New Infrared Bands in Neutron-Irradiated Si

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Abstract
This paper reports Infrared Spectroscopy (IR) studies of defects introduced in Cz-grown Si samples by fast neutron irradiation at room temperature, followed by thermal anneals. Two new Localized Vibrational Modes (LVMs) at 914 and 1000 cm⁻¹ were detected and studied. They were correlated to intermediate defect stages between VO and VO₂ centers. The most strong candidate appears to be a [VO+O₁] structure where a VO pair is trapped near an interstitial oxygen atom. Semiempirical calculations for the frequency shifts of the isolated O₁ and VO centers when they come together to a [VO+O₁] structure are generally in accord with such an assignment. A model for the formation of intermediate stages of defects is also discussed.

Introduction
Oxygen is the main unintentionally added impurity in the silicon material, incorporated interstitially in the lattice. Its interactions with various imperfections in silicon is an important issue of semiconductor technology. Some aspects of this issue, as for example the details of oxygen complexing with lattice vacancies has not yet completely clarified.

Upon irradiation of Cz-grown Si the most dominant defect formed is VO pair [1], where oxygen occupies an off-center substitutional site and in the neutral charge state it gives rise to a LVM at 827 cm⁻¹. Upon annealing around 300°C the amplitude of 827 cm⁻¹ line begins to diminish and another line at 883 cm⁻¹ assigned to VO₂ defect begins to emerge in the spectra. In a recent
paper [2] we have reported the observation of two LVMs at 914 and 1000 cm\(^{-1}\) which were tentatively attributed to an intermediate defect structure [VO+O\(_i\), formed during the transformation process of VO to VO\(_2\) defect. In the present work we further investigate this structure and the formation in general of intermediate defect stages.

**EXPERIMENTAL**

Samples with [O\(_i\)]=1x10\(^{18}\) cm\(^{-3}\) were irradiated by fast neutrons at a dose of \(~1x10^{17}\) n cm\(^{-2}\). The effect of thermal neutrons was eliminated by covering the samples with Cd. 15min isochronal annealings were carried out up to the temperature of 650°C, in ~10 degrees steps, and the IR spectra were recorded at room temperature with a JASCO-IR 700 dispersive spectrometer. Intrinsic absorption was subtracted during scanning by using control samples from Float-Zone material of equal thickness with the Cz-grown ones.

**RESULTS AND DISCUSSION**

Fig 1 exhibits the IR spectra of Si after neutron irradiation and at some characteristic temperatures during the isochronal annealings. As we mentioned previously the 827 cm\(^{-1}\) (fig.1-a) band arises from the VO defect. At about 290°C the band begins to decay and another one at 883 cm\(^{-1}\) begins to emerge (fig.1-c). However, in our spectra, two additional lines at 914 cm\(^{-1}\) and 1000 cm\(^{-1}\) emerge simultaneously at intermediate temperature (fig.1-b), prior to the appearance of the 883 cm\(^{-1}\) band. Traces of both defects appear in the spectra around 260°C. A possible defect that could be correlated with 914 cm\(^{-1}\) and 1000 cm\(^{-1}\) bands is \((O_i)_2Si\), for which a theoretical analysis has forseen two associated LVMs in this range [3]. As it is well known O\(_i\)Si\(_i\) [4] is formed
during irradiation and migrates at room temperature. It can be trapped therefore by an $O_1$ to form $(O_1)_2Si_1$ complex $(O_1Si_1 + O_1 -> (O_1)_2Si_1$). However, such a defect would appear in the spectra at room temperature and not above 260°C. Pomozov et al. [5] have considered 914 and 1000 cm$^{-1}$ lines as intermediate stages in the transformation process of VO to VO$_2$. Noticeably, there is a variety of such defects that could be formed at this temperature range. Among them is for example [VO+V] structure which is likely to form by the attachment of a vacancy near a VO center. Its candidacy however, should be disregarded on the grounds that such a defect is not expected to produce more than one LVM in this frequency range. Another candidate is the [VO+O$_1$] defect [2](fig.3) formed by the trapping of a VO center near an O$_1$ atom. In principle, such a structure is expected to give rise to two vibrational frequencies.

![Fig.2: Suggestive structure for the (VO+O$_1$) intermediate defect.](image)

![Fig.3: Schematic illustration of the formation mechanism of [VO+O$_1$] defect.](image)

The formation mechanism of this defect is phenomenologically depicted in the sketch of (fig.3). The main idea is the following. In order a defect to begin to migrate it has to overcome a potential barrier $E_1$ the magnitude of which depends mainly on the particular defect, its site in the lattice and the crystal environment. However, this energy may not be adequate for the defect to form a complex with another defect. An additional energy ($E=E_2-E_1$) may be needed in order the two partners accommodate themselves in the final
arrangement. In other words an additional barrier may exist, possibly due to Coulomb or/and strain fields, that prevents the immediate complexing of the two defects. If the temperature is not sufficient for this extra barrier to be surpassed, it is likely the defects partners to arrange themselves in an intermediate geometry providing that it is energetically favourable. The resulted structure appears as precursor defect to the VO₂ center forming intermediately during the transformation of VO to VO₂.

