The effect of high pressure - high temperature treatment on neutron irradiation induced defects in Czochralski silicon

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ABSTRACT

Czochralski-grown (Cz-grown) silicon crystals of the same initial oxygen content (8.33×10^{17} cm^{-3}) were subjected to various high temperature - high pressure (HTHP) treatments for different time durations. Subsequently, the crystals were irradiated by fast neutrons at ~50°C. One of the main defects form is VO pair (A-Center) usually identified in the Infrared (IR) Spectra by the 830cm^{-1} Localized Vibrational Mode (LVM) band. Upon annealing, this defect is converted to the VO_2 defect responsible for a LVM band at 887cm^{-1}. The purpose of this work is to study the effect of various combinations of HTHP treatment prior to irradiation on the annealing behaviour of the VO defect and particularly on its conversion to the VO_2 defect. We have concluded that the conversion of VO to VO_2 depends on the forms of oxygen impurity (i.e. oxygen aggregates, precipitates etc.) and on other defects created in the sample after the HTHP treatment, as for example dislocations and stacking faults.

Keywords: high temperature - high pressure treatments, annealing, neutron irradiation.

1. INTRODUCTION

Oxygen is one of the two main impurities (the other is Carbon) always present in Cz-grown Si and oxygen-related defects in Si have been studied for years[1]. One family of such defects is a series of oxygen-vacancy complexes formed in silicon upon irradiation and subsequent thermal anneal. The first member of this series is the well-known A-center where an oxygen atom is positioned nearly substitutionally in a lattice vacant site. The neutral charge state of this defect gives rise to a LVM band at ~830cm^{-1} which is its fingerprint in the IR-Spectra[2]. Upon thermal anneal this defect is converted to VO_2 center. In this process, a migrating VO pair is captured by an oxygen interstitial atom to form a dioxygen-vacancy center giving rise to an IR band[2] around 887cm^{-1}. Further anneals lead to more complex centers generally labeled[3,4] as V_nO_m complexes.

It is well-known in the literature that heat treatments of the silicon crystals prior to irradiation cause considerable changes in the annealing behaviour of the irradiation-induced defects. More specifically, it has been observed that, due to heat treatments at 600°C, the annealing temperature of A-center could be changed depending[5] on the annealing duration as well as the initial oxygen content of the samples. It has been found that a critical value of the oxygen interstitial content, $[O]_{crit}$, exists about $7x10^{17}cm^{-3}$ and samples with oxygen concentration above this value exhibit a substantial decrease of the annealing temperature of A-centers. The whole process has been explained[5,6] as a result of the oxygen precipitation induced in the heat-treated samples with oxygen content larger than the critical one.

External stress, applied during the course of thermal treatment prior to irradiation, is another important parameter which is reasonably expected to affect the annealing behaviour of the radiation-induced defects. Enhanced hydrostatic pressure during gas ambient annealing is known to affect the formation of oxygen precipitates and of other

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defects created in Cz-Si, due to the stress related change of oxygen diffusivity rate[7,8], stress-stimulated creation[9] of nucleation centers for oxygen precipitation, and stress-stimulated oxygen precipitation[10] as well as of large differences in the compressibilities between Si and SiO_2 phases[11]. Therefore the HTHP treatments prior to irradiation are obviously expected to affect the annealing behaviour of the radiation-induced defects and the purpose of the present paper is to examine the effect of various combinations of HTHP treatments on the evolution of VO defect and its conversion to VO_2 defect.

2. EXPERIMENTAL DETAILS

Six silicon samples of $15x10x2mm^3$ dimensions were cut from a commercially obtained Cz-grown wafer with initial oxygen interstitial concentration $\sim 8.33x10^{17}cm^{-3}$. The samples were subjected to a four stage treatment i) Firstly, they were subjected to HTHP treatments. More specifically, they were annealed under different hydrostatic pressures (1 bar[1 atm] up to 12Kbar in argon ambient), at temperatures in the range of (900-1027)°C, for various time durations (3-10)h, (the conditions of the HTHP treatments of each sample are shown in the tables cited in section 3), ii) afterwards, they were irradiated by fast neutrons at a dose of $\sim 10^{17}n/cm^2$, at T=50°C, iii) after the irradiation, they were subjected to a heat treatment at 220°C for 150h for the purpose of complete annealing of large clusters of defects and disordered regions, and iv) finally, to a thermal anneal at 420°C for 4 hours to study the conversion of A-centers to VO_2 defects. Infrared spectroscopy measurements were performed after each stage of the above procedure.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 1 shows the IR spectra, for each sample, after a HTHP treatment, after neutron irradiation, after the anneal at T=220°C for t=150h and after the isothermal anneal at T=420°C for t=4h. The curve (a) of Fig.1 (S_1) refers to a sample which has not been subjected to HTHP treatment and therefore the corresponding spectra prior to irradiation represent also the spectra of any of the six as received samples in the present experiment.

