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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 1000cm^{-1} were detected and studied. They were correlated to intermediate defect stages between VO and VO_2 centers. The most strong candidate appears to be a [VO+O_i] structure where a VO pair is trapped near an interstitial oxygen atom. Semiempirical calculations for the frequency shifts of the isolated O_i and VO centers when they come together to a [VO+O_i] structure are generally in accord with such an assignement. A model for the formation of intermadiate 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 827cm^{-1}. Upon annealing around 300°C the amplitude of 827cm^{-1} line begins to diminish and another line at 883cm^{-1} assigned to VO_2 defect begins to emerge in the spectra. In a recent

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paper [2] we have reported the observation of two LVMs at 914 and 1000cm^{-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 [Oi]=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 substructed 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 827cm^{-1} (fig.1-a) band arises from the VO defect. At about 290°C the band begins to decay and another one at 883cm^{-1} begins to emerge (fig.1-c). However, in our spectra, two additional lines at 914cm^{-1} and 1000cm^{-1} emerge simultaneously at intermadiate temperature (fig.1-b), prior to the appearance of the 883cm^{-1} band. Traces of both defects appear in the spectra around 260°C. A possible defect that could be correlated with 914cm^{-1} and 1000cm^{-1} bands is $(O_i)_2Si_i$ for which a theoretical analysis has forseen two associated LVMs in this range [3]. As it is well known O_iSi_i[4] is formed

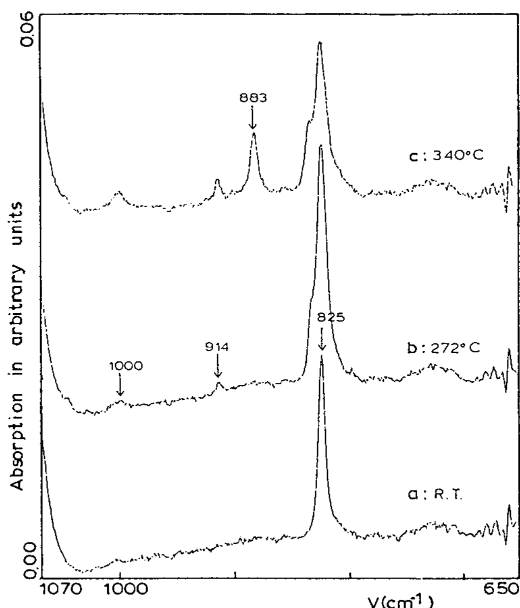

Fig.1:IR spectra of neutron irradiated Silicon at selective temperatures in a 15min isochronal annealing sequence.

during irradiation and migrates at room temperature. It can be trapped therefore by an O_i to form $(O_i)_2Si_i$ complex $(O_iSi_i+O_i \longrightarrow (O_i)_2Si_i)$. However, such a defect would appear in the spectra at room temperature and not above 260°C. Pomozov et.al. [5] have concidered 914 and $1000cm^{-1}$ 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 $[VO+O_i]$ defect [2](fig.2) formed by the trapping of a VO center near an O_i atom. In principle, such a structure is expected to give rise to two vibrational frequencies.

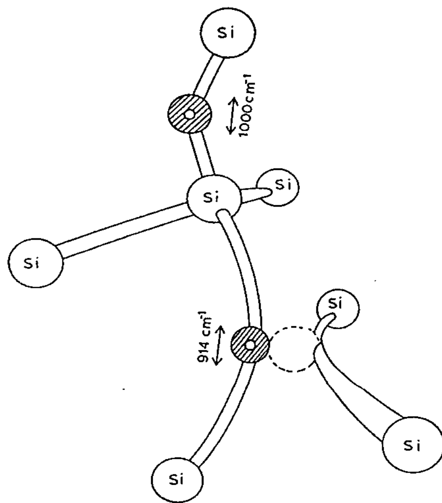

Fig.2: Suggestive structure for the $[VO+O_i]$ intermediate defect.

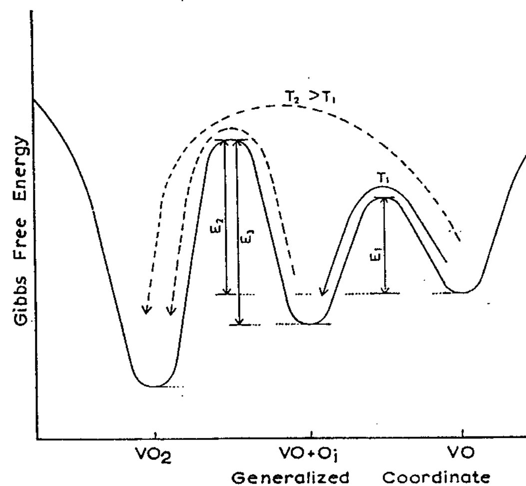

Fig.3: Schematic illustration of the formation mechanism of $[VO+O_i]$ defect

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 enviroment. 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 final complex. In this sense [VO+O_i] is a precursor defect state to the VO_2 center forming intermediately during the transformation of VO to VO_2.

Reasonably, 914cm^{-1} and 1000cm^{-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 1100cm^{-1} to 1000cm^{-1}). On the other hand the force constants of oxygen atom of the VO center increase resulting in a increase in the vibrational frequency (here, from 827cm^{-1} to 914cm^{-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:

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

suitable for representing a homopolar bond [6].
In the case of [VO+O_i] structure the above potential for O_i take the form:

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

where parameter λ_- 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:

$$U'(r)=4\varepsilon'\left[\left(\frac{\sigma}{r}\right)^4-(1-\lambda_+)\left(\frac{\sigma}{r}\right)^2\right] \qquad (2)$$

where λ_+ is a measure of the extra attraction that the oxygen atoms of VO feels due to the presence of O_i. The appearence 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 $[VO+O_i]$ structure. This marix element is related to the metalic 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:

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

where V_2 is the covalent energy [7] and ζ is a parameter that measures the effect of its enviroment. 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 $a_m=(3*0.81+1*0.4)/4$ 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 $a_m'=(2*0.81+2*0.4)/4$ because now a Si atom is replaced by an oxygen atom. This new a_m' value corresponds to a new ζ' value. The difference in metallicities leads to a difference in ζ's, that is

$$\zeta-\zeta'=(1-\sqrt{1-0.71})-(1-\sqrt{1-0.6})\cong0.094$$

Apparrently, $\zeta-\zeta'$ is related to λ_-, since the later expresses the difference in the attractive part of the potential between O_i and its neighboring Si atoms before and after the formation of $[VO+O_i]$. Noticeably, the actual value of λ_- should be taken as half of this value, i.e. $\lambda_-\cong0.05$, since O_i bonds directly with two silicon atoms. In a similar way of thinking we can estimate λ_+. Using the experimental frequencies of $[VO+O_i]$ as well as the well known frequencies of the isolated VO and O_i, parameters $\lambda_\mp$ are obtained from equation $\frac{\Delta\nu}{\nu_o}=(1\mp\lambda_\mp)^{3/2}-1$, which gives the frequency shift. This formula is easily derived by taking into account that the vibrational frequency is propotional 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 $\lambda_\mp\cong0.07$. This result in consistent with the estimating value of $\lambda_\mp\cong0.05$

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 combonents and the existence of a geometrical configuration which is energetically feasible, where they accommodiate 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 experimemtal observations.

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