Reasonably, 914 cm⁻¹ and 1000 cm⁻¹ modes arise from the VO and O i vibrations respectively, in the [VO+O i] structure. Oxygen interstitial is the less roomy configuration and VO the more roomy one of the oxygen atom in the Si lattice. Therefore, when they come together, oxygen interstitial bonds tend to expand and oxygen bonds in the VO center tend to contract. This means that the force constants of O i in the [VO+O i] structure decrease in comparison with that of the isolated oxygen interstitial atom. Consequently, its vibrational frequency is expected to decrease (here, from 1100 cm⁻¹ to 1000 cm⁻¹). On the other hand the force constants of oxygen atom of the VO center increase resulting in an increase in the vibrational frequency (here, from 827 cm⁻¹ to 914 cm⁻¹). In the following we have tried semiempirical calculations in order to estimate this frequency changes of O i and VO defects when they come together to a [VO+O i] structure.

For the purpose of this analysis is sufficient to consider that oxygen atoms oscillate under the influence of a potential of the type:

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

suitable for representing a homopolar bond [6].

In the case of [VO+O i] structure the above potential for O i take the form:

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

where parameter \( \lambda_\downarrow \) is a measure of the change in the attractive interaction between O i and the neighboring enviroment due to the presence of VO. Respectively, the potential for VO takes the form:

\[ U^\prime(r) = 4 \epsilon \left[ \left( \frac{\sigma}{r} \right)^4 - (1 - \lambda) \left( \frac{\sigma}{r} \right)^2 \right] \] (2)

where \( \lambda_\uparrow \) is a measure of the extra attraction that the oxygen atoms of VO feels due to the presence of O i. The appearance of a modified attractive part
in the above equations comes from the change in the matrix element of the Hamiltonian between the hybrids of the Si atom that bonds with the two oxygen atoms of the [VO+O\textsubscript{i}] structure. This matrix element is related to the metallic energy [6] that was used to correct the bond orbital approximation [7,8]. The potential that this Si atom is subjected, could be expressed in a form:

\[ U(r)=2V_2\left[\left(\frac{\alpha}{r}\right)^4-(1-\zeta)\left(\frac{\alpha}{r}\right)^2\right] \]

where \( V_2 \) is the covalent energy [7] and \( \zeta \) is a parameter that measures the effect of its environment. For such a potential we get a binding energy \( E_b=V_2(1-\zeta)^2 \). However, this \( E_b \) has the expression \( E_b=V_2(1-a_m) \) [7] where \( a_m \) is the metallicity of the Si atom. The value of \( a_m \) is taken as \( a_m=(3\times0.81+1\times0.4)/4 \) because Si atom is surrounded by three other Si atoms and one oxygen atom. We have corrected the metallicity value of 0.81 of the Si atom in the pure Si lattice, assuming an average metallicity due to the presence of the oxygen atom. In this approximation oxygen effect has been simulated by that of carbon, on the grounds that both atoms belong to the same period of the periodic table. On the other hand, the presence of VO modifies the metallicity of this Si atom to a new value \( a_m=(2\times0.81+2\times0.4)/4 \) because now a Si atom is replaced by an oxygen atom. This new \( a_m \) value corresponds to a new \( \zeta' \) value. The difference in metallicities leads to a difference in \( \zeta' \)s, that is

\[ \zeta-\zeta'=(1-\frac{1}{1-0.71})-(1-\frac{1}{1-0.6})=0.094 \]

Apparently, \( \zeta-\zeta' \) is related to \( \lambda_\pm \), since the latter expresses the difference in the attractive part of the potential between O\textsubscript{i} and its neighboring Si atoms before and after the formation of [VO+O\textsubscript{i}]. Noticeably, the actual value of \( \lambda_\pm \) should be taken as half of this value, i.e. \( \lambda_\pm=0.05 \), since O\textsubscript{i} bonds directly with two silicon atoms. In a similar way of thinking we can estimate \( \lambda_\mp \). Using the experimental frequencies of [VO+O] as well as the well known frequencies of the isolated VO and O\textsubscript{i}, parameters \( \lambda_\pm \) are obtained from equation \( \frac{\Delta\nu}{\nu_0}=(1+\frac{1}{\lambda_\pm})^{3/2}-1 \), which gives the frequency shift. This formula is easily derived by taking into account that the vibrational frequency is proportional to the square root of the force constant. The latter is the second derivative of the potential, at the equilibrium position. The values we get are \( \lambda_\pm=0.07 \). This result is consistent with the estimating value of \( \lambda_\pm=0.05 \).
CONCLUSIONS

We have observed two new bands at 914cm$^{-1}$ and 1000cm$^{-1}$ in the IR spectra of neutron irradiated Cz-grown Si. These bands were assigned to a [VO+O$_i$] structure which is considered as an intermediate defect stage in the transformation process of VO to VO$_2$. Prerequisites for the formation of such stages is the presence of an extra barrier that prevents the immediate complexing of the defect components and the existence of a geometrical configuration which is energetically feasible, where they accommodate themselves prior to the final arrangement. Semiempirical calculations of the frequency shifts of O$_i$ and VO defects in the [VO+O$_i$] structure agree fairly well with the experimental observations.

REFERENCES