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# A Study of the Conversion of the VO to the $VO_2$ Defect in Heat-Treated Silicon under Stress

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## Abstract

We report infrared studies concerning the annealing behavior of the VO defect in neutron irradiated Cz-grown Si. The VO center is the major radiation-induced defect in oxygen-rich Si. Upon annealing of the IR band at 829 $cm^{-1}$ related to the VO defect, another band at 890 $cm^{-1}$ generally attributed to the $VO_2$ center emerges in the IR spectra. The purpose of this work is to study the conversion of the VO to the $VO_2$ defect on samples subjected to various combinations of high temperature-high pressure (HT-HP) treatments prior to irradiation. The observed differences in the annealing behavior are discussed by considering the two main reactions $VO+Si_I \rightarrow O_i$ and $VO+O_i \rightarrow VO_2$, taking place in parallel during the process. The contribution of each reaction to the whole annealing process is discussed by taking into account that the state of the self-interstitials, adjacent to precipitates due to the HT-HP treatment, is different for each sample because of the different treatments. Otherwise, the contribution of each one of the two reactions in the annealing of the VO defects is different in each sample due to the different HT-HP pre-treatment they were subjected to.

## Introduction

A-centers are created as the dominant defects in Czochralski silicon, Cz-Si, by any kind of irradiation. The main reason is that the silicon monovacancies,V, produced by irradiation, are mobile at room temperature and, besides annihilation by silicon interstitials or by pairing with each other to produce divacancies, $V_2$, are trapped by interstitial oxygen atoms ,$O_i$, to form vacancy-oxygen pairs, VO, the well-known A-centers. The presence of such pairs in Cz-Si is manifested by an infrared absorption band at 828 $cm^{-1}$ . They are stable up to ~300° C. Annealing at this temperature results in decreasing the intensity of the 828 $cm^{-1}$ band and in revealing of another absorption band at 890 $cm^{-1}$, generally attributed to the $VO_2$ defect [1,2]. Other defects are also formed at these temperatures [3].

It is well-established that heat treatments of silicon at various temperatures leads to the formation [4,5] of thermal donors, oxygen precipitates and various structural defects as, for example, rod-like defects, dislocations, stacking faults etc. Apparently, the presence of these defects is expected to affect the annealing behavior of radiation-induced defects. Concerning the VO defect, investigations [6] of its behavior have shown substantial changes in the annealing temperature of this center. It has been concluded that oxygen-related precipitates and structural defects, which can trap and release vacancies and self-interstitials, have a profound effect in the annealing temperature of the A-centers. Note that the clustering and precipitation of oxygen in silicon is accompanied [7] by the emission of self-interstitials which are expected [8] to aggregate adjacent to the precipitates. On the other hand, the application of hydrostatic stress can induce [9] changes in the defect structure. More specifically, uniform stress applied at various temperatures has [10] significant influence in the precipitates and

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the structural defects in general. It is therefore expected that treatments of Si crystals under various combinations of high temperature-high pressure would affect the annealing behavior of the VO defect. The study of this phenomenon is the main object in this work.

## Experimental details

Six samples cut from a 2mm thick, 001 oriented wafer, were used. Their initial oxygen concentration was $[O_i]_o \sim 8.3x10^{17}$ $cm^{-3}$. The samples were subjected to various combinations of HT-HP treatments as shown in Table I and then irradiated by fast neutrons to a fluence of $\sim 1x10^{17}$ $cm^{-2}$, at $T \approx 50°C$. Afterwards they were subjected to a heat treatment at 220 °C for 150 min aiming at a complete annealing of the large cluster of defects and disordered regions, present in neutron-irradiated material. As it is expected[3] this process resulted in changes in the VO and $[O_i]$ intensities due to the liberation of vacancies which react with oxygen atoms to form additional VO centers. The establishing values of $O_i$ and VO intensities after this process are also shown in Table I. Finally, the samples were subjected to a heat treatment at 400°C , for 4 h, for the purpose of complete conversion of the VO to the $VO_2$ defects. Infrared spectra were taken at room temperature by a dispersive kind of spectrometer.

**Table I.** The oxygen interstitial concentration, the $N_{VO}$ and the $N_{VO_2}$ intensities and the intesity ratio $N_{VO} / N_{VO_2}$ for the various samples used.

| | A | B | C | D |
|---|---|---|---|---|
| SAMPLE T(°C),P(Kbar),t(h) | $[Oi]x10^{17}$ $[cm^{-3}]$ | $N_{VO}$ [a.u] | $N_{VO_2}$ [a.u] | $N_{VO} / N_{VO_2}$ |
| S1 Untreated | 7.78 | 0.0788 | 0.0380 | 2.074 |
| S2 900,3,3 | 7.71 | 0.0771 | 0.0370 | 2.084 |
| S3 900,12,5 | 5.95 | 0.0681 | 0.0228 | 2.987 |
| S4 1027,12,5 | 4.82 | 0.0612 | 0.0172 | 2.363 |
| S5 900,12,10 | 3.91 | 0.0424 | 0.0105 | 4.038 |
| S6 957,12,10 | 3.02 | 0.0304 | 0.0042 | 7.238 |

## Results and Discussion

Fig.1 presents the variations of the intensities of (a) the VO defect (b) the $VO_2$ defect and (c) the intensity ratio $N_{VO} / N_{VO_2}$ versus the oxygen concentration of the samples prior to the annealing stage at 400°C, for 4h. As it is seen, the $VO_2$ defect exhibits an almost linear dependence versus $[O_i]$ although the VO shows a more complicated behavior. On the other hand the intensity ratio $N_{VO} / N_{VO_2}$ is not the same for the various samples. In the following we shall try to understand the above exhibiting behavior firstly by modeling of the anneals and then by considering the effects of the various HT-HP pre-treatments on the annealing curves.

