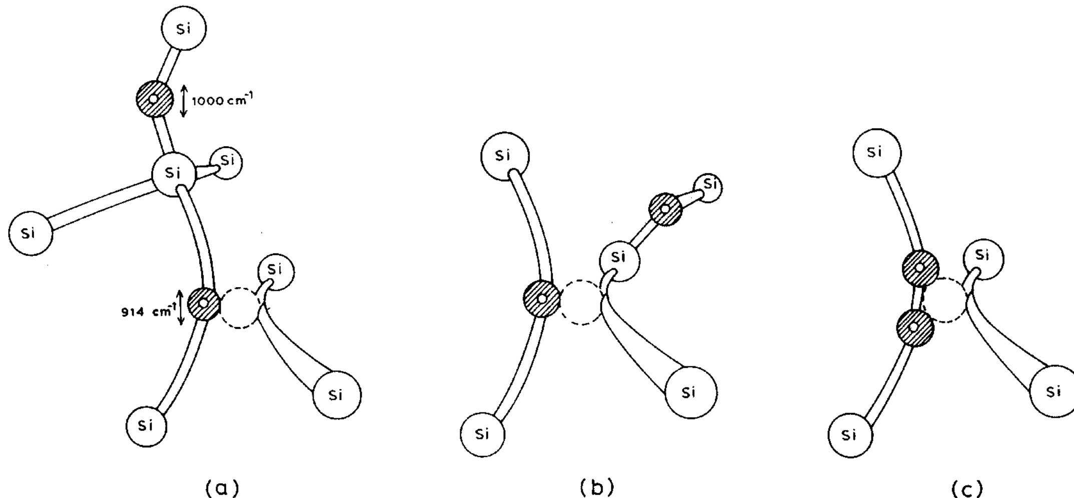

FIG. 2. Various geometries of the $[VO+O_i]$ defect.

the attractive part of the potential of O_i is equal to the average relative change of attractive parts of the potentials of its two neighboring Si atoms. Since from these two atoms only the potential of the intermediate one is expected to change, the λ_- value could be taken as half of the $|\zeta_f-\zeta_i|$ value, i.e., $\lambda_-=0.075$.

In a similar manner the 914-cm^{-1} band can be associated with the oscillation of the oxygen atom of the VO center in the presence of a nearby interstitial oxygen atom. The interstitial oxygen, in this case, exerts an extra attraction. Thus, the oscillation of the oxygen atom of the VO defect in $[VO+O_i]$ can be described by using a potential $U_+(r)$:

$$U_+(r)=4\epsilon'\{(\sigma'/r)^4-(1+\lambda_+)(\sigma'/r)^2\}, \quad (6)$$

where the λ_+ parameter is a measure of this extra attraction that the oxygen atom of VO feels due to its modified environment. Since λ_+ and λ_- are both related to the coupling between the hybrids of the intermediate Si atom, we assume that their values are almost the same. This means that the frequency of O_i is expected to downshift by an amount equal to the uppershift of VO frequency when they come together to the $[VO+O_i]$ structure.

Using the forms of Eqs. (2) and (6), we easily get by differentiation the following expression for the bond distance:

$$r_0=\sigma\sqrt{2/(1\mp\lambda_\mp)}. \quad (7)$$

Since the force constant is equal to the second derivative at the equilibrium position, differentiating once again we have

$$(d^2U/dr^2)(r_0)=(4\epsilon/\sigma^2)(1\mp\lambda_\mp)^3. \quad (8)$$

As the vibrational frequency is proportional to the square root of the force constant, we can easily find that the relative frequency shift is

$$\Delta\nu/\nu_0=(1\mp\lambda_\mp)^{3/2}-1, \quad (9)$$

whereas the relative change in the bond length is

$$\Delta r_0/r_0=1/\sqrt{1\mp\lambda_\mp}-1. \quad (10)$$

Substituting the estimated values, $\lambda_\mp=0.075$, in Eq. (9) we get that the frequency shift for the 827-cm^{-1} band of VO is approximately $+95\ cm^{-1}$, whereas for the 1110-cm^{-1} band of O_i it is approximately $-122\ cm^{-1}$. Accordingly, the estimated LVM frequencies of $[VO+O_i]$ are 988 and 922 cm^{-1}. These values compare favorably (within $\pm1\%$) with the experimental frequencies of 1000 and 914 cm^{-1}.

