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CORRELATIONS OF VIBRATIONAL FREQUENCIES WITH VO_4 DEFECT IN IRRADIATED SILICON

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SUMMARY

This paper reports Infrared spectroscopy studies on oxygen related defects in Czochralsky grown neutron irradiated Silicon material subsequently submitted to heat treatment. The sequential formation of various VO_n *(n=1,2,3,4) defects according to the reaction process* $VO \rightarrow VO_2 \rightarrow VO_3 \rightarrow VO_4$ *is investigated. We argue that on increasing the annealing temperature different sites for the addition of oxygen atoms become available, triggering for n>2 two parallel formation sequencies in relation with* VO_3 *and* VO_4 *defects. Thus in the first sequence the oxygen atoms are added in adjacent sites to* VO_2 *defect although in the second sequence the oxygen atoms are added in the same vacant site of* VO_2 *defect.*

1. Introduction

The VO pair is the main defect in Cz-grown irradiated silicon giving rise to an infrared band around 830cm^{-1}. On annealing, the defect signal begins to decay at ~300°C and another signal at 885cm^{-1} begins to arise in the spectra attributed to VO_2 defect /1/. On further annealing at ~450°C three bands /1/ at 904, 968 and 1000cm^{-1} begin to emerge in the spectra as VO_2 signal diminishes. These bands were attributed to a VO_3 center when a oxygen atom is added in an adjacent site to VO_2 center. At a slightly higher temperature another peak appears at ~984cm^{-1}, tentatively attributed /2/ to a modified VO_3 defect. At about 550°C the peaks related to VO_3 and VO_3 modified center anneal out and two other peaks at 983 and 1004cm^{-1} appear in the IR spectra /3/ of oxygen implanted silicon. These peaks have been attributed to a VO_4 $[VO_2+2O_i]$ structure when an additional Oi is trapped by VO_3 $[VO_2+O_i]$ defect. Remarkably, two other peaks at 1032 and 1043cm^{-1} have also been attributed /4/ to this VO_4 $[VO_2+2O_i]$ defect from results in neutron irradiated Silicon. In this work theoritical calculations for the vibrational frequencies. of VO_4 $[VO_2+2O_i]$ defect are attempted. The main object of the paper is to make the correct band assignment in regard to VO_4 defect.

2. Experimental details

Oxygen-rich samples produced by the Czochralski technique with initial oxygen concentration $[O_i]_o$~10^{18}cm^{-3} where irradiated by fast neutrons at temperatures not exceeded 50°C. After that, the samples were submitted to thermal treatment by isochronal anneals of 15min duration and ~10 degrees steps. Optical absorption measurements of the Localized Vibrational Modes of the various defects were conducted with a JASCO IR-700 double beam dispersive spectrometer.

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3. Experimental results and discussion

Fig.1 gives the evolutions with temperature of the VO_3, VO_4 defects. The experimental values for the various peaks as appeared in our studies /4/ are indicated in the figure. Oxygen interstitial 9μ line was detected at ~1100cm^{-1}. In the following we shall focus our attention to VO_4 defect.

VO_4 defect

In a previous work /5/ we studied the effect caused in the LVM ferquency due to the attachment of an O_i atom next to the Si-O-Si unit of the VO defect. In that investigation the change in the LVM frequency was estimated in terms of the change in the metallicity /6/ of the Si atom that bonds with both O atoms in the formed Si-O_i-Si-O-Si chain, where O_i is the initial oxygen interstitial atom in the Si-O_i-Si subunit and O the attached to the vacancy atom to form the chain. We reached to the conclusion /5/ that the relative frequency shift is given by the following expression

$$\frac{\Delta\nu}{\nu_0} = \left(1 \mp \lambda_{\mp}\right)^{\frac{3}{2}} - 1 \qquad (1)$$

where ν_0 is the LVM frequency of the undistorted Si-O-Si unit and $\lambda_{\mp}$ is a measure of the modification of the attractive interaction between each oxygen atom (λ_- for O_i , λ_+ for O) in the Si-O_i-Si-O-Si chain and its neighboring Si atoms. In this investigation we shall further apply the above model in an attempt to evaluate the LVM frequencies of VO_3 and VO_4 defects. In our studies VO_3 defect, begins to manifest its presence in the spectra at about 450°C. In the VO_2 structure the two oxygen atoms are equivalent and the defect gives rise only to one LVM frequency (883cm^{-1}). When the additional O_i atom joins VO_2 unit form VO_3 (VO_2+O_i) structure, Fig.2, it renders the three O atoms inequivalent resulting in three LVM frequencies (899, 962, 993cm^{-1}). At a slightly higher temperature (~470°C), as compared with that of the appearence of the three bands of VO_3 defect (~440°C), another band at 978cm^{-1} (986cm^{-1} in