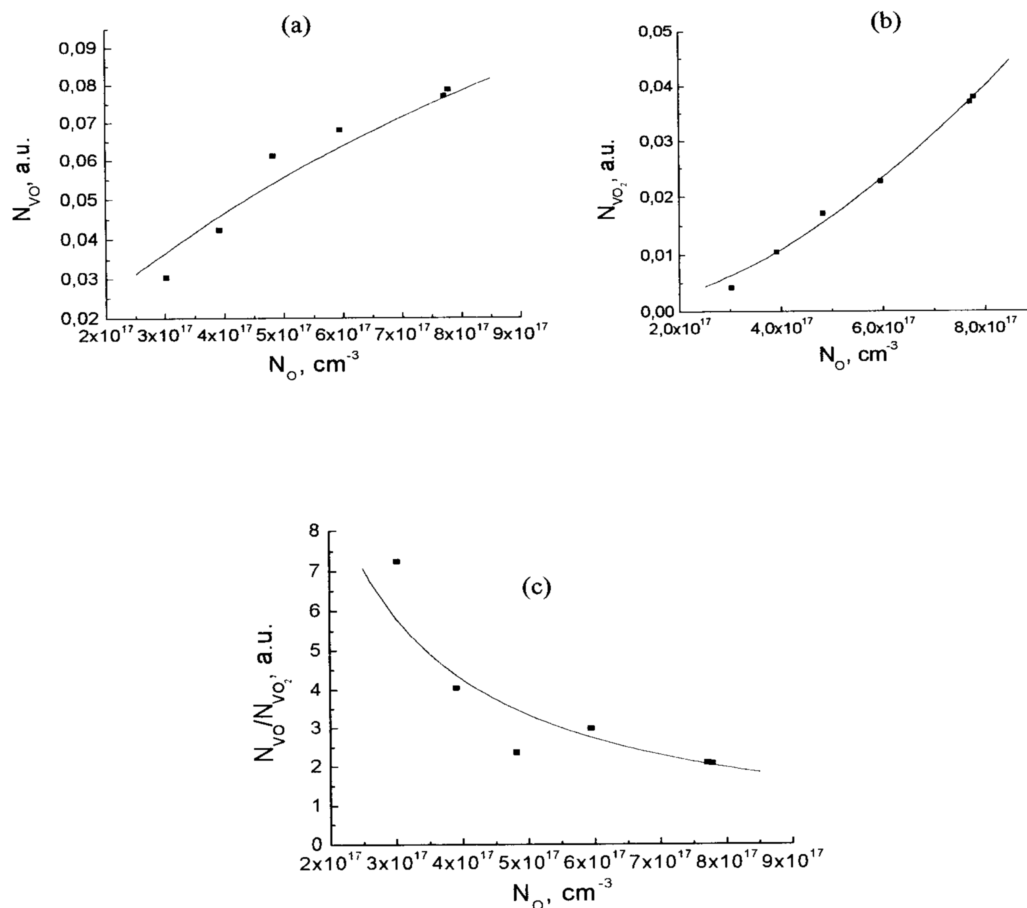


Fig 1. (a)-(b) The variation of the VO concentration, ($N_{VO}$) and the $VO_2$ concentration ($N_{VO_2}$) of each sample versus the oxygen concentration ($N_O$) prior to the conversion of the VO defect to the $VO_2$ defect. (c) The variation of the $N_{VO} / N_{VO_2}$ ratio of each sample correspondingly versus $N_O$.

The most important reactions occurring during the decay of the VO defect and the growth of the $VO_2$ defect are the following:

$$VO + Si_I \xrightarrow{k_1} O_i \tag{1}$$

where $k_1, k_2, k_3, k_4, k_5$ are the proportionality constants characterizing each one of the above reactions, respectively. We assume that equations (1)-(5) constitute a more or less complete reaction scheme describing the phenomenon. Thus, the whole process concerning the VO defects is represented correspondingly by the following rate reactions:

$$\frac{dN_{VO}}{dt} = k_4 N_O N_V - k_1 N_{VO} N_{Si_I} - k_2 N_{VO} N_O - k_3 N_{VO} N_V \tag{6}$$