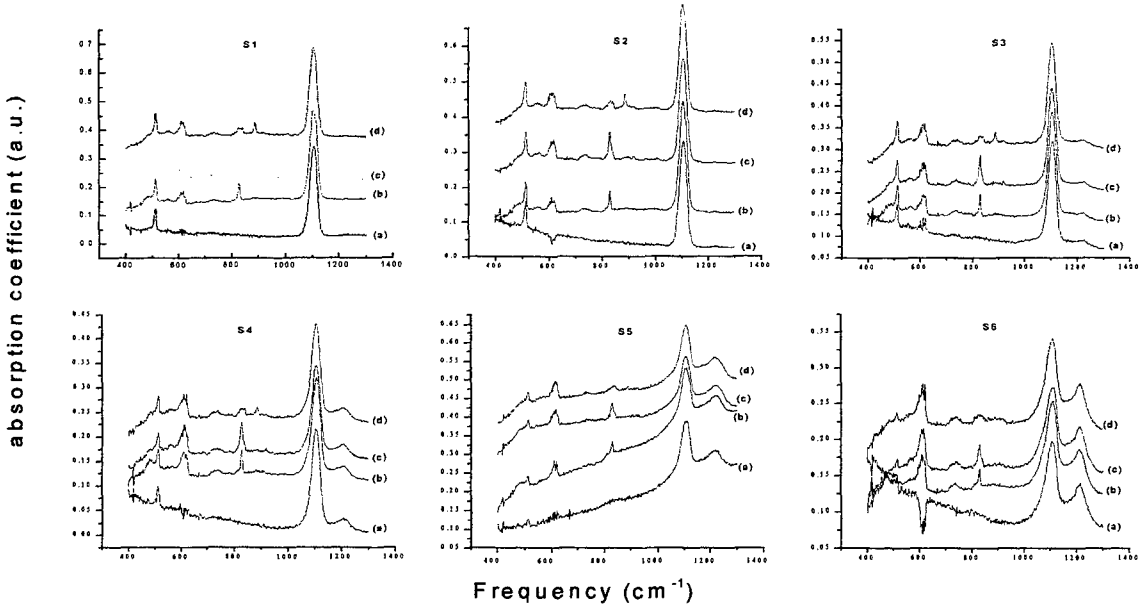

Fig. 1 IR Spectra for the investigated samples, (a) just after HTHP treatment, (b) after neutron irradiation, (c) after heat treatment at 220°C,1 bar, for t=150h, (d) after additional heat treatment at 420°C,1 bar, for t=4h

Tables I,II and III summarize all the results containing the changes of the parameters which are of interest in this work. Particularly, table I presents the variation of oxygen for each sample for the above four stages of the whole procedure. The concentration of oxygen was calculated from the Oi absorption band at 1106cm^{-1}. Table II presents the variations of oxygen precipitates for the four stages correspondingly as in table I. Table III presents VO variations after irradiation, after the heat treatment, T=220°C, t=150h and after the isothermal anneal (T=420°C, t=4h) for each sample. It also presents the amplitudes of VO_2 defect appearing in the spectra after the (T=420°C, t=4h) isothermal anneal.

Table I. The variations of the oxygen interstitial concentration of the samples in the course of the four stages of the experimental procedure.

	A	B	**A-B**	C	**B-C**	D	**C-D**	E	**D-E**
SAMPLE T(°C),P(Kbar),t(h)	[Oi]x10^{17} initial	[Oi]x10^{17} after HTHP (bef. irrad)	**$(\Delta Oi)_1$ x10^{17}**	[Oi]x10^{17} (after irrad)	**$(\Delta Oi)_2$ x10^{17}**	[Oi]x10^{17} before transition VO-->VO2	**$(\Delta Oi)_3$ x10^{17}**	[Oi]x10^{17} after transition VO-->VO2	**$(\Delta Oi)_4$ x10^{17}**
S1 untreated	8.33	8.33	**0**	8.16	**0.17**	7.78	**0.38**	8.01	**-0.23**
S2 900,3,3	8.33	7.94	**0.39**	8.24	**-0.30**	7.71	**0.53**	7.86	**-0.15**
S3 900,12,5	8.33	6.28	**2.05**	6.40	**-0.12**	5.95	**0.45**	6.18	**-0.23**
S4 1027,12,5	8.33	5.33	**3.00**	5.24	**0.09**	4.82	**0.42**	5.10	**-0.28**
S5 900,12,10	8.33	4.17	**4.16**	4.25	**-0.08**	3.91	**0.34**	4.20	**-0.29**
S6 957,12,10	8.33	3.06	**5.27**	3.26	**-0.20**	3.02	**0.24**	3.17	**-0.15**