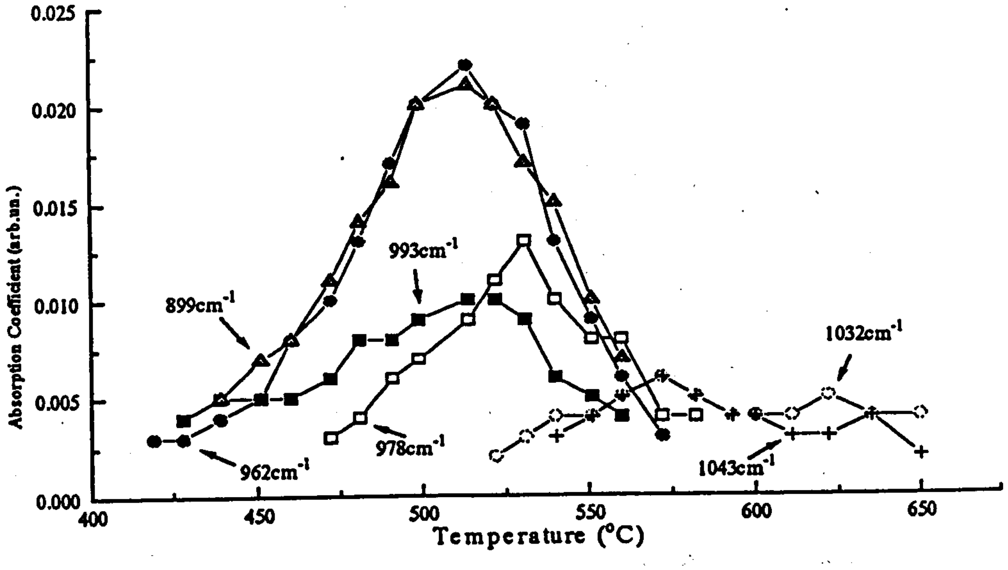

Fig.1: The evolution with temperature of VO_3 and VO_4 bands

ref.2) emerges in our spectra fig.1. This band has been previously tentatively attributed to a modified VO_3 structure /2/ with one more oxygen atom attached. Another possibility is that in which the three oxygen atoms arrange themselves around the vacant site (fig.2). Such a structure has a special interest for this work, in relation with the accumulation of oxygen atoms and the possibility of various kinds of VO_4 defect and the processes of its formation, as discussed below.

The decay of VO_3 bands in our spectra was accompanied by the emergence of two bands at 1032 and $1043cm^{-1}$ respectively. Within the lines of Corbett et al.'s model /1/ , VO_4 defect is expected to form as a result of the attachment of an O_i atom to VO_3 center ($VO_2+2O_i \rightarrow VO_4$) fig.2. The attachment of another oxygen atom in the other leg of VO_3 defect renders the structure symmetric again. Thus, the two oxygen atoms O_2, O_3 become again equivalent . O_1 and O_4 atoms are also equivalent. Apparently, two LVMs are expected from this structure. Again atoms O_3 and O_4 as well as O_1 and O_2, belong to a Si-O_i-Si-O-Si chain . According to eq.(1), the LVM frequencies obtained for the VO_4 defect are expected to have the following values:

$$\nu_1^{VO_4} = \nu_3^{VO_3}(1-\lambda_+)^{\frac{3}{2}} = 899cm^{-1}(1-\lambda_+)^{\frac{3}{2}} = 1002cm^{-1}$$

$$\nu_2^{VO_4} = \nu^{O_i}(1-\lambda_-)^{\frac{3}{2}} = 1100cm^{-1}(1-\lambda_-)^{\frac{3}{2}} = 984cm^{-1}$$

Moticeably, these values are quite different from our experimental findings but in very good agreement with the valus 1004 and $983cm^{-1}$ found by Stein /3/ for VO_4 structure in oxygen implanted silicon. There is a possibility that the two bands reported by Stein to be related with O^{18} isotope oxygen in VO_4 structure. Actually the application of the isotope effect formula

$$\nu_{O_{16}} = \nu_{O_{18}}\sqrt{\frac{m_{O_{18}}}{m_{O_{16}}}} \qquad (2)$$

for 983 and $1004cm^{-1}$ bands leads to the values 1043 and $1065cm^{-1}$ respectively which are close to our experimental values for VO_4 defect. Disregarding this likehood, a question raises: which is the defect that gives rise to 1032 and $1043cm^{-1}$ bands? There is a possibility that these bands originate from a VO_4-modified defect which forms when $978m^{-1}$ band of VO_3-modified defect dies out.