$$\frac{dN_{VO2}}{dt} = k_2 N_{VO} N_O - k_5 N_{VO_2} N_{Si_I} . \tag{7}$$

In the steady state, the concentrations are given by the equations

$$k_4 N_O N_V - k_1 N_{VO} N_{Si_I} - k_2 N_{VO} N_O - k_3 N_{VO} N_V = 0 \tag{8}$$

$$k_2 N_{VO} N_O - k_5 N_{VO_2} N_{Si_I} = 0 \tag{9}$$

from which we receive

$$N_{VO} = \frac{k_4 N_V N_O}{k_1 N_{Si_I} + k_2 N_O + k_3 N_V} \quad (10)$$

$$N_{VO2} = \frac{k_2 N_{VO} N_O}{k_5 N_{Si_I}}. \quad (11)$$

Putting $k_2/k_4N_V = \alpha_1$ and $( k_1 N_{Si_I} + k_3 N_V )/k_4 N_V = a_2$ eq. (10) becomes

$$N_{VO} = \frac{N_O}{a_1 N_O + a_2}. \quad (12)$$

Upon replacing eq.(12) to eq. (11) and putting $\alpha_1 k_5 N_{Si_I} /k_2 = \alpha_3$ and , $\alpha_2 k_5 N_{Si_I} /k_2 = \alpha_4$ , we get

$$N_{VO2} = \frac{N_O^2}{a_3 N_O + a_4}. \quad (13)$$

Upon dividing eq.(12) and (13) we get

$$\frac{N_{VO}}{V_{VO_2}} = \frac{a_3 N_O + a_4}{a_1 N_O^2 + a_2 N_O}. \quad (14)$$

We have solved numerically equations, (12), (13) and (14) and the results for parameters $\alpha_1 = 2.8$, $\alpha_2 = 7.6\text{x}10^{18}$, $\alpha_3 = 3.4\text{x}10^{18}$, $\alpha_4 = 1.33\text{x}10^{37}$ are depicted in the Fig. 1 (a), (b) and (c), as curves for the $N_{VO}$, the $N_{VO_2}$ and the ratio $N_{VO} / N_{VO_2}$ respectively, versus the oxygen concentration of each sample prior to the (400° C, 4h) annealing stage. As one can see from these figures, the experimental results fit well the theoretical ones.

Physically, the decay of the VO defects occurs [2] mainly through the destruction of the VO by the self-interstitials (eq.1) and the coupling of the VO with the $O_i$ , for the production of the $VO_2$ defects (eq.2). The first reaction depends on the number of the self-interstitials, being present at the aggregates adjacent to the interface of the precipitates and the Si matrix, and their ability to release from these aggregates. If the activation energy for the liberation of the self-interstitials, in order to

break away from the agglomerates and destroy the VO centers, is smaller than the activation energy for the VO movement, in order to trap an $O_i$ atom to form the $VO_2$ defect, then the reaction $VO+Si_I \rightarrow O_i$ occurs earlier than the reaction $VO+O_i \rightarrow VO_2$ .Of course, there appears no reason why both reactions cannot operate in parallel, at least for a part of the annealing process. Notice, that the first reaction will stop when the supply of the self-interstitials is ceased. On the other hand, the number of the self-interstitials and their ability to participate in the reactions depend on the form, the shape and the density of the precipitates, which in turn depend on the HT-HP treatment performed on each sample before irradiation. This means that the effectiveness of the reaction $VO+Si_I \rightarrow O_i$ differs according to the treatment each sample has been given and therefore the number of the VO reacting with the $O_i$ for producing the $VO_2$ defects is also different. In other words, the ratio $N_{VO} / N_{VO_2}$ is expected to be different for the different samples, as it is observed experimentally.

The decrease in the oxygen concentration in the samples S2 – S6 in comparison with the sample S1 is caused by the formation of the oxygen precipitates during HP-HT treatments. The utilization of high pressure stimulates the precipitation process (increase the concentration of oxygen in precipitates) and leads to a higher concentration of the precipitates in silicon [11]. Thus, the lower Oi concentration we have in the samples after HT-HP treatments, the more oxygen precipitates are created and therefore, the higher the number of the self-interstitials, which are rejected from precipitates and collected in agglomerates.

The neutron irradiation introduces high concentration of self-interstitials as well. But they annihilate very effectively with vacancies at the first annealing stage (at 220°C) and the VO to the $VO_2$ conversion will be determined first of all by the self-interstitials accumulated in agglomerates during HT-HP treatments. The increase in the self-interstitial concentration and the decrease in the Oi concentration lead to a more important role of reaction (1) in comparison with reaction (2), which is clearly seen by the increase of the ratio $N_{VO} / N_{VO_2}$ (Fig. 1 (c)).

## Summary

It has been shown that HT-HP treatments of Si samples prior to irradiation affect the annealing behavior of the VO defect. More specifically, HT-HP treatments affect the state of the self-interstitials adjacent to the precipitates, participating in the annealing of the VO defect. As a result the particular contribution of the two main reactions $VO+O_i \rightarrow VO_2$ and $VO+Si_I \rightarrow O_i$ in the whole annealing process differs for each HT-HP treatment, leading finally to different annealing behavior of the VO center in each sample.

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