It is interesting also to note that by putting $\lambda_\mp=0.075$ in Eq. (10) we get $(\Delta r_0/r_0)_\mp\approx\mp4\%$. Such a change in bond length is very small and confirms that the geometry of $[VO+O_i]$ is almost the same as that of an O_i and VO defect in close proximity. Moreover, considering that the calibrating factors of O_i ($3.14\times10^{17}\ cm^{-1}$) (Ref. 11) and VO ($6.1\times10^{16}\ cm^{-1}$) (Ref. 12) remain unaffected when they come together to form $[VO+O_i]$, one would expect the absorption amplitude of 914 cm^{-1} related to VO vibration to be stronger than that of the 1000-cm^{-1} line related to O_i vibration, as it is experimentally observed.

Thus calculations of the LVM frequencies of the $[VO+O_i]$ structure are in accord with the experimental findings, posing a strong argument in favor of the assignment of 914- and 1000-cm^{-1} lines to the $[VO+O_i]$ complex. In this line of thinking any other defect that may be correlated with 914- and 1000-cm^{-1} peaks should be considered and discussed. In addition, defect reactions that may involve structures that could be considered as intermediate stages correlated with the two peaks should also be examined. Note that theoretical studies have shown that other defects, as, for example, the $(O_i)_2Si_i$ defect,[13] may produce similar LVM frequencies. Calculations have given two LVM's for $(O_i)_2Si_i$ at 984 and 901 cm^{-1} that are close to our experimental data. As is well known,[14] the O_iSi_i pair is formed upon irradiation and is mobile at room temperature. Not unreasonably, therefore, one could envisage for the $(O_i)_2Si_i$ defect the following formation procedure: $(O_iSi_i)+O_i\rightarrow(O_i)_2Si_i$. However, if 914- and 1000-cm^{-1} bands were related with the $(O_i)_2Si_i$ complex they should have been observed in the spectra immediately after irradiation and not at $\sim250\ ^\circ C$. Similar arguments could be put forward against other defect geometries, such as $(O_i)_2(Si_i)_2$ $[O_iSi_i+O_iSi_i\rightarrow(O_i)_2(Si_i)_2]$ or VO_2Si_i $[VO+O_iSi_i\rightarrow VO_2Si_i]$, for being candidates for the 914- and 1000-cm^{-1} lines.

Notice that a variety of defect morphologies of the general type (V_nO_m) could be formed in the temperature range (250–300 °C) in RT irradiated Cz-Si. Models for these multivacancy-oxygen complexes have been constructed from electron paramagnetic resonance data[15] and some correlations with IR absorption features have been attempted.[16] First, since (V_nO) defects are expected to give rise to one LVM, only $(V_nO_m,\ m\geqslant2)$ structures should be considered. Second, defects with more than two oxygen atoms are expected in general to give rise to more than two LVM's. Moreover, they form[15] above 400 °C. This narrows it down to V_nO_2 complexes. Among them V_2O_2, V_3O_2, and V_4O_2 deserve particular attention. In fact, a LVM at 1000 cm^{-1} has been tentatively attributed[16] to a V_2O_2 defect that is expected to give rise to one LVM caused by two equivalent Si-O-Si bonds. However, in our case we found two LVM's showing the same annealing behavior and therefore most likely originated from the same center. Notice, in addition, that V_2O_2 is created[15] from V_2O by capturing an O_i and V_2O anneals out[15] at the same temperature range as VO. Thus, one could suggest the following reaction process: $V_2O+O_i\rightarrow[V_2O+O_i]\rightarrow V_2O_2$. In this scheme $[V_2O+O_i]$ is considered as an intermediate defect stage prior to the formation of V_2O_2. More specifically, since V_2O is expected to give rise to a LVM near VO, it may be argued that $[V_2O+O_i]$ is, in principle, a potential candidate for the 914- and 1000-cm^{-1} bands. However, according to our calculations the frequency shifts of V_2O and O_i in the $[V_2O+O_i]$ structure are expected to be smaller than those for $[VO+O_i]$, because of the fact that V_2O is more roomy than VO, implying a weaker interaction between the oxygen atoms of V_2O and O_i. Moreover, since V_2O and V_2O_2 have not been detected in our studies, it does not make much sense to discuss correlations of the two bands with an intermediate stage between V_2O and V_2O_2. On the other hand, V_3O_2 also forms[15,17] above 350 °C from V_2O_2 by trapping a vacancy.[15] If the frequency[15] of V_2O_2 is 1000 cm^{-1}, then within the context of the above calculations $[V_2O_2+O_i]$ is not expected to produce LVM's with frequencies at 914 and 1000 cm^{-1}. Additionally, such a center would produce three