Table II. The variations of the oxygen precipitates strength of of the samples in the course of the four stages of the experimental procedure.

	A	B	**B-A**	C	**C-B**	D	**D-C**
SAMPLE T(°C),P(Kbar),t(h)	O_{precip} (a.u) before irrad.	O_{precip} (a.u) after irrad	**ΔO_{precip} (a.u.)**	O_{precip} (a.u) before transit.	**ΔO_{precip} (a.u.)**	O_{precip} (a.u) after transit.	**ΔO_{precip} (a.u.)**
S1 untreated	–	–	–	–	–	–	–
S2 900,3,3	–	–	–	–	–	–	–
S3 900,12,5	0.01548	0.01503	**-0.0004**	0.01423	**-0.0008**	0.01610	**0.00187**
S4 1027,12,5	0.02077	0.0237	**0.003**	0.02630	**0.0026**	0.02581	**-0.00049**
S5 900,12,10	0.05491	0.06139	**0.0065**	0.06391	**0.0025**	0.06659	**0.00268**
S6 957,12,10	0.05946	0.06042	**0.0009**	0.06190	**0.0014**	0.06207	**0.00017**

Table III. The variation of the intensities of the VO and the VO_2 defects in the samples in the course of the last three stages of the procedure.

	A	B	**B-A**	C	**C-B**	D
SAMPLE T(°C),P(Kbar),t(h)	VO (a.u) after irrad.	VO (a.u) before trans.	**ΔVO (a.u.)**	VO (a.u) after trans.	**ΔVO (a.u.)**	VO_2 (a.u) after trans.
S1 untreated	0.06025	0.0788	**0.01855**	0.0246	**-0.0542**	0.038
S2 900,3,3	0.05671	0.0771	**0.02039**	0.0227	**-0.0544**	0.037
S3 900,12,5	0.0505	0.0681	**0.0176**	0.0157	**-0.0524**	0.0228
S4 1027,12,5	0.04806	0.0612	**0.01314**	0.0151	**-0.0461**	0.0172
S5 900,12,10	0.03799	0.0424	**0.0044**	0.0149	**-0.0275**	0.0105
S6 957,12,10	0.02492	0.0304	**0.00548**	0.0106	**-0.0198**	0.0042

At first, we observe that the largest the change of the oxygen content of each sample due to the HTHP treatment, the larger the amplitude of the oxygen precipitation peak around $1220cm^{-1}$. This could be somehow expected since most of the oxygen interstitial atoms that remove from the solution due to the above treatments precipitate. It is also known[12] that a fraction of oxygen atoms is trapped near oxygen precipitates during the treatment. We also observe (Table II) that neutron irradiation does not affect virtually the amplitude of the oxygen precipitation peak around $1220cm^{-1}$ which alternatively means that the preformed irradiation did not result in dissolution of oxygen atoms from precipitates. This conclusion is in agreement with previous reports[12] concerning 3MeV electron irradiation. It is worth noting that after irradiation the oxygen content of the samples increases (apart for sample S_4, for which however, the oxygen variation seems to be within experimental error). Most possibly this occurs because oxygen atoms trapped near precipitates are liberated and the number of these oxygen atoms is larger than the number of oxygen interstitials participating in the formation of VO defects. Furthermore, we see that the larger the amplitude of the oxygen precipitate the smaller the VO amplitude which is something also expected since the initial oxygen concentration of the samples after the HTHP treatment is smaller.

