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An IR Study of the Annealing Behaviour of A-Center in Silicon

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Abstract. The current understanding of the vacancy-oxygen (VO) pair, the so-called A-center in silicon is more than satisfactory. However, the annealing behaviour of the center exhibits some features which need proper explanation in order that the whole picture for the defect becomes more clear. To this end, we investigated the evolution of the infrared signal of the center (828cm^{-1} LVM band) created in Cz-grown Si by neutron irradiation, as a function of the heat treatment. The amplitude of the band appears to be stable up to 200°C where it begins to increase reaching a maximum value at ~280°C and then begins to decrease rapidly up to ~400°C, although a small portion of it lingers in the spectra up to 550°C. The inverse annealing stage (200-280°C), the mechanisms and the annealing kinetics of the defect as it decay out (300-400°C) and the stabilization of the defect signal (400-500°C) are the main points which concern the present investigation. After completing the annealing sequence and re-irradiating the material, the inverse annealing stage is absent. This led us to surmise the presence of an unknown defect (X-defect) which compete with O_i in capturing vacancies. The stabilization of the 828cm^{-1} band amplitude above 400°C has been tentatively ascribed to the trapping of a number of A-centers near disordered regions or large defects. This fact results to a larger binding energy of the corresponding defects.

Introduction. Understanding defects has become one of the highest priority fields in Semiconductor Physics and Technology. Information concerning the microscopic origin and their macroscopic appearance and behaviour is very important for the purpose of defect control and consequently for improving the device performance.

Silicon is the basic material in the current stage of electronic technology. Wafers grown by the Czochralski (Cz) pulling technique contain oxygen impurities in a concentration close to 10^{18}cm^{-3}. One of the most interesting aspects of oxygen defect in Si is its tendency to cluster and to form complexes with lattice defects and impurities thus altering the electrical and optical properties of the crystal. Apparently the exact knowledge of these defects and their properties is of paramount significance in Si technology. Important among oxygen defects is its complexing with the lattice vacancy to form the VO pair.

VO pair is a well known fingerprint of any kind of irradiation of Cz-grown Si. It is a quasi-Os defect manifesting its presence in the Infrared spectra with a Localized Vibrational Mode (LVM) band at about 828cm^{-1}, in the neutral charge state [1]. Although a lot of information has been gathered about its structure, its electronic and optical properties, etc, there are some aspects in its annealing behaviour that are not fully understood. It is therefore reasonable to investigate this behaviour and the aim of the present work is to elucidate certains points concerning the evolution of A-center as a function of the heat treatment. Various explanations are considered and discussed.

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Experimental Details. Cz grown Si samples, not subjected to any postgrowth heat treatment, with typical dimensions of 20x12x2 mm were used. Their initial oxygen concentration [O_i] was $1.2x10^{18}cm^3$ as it was found by measurements of the 9μ absorption band according to the relevant ASTM procedures [2]. Fast neutrons irradiations were done inside a water pool at 40°C, at a dose of $6.5x10^{16}$ $n.cm^{-2}$. The samples were wrapped in Cadmium foils to eliminate thermal neutrons and were put inside quartz amboules to avoid water contamination. 15 minute isochronal anneals in ~10°C increaments, over the range R.T.-700°C, were performed in open furnaces. Measurements were carried out at R.T. with a JASCO-IR 700 double beam dispersive spectrometer. The two phonon absorption was always substracted by using reference samples from FZ material of equal thickness.

Experimental Results and Discussion. Fig.1a exhibits the evolution with temperature of VO band of silicon appearing in our infrared spectra after irradiation and located at $828cm^{-1}$. As it is seen at a first glance, the strength of the band increases from ~200°C onwards up to ~280°C. From ~300°C onwards the band signal diminishes rapidly up to ~400°C but it does not die out. Above 400°C the band somehow stabilizes with small fluctuations in its amplitude and maintain its presence in the spectra up to ~550°C.