LVM's due to the fact that the two oxygen atoms of V_2O_2 in the [$V_2O_2+O_i$] defect would not be equivalent any more. Alternative formation processes of V_3O_2 as, for example, $V_2O+VO \rightarrow V_3O_2$ or/and $V_3O+O_i \rightarrow V_3O_2$ could also be suggested. Since V_2O and V_3O do not have so far well-established LVM frequencies we cannot make any definite correlations between our bands and [V_2O+VO] or [V_3O+O_i] intermediate structures, if such structures could really exist. More particularly, a structure like [V_2O+VO] with V_2O frequency in the region of VO is not expected to give signals at 914 and 1000 cm^{-1}. Also, [V_3O+O_i] is assumed according to our calculations to have smaller frequency shifts than those for [$VO+O_i$] because the oxygen in V_3O is in a more roomy environment than the oxygen in VO and therefore a smaller coupling between the vibrating oxygen atoms is expected. Similar arguments could be invoked for the V_4O_2 (Ref. 17) defect. All these bring it down to the [$VO+O_i$] structure. In other words, the attribution of 914- and 1000-cm^{-1} peaks to [$VO+O_i$] sounds the most likely and acceptable. All the evidence, though circumstantial, points in this direction.

An alternative geometry of the [$VO+O_i$] defect may be that illustrated in Fig. 2(b), where the two oxygen atoms of the structure belong to different bond chains. It is known, however, from the VO_2 defect that shows a frequency shift from VO about +58 cm^{-1}, that the interaction between the two oxygen atoms, which incidentally does not belong to the same chain, is very weak. In the case of Fig. 2(b), where the oxygen-oxygen interaction is expected to be even weaker due to the larger distances, the two vibrational frequencies would be expected to be near those of the isolated O_i and VO centers, contrary to the experimental observations of this work. A geometry like that of Fig. 2(c) for the intermediate state also seems unlikely since the T_d symmetry of the vacant site imposes that the two oxygen atoms arrange themselves in the usual VO_2 configuration.[1]

The phenomenon of the existence of intermediate defect stages could be understood if one uses the concept of an extra barrier that has to be overcome in order that defect partners, when they begin to move, accommodate themselves to the energetically most favorable configuration. In the general case we consider that, besides the energy E_m that the moving partner needs in order to begin to migrate, an additional energy E_a is required for the complex constituents in order to arrange themselves in the final structure. The value of E_a depends on the strength of the interaction potential between the defect components and its origin (i.e., Coulombic or/and strain field). It depends also on their size, their charge states, and perhaps the diffusion mechanism of the moving partners. All these factors may give rise to an E_a value too high to be overcome immediately after the beginning of the migration. If the components of the complex could somehow arrange themselves to form an intermediate structure that thermodynamically is not prohibited, then the creation of a precursor defect becomes feasible. We believe that this is the case of the [$VO+O_i$] structure occurring as the migrating VO center meets an oxygen atom towards the formation of VO_2 defect. Admittedly, the phenomenon is not expected to appear in all reaction processes since E_a may be too small or/and intermediate geometries may not exist. On the other hand, when an intermediate configuration is established it has its own LVM frequencies and annealing behavior. Thus, irrespective of the increase of temperature that makes the immediate conversion VO to VO_2 feasible, the [$VO+O_i$] structure continues to exist. This explains the presence of 914-cm^{-1} and 1000-cm^{-1} peaks in the spectra even after the appearance of the 885-cm^{-1} peak of the VO_2 (Fig. 1). Notice that the zero-point LVM energy ($1000/2+914/2=957$ cm^{-1}) of the [$VO+O_i$] defect lies between the corresponding zero-point energies of the isolated O_i and VO defects ($1110/2+827/2\approx 969$ cm^{-1}) and of the VO_2 center (885 cm^{-1}) as one would expect for an intermediate structure, provided that other contributions to the energy are negligible.

In conclusion, our observations indicate that the transformation process of VO to VO_2 is characterized by a well-defined stage in its development. In this stage a VO pair is placed near an O_i atom and the two components are accommodated to a [$VO+O_i$] structure. This structure has its own properties and behavior. There is convincing evidence that 914- and 1000-cm^{-1} bands should be assigned to the [$VO+O_i$] defect. Theoretical calculations are in accord with such an assignment.

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