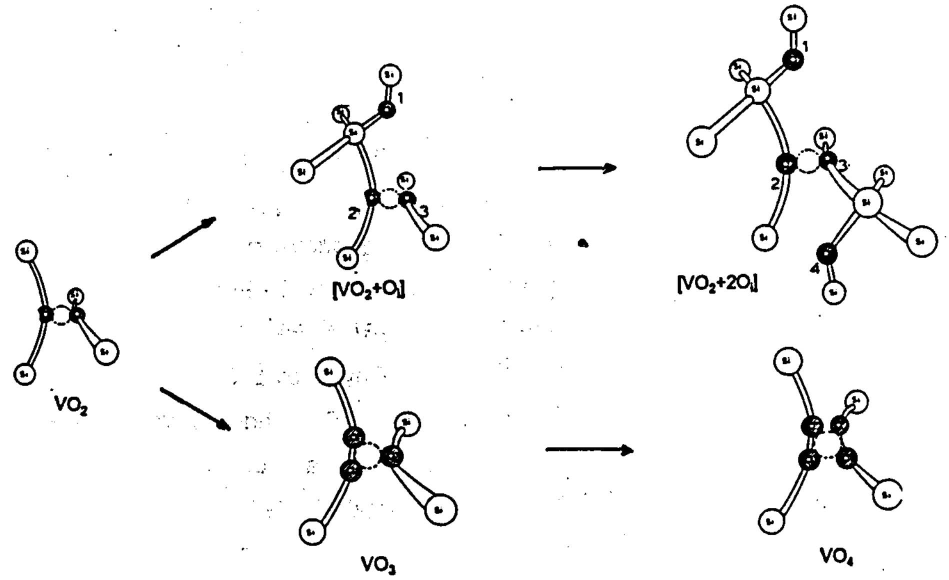

Fig.2: The two suggested parallel formation processes for VO_3,VO_4 structures.

Such a defect may have a structure similar to that previously discussed by Chadi /7/ where four oxygen atoms arrange themselves around a vacant site. Then two parallel reaction processes for the formation of VO_3, VO_4 defect could be envisaged. VO_3, VO_4 defects form from VO_2 defect i) by the addition of oxygen atoms next to silicon atoms arround VO_2 defect i.e. $VO_2 \rightarrow [VO_2+O_i] \rightarrow [VO_2+2O_i]$ and ii) by the addition of oxygen atoms in the region of the vacant site where the initial two oxygen atoms are positioned i.e. $VO_2 \rightarrow VO_3 \rightarrow VO_4$, with the later reaction sequence pending further experimental verification. Reaction (ii) is expected to occur at higher temperatures assuming that the energy barrier that has to be overcome for the formation of VO_3 and VO_4 geometries is larger than that of $[VO_2+O_i]$ and $[VO_2+2O_i]$ geometries respectively. Furthemore, $[VO_2+2O_i]$ bands (983 and 1004cm^{-1}) are most possibly very weak, and could be seen only in oxygen implanted silicon where oxygen content is increased due to the ion implantation. The bands at 1032 and 1043cm^{-1} may be more favourable to appear in neutron irradiated Si.

4. CONCLUSIONS

In this paper we have studied VO_3 and VO_4 defects in Silicon. Experimental values of the LVM frequencies of two bands of VO_3 defect at 962 and 993cm^{-1} are in agreement with our semiempirical calculations for the evaluation of the vibrational freqencies. Our calculations for the LVM of VO_4 defect support the assignement of two bands at 983 and 1004cm^{-1}, previous correlated by Stein /3/ with this defect, in oxygen implanted silicon. In our experiments however, in neutron irradiated silicon, we found two bands at 1032 and 1043cm^{-1} to arise in the spectra when VO_3 bands decay. Defect structures that could be correlated with these two bands were discussed. Two parallel reaction sequences in the oxygen accumulations processes in relation with VO_4 defect were envisaged

i) $VO \rightarrow VO_2 \rightarrow [VO_2+O_i] \rightarrow [VO_2+2O_i]$

ii) $VO \rightarrow VO_2 \rightarrow VO_3 \rightarrow VO_4$.

In the latter case all oxygen atoms share the same vacant site. Further experiments by various techniques are needed in order to verify our suggestions.

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