In the first place we shall try to explain the gradual enhancement of A-center amplitude in the temperature range of 200-280°C. The increase of A-center signal could reasonably be attributed to the formation of additional VO pairs as a result of vacancy production; these vacancies are readily captured by oxygen atoms. Notice that oxygen concentration decreases during this stage. A source of the additional vacancies may be large defect clusters [3] usually formed in neutron irradiated Silicon. At elevated temperatures these clusters liberate vacancies which are subsequently trapped by oxygen atoms. On the other hand, divacancies which are partially dissociated at these temperatures could also be considered as potential vacancy sources.

At about 700°C all the signals from the various V_nO_m defects were gone, in agreement with previous reports in the literature [1]. As a next step, these samples were irradiated again under exactly the same conditions and the isochronal annealing routine was repeated. Fig.1b represents the evolution curve of VO defect in this case.. The increase of VO signal in the temperature range of 200-280°C has disappeared. That is an indication that additional A-centers were not formed. Oxygen concentration in this temperature range shows generally a tendency to decrease but in a much slighter fashion in comparison with the corresponding change in Fig.1a. In an attempt to explain this behaviour we notice at first that the re-irradiated material after finishing the first annealing sequence is not exactly the same as the initial one. The following arguments could be invoked to corroborate this aspect:

i) oxygen precipitation occurs at the later stages of the anneals.
ii) some of the defects that disappear from the spectra may go irreversibly to some unseen configurations. This does not mean that they do not exist.
iii) also, at the higher temperatures large clusters of defects or mixture of point defects with extensive defects are formed. Such configurations may be infrared inactive and therefore they pass undetected in the spectra.

It is difficult to resist the notion that some kind of defects (we label them as X-defects) exist at the end of the first annealing sequence [4]. Apparently, these X-defects have the tendency to trap vacancies. After the re-irradiations, while increasing the annealing temperature, they reconstruct and in the range (200-280°C) they compete with oxygen in trapping the additional vacancies. This may explain the absence in the increase of A-center signal.

X-defects are expected to be destroyed at higher temperatures. After completion the second annealing sequence the samples were submitted [4] to a heat treatment at 900°C for 30min. Then, they were irradiated for a third time and the same annealing sequence was

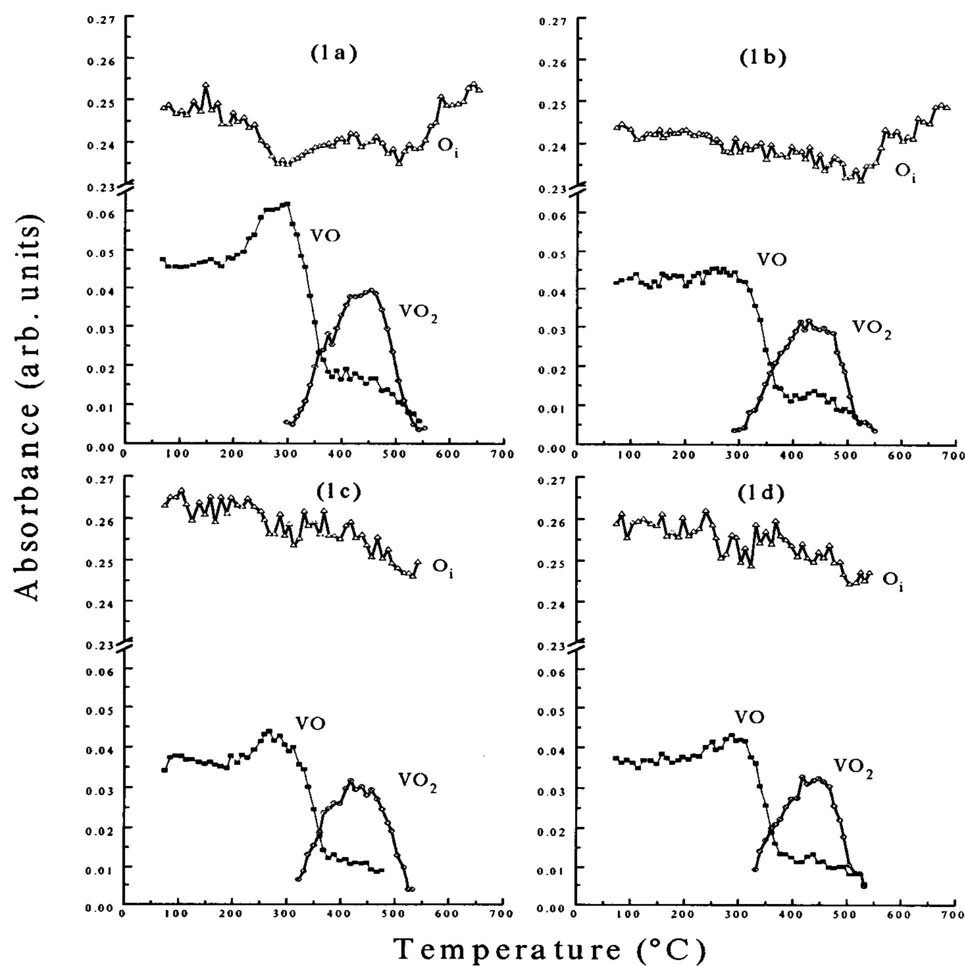

Fig. 1a: The evolution of VO center after initial irradiation .
Fig. 1b: The evolution of VO center after completion the annealing sequence described in Fig. 1a and re-irradiation.
Fig. 1c: The evolution of VO center after completion the annealing sequence described in Fig. 1b, then carrying out a heat treatment at 900°C for 30 min and then re-irradiation
Fig. 1d: The evolution of VO center after an initial heat treatment at 600°C for 5h and irradiation.
In all the Figures the evolutions of Oi and VO_2 are also presented.

carried out. The corresponding evolution curve is demonstrated in Fig.1c. The inverse annealing stage has now reappeared although the increase in VO is less than that in Fig.1a. This is an indication that the (900°C, 30min.) heat treatment was not adequate to destroy all the X-defects. It is also possible that the increase of VO in the (200-280°C) temperature range may be related [5] to two processes occuring in parralel and the above heat treatment has neutralize only the one of them.

Another question pertiment to the above problem concerns the effect of a pre-irradiation heat treatment on the evolution curve of A-center. Fig.1d exhibits the corresponding behaviour of a silicon sample of the same initial oxygen concentration which was subjected to an initial heat treatment at 600°C for 5h and then submitted to the same neutron irradiation and annealing procedure. The inverse annealing stage at (200-280°C) of A-center in this case manifests its presence with minor strength than that of fig.1a. Similar conclusions to that drawn for the procedure leading to fig.1c could again be derived.

From 300°C onwards VO signal decreases rapidly. The data fit with a second order kinetics and a possible reaction process is $VO+Si_i \rightarrow Oi$, where Si_i are liberated [3] from defect clusters. This fact is corroborated by the observed increase of Oi concentration. The decay of VO is accompanied in the spectra by the growth of a band at 887cm^{-1} generally attributed [1] to VO_2 defect. A possible process is $VO+O_i \rightarrow VO_2$ which is a first order reaction (since $[O_i]>>[VO]$). Another posibility is $VO+VO \rightarrow VO_2+V$ reaction, which has been tentatively suggested previously [6]. This is apparently a second order process. In table (I) we register activation energies E_1 and E_2 refering either to a combination of reaction (a) and reaction (b) or of reaction (a) and reaction (c) for the decay of VO and the growth of VO_2 defects respectively. Table (II) is the corresponding of table (I) for the re-irradiated materials. The decay of VO again follows a second order process. However, reaction $VO+Si_i \rightarrow O_i$ cannot been invoked in this case, since O_i concentration is not increased in this temperature range. In the first case we concider a combination of reactions $VO+VO \rightarrow VO_2+V$ and $VO+O_i \rightarrow VO_2$. In the second case reaction $VO+VO \rightarrow VO_2+V$ is considered to account for the whole phenomenon (the left side of reaction refers to the decay of VO and the right side to the growth of VO_2).

Table I: *Activation energies for VO decay and VO_2 growth in neutron irradiated Si.*

Case	*Activation* energy	*correlation* coefficient
(I)		
$VO+Si_i \rightarrow O_i$ (a)	$E_1=(1.63\pm0.22)$eV	$r_1=0.919$
$VO+O_i \rightarrow VO_2$ (b)	$E_2=(1.36\pm0.22)$eV	$r_2=0.950$
(II)		
$VO+Si_i \rightarrow O_i$	$E_1=(1.63\pm0.22)$eV	$r_1=0.919$
$VO+VO \rightarrow VO_2+V$ (c)	$E_2=(1.95\pm0.23)$eV	$r_2=0.950$

Table II: *Activation energies for VO decay and VO_2 growth in neutron re-irradiated Si.*

Case	*Activation energy*	*correlation coefficient*
(I)		
$VO+VO \rightarrow VO_2+V$	$E_1=(1.90\pm0.23)$eV	$r_1=0.945$
$VO+O_i \rightarrow VO_2$	$E_2=(1.27\pm0.24)$eV	$r_2=0.870$
(II)		
$VO+VO \rightarrow VO_2+V$	$E_2=(1.93\pm0.23)$eV	$r_2=0.944$

The activation energy E_2=1.36eV (table I) which was estimated from the data fitting in case (I) cannot be an acceptable value for the movement of A-centers, although the trapping of VO by Oi atoms is reasonably expected. The activation energy E_2=1.95eV estimated from the data fitting in case (II) is an acceptable value although reaction (c) has not been so far experimentaly verified. More probable would be a combination of reactions (a), (b) and (c) which could describe the phenomenon in a more complete fashion. Similar arguments could be put forward for the re-irradiated material (table II) and case II gives more acceptable values for the activation energies.

As it is seen from the Fig.1a and Fig.1b the amplitude of VO decreases rapidly in the range 300-400°C, but it does not die out. It stabilizes at low values around 10% of the maximum amplitude and preserves its presence in the spectra up to ~550°C with small fluctuations. This behaviour may be considered as the manifestation of the existence of two involved opposite processes; the first one is related to the destruction of VO pairs and the second with the generation of new VO pairs. If the two rates of destruction and regeneration are of the same value they counterbalance each other. Therefore an almost stable number of A-centers survives, as it is indicated by the stable amplitude of the defect. In this way of thinking, it may be argued that vacancies liberated from defect clusters while increasing the temperature, will lead to the formation of A-centers compensating for their destruction due to the anneals.

An alternative explanation may be the following. Although A-centers are in general isolated defects, a number of them especially in neutron irradiated material may be trapped near larger defects. Due to the increased elastic stresses in the vicinity of such defects the binding energy of VO becomes larger, which in effect enhance the thermal stability of the trapped A-centers. In such a situation the annealing temperature of the defect is increased. Notice that in DLTS studies [7] of the E_c-0.18eV A-center peak in electron irradiated material the defect disappears around 400°C without showing any further stabilization of its signal. This behaviour might indicate that, either in this kind of irradiation A-centers are not trapped near larger defects or that if some of them are trapped, they become electrically inactive and they are not seen in the DLTS spectra. On the other hand it appears that these special A-centers undergo only slight changes in their structure and therefore their LVM band is not shifted from the initial A-band signal to be detected separetely in the IR spectra.

Conclusions. The evolution of VO center as a function of heat treatment has been studied. An inverse annealing stage in the temperature region 200-280°C has been attributed to the capturing of additional vacancies liberated from defect clusters by isolated oxygen atoms. The existence of an unspecified defect cluster (X-defect) has been invoked to explain the absence of the inverse annealing stage in the re-irradiated material. There may be a problem however that remains in terms of the existence of one or two sources that contribute in parallel, to the production of the inverse stage. The annealing kinetcs of VO has been investigated and activation energies have been derived. A stabilization of VO signal in the infrared spectra up to ~550°C has been tentatively attributed to the trapping of some of the VO pairs in the vicinity of larger defects thus increasing the thermal stability of the A-centers.

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