It is known that in neutron-irradiated Si, large defect aggregates and disordered regions are formed which generally trap vacancies. These vacancies are released[13,14] upon annealing at ~200°C. This release could be studied in Cz-grown Si indirectly, by monitoring the increase of A-centers since the liberated vacancies are readily captured by oxygen interstitial atoms. To this end, the samples were kept at T=220°C for t=150h. In the first 15h of this process the A-center peak amplitude in the spectra was increased substantially in all the samples and then stabilized. Thus, a time duration of about 15h is adequate for all the samples. However, the annealing at this temperature was extended to time durations up to 150h to investigate any other changes in the spectra, particularly in the peak amplitude of the VO and the O_i defects. No changes were observed for any sample. It is an indication that the HTHP treatment prior to irradiation does not affect the structure and the behaviour of the formed disordered regions. Table III contains the changes in the VO concentration of each sample occurring in the course of this annealing stage. The oxygen concentration of the samples was decreased (Table I) during the same stage as was expected due to the participation of oxygen atoms in the formation of VO defects. It is worth noting that during this stage the oxygen precipitation peak amplitude remained practically unaltered (Table II), an indication that oxygen atoms from precipitates do not participate in the above process, as it is reasonably expected for these low temperature anneals.

In the final stage of the whole process the samples were subjected to an isothermal anneal at T=420°C for t=4h.As it is seem from fig.1 and table III the conversion of VO to VO_2 is not the same in all the samples. This will be discussed below in connection with fig.2. Another observation is that in all the samples the oxygen content was increased. This strongly suggests that apart for the reaction $VO + O_i \rightarrow VO_2$ which characterizes the conversion VO to VO_2, another reaction occurs parallel which is the source of the additional oxygen atoms. This reaction is: $VO + Si_i \rightarrow O_i$ describing the destruction of VO by silicon self-interstitials. At this temperature both components of this reaction are mobile. The

self-interstitials interacting with A-centers are liberated from some traps in the crystal. Another possibility is that A-centers migrate to the traps containing self-interstitials which in turn can annihilate with A-centers.

Fig. 2 presents, for each sample, the remaining VO defects and the created VO_2 defects after the final stage, versus the difference (ΔO_i) of the total oxygen concentration . More specifically (ΔO_i) is the difference between the initial oxygen concentration, which is the same for all samples, and their concentration of each sample after the final (T=420°C, t=4h) isothermal treatment. Notice that VO_2 exhibits a linear dependence on (ΔO_i) although the corresponding dependence of VO is more complicated and certainly not linear. This behavior of the VO_2 defect could be understood if one looks at the formation reaction $VO+Oi \rightarrow VO_2$ which entails a proportionality between the concentrations of VO_2 and

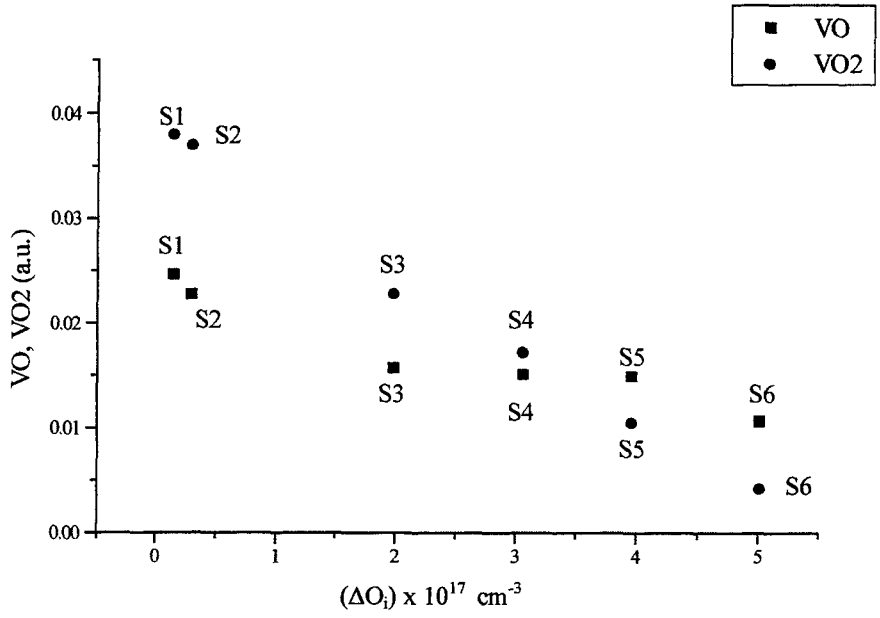

Fig. 2 The variation of the intensities of the VO and the VO_2 defects as a function of the total oxygen interstitial concentration change between the initial value and the final value after the four stages procedure.

O_i defects. According to this reaction, VO_2 concentration is also expected to be proportional to the concentration of the VO defect. However, this is not the case as it is seen, if one looks at columns (C-B) and D of Table III. In general, it is expected a difference in the behavior of VO and VO_2 defects, since VO participate[3],[4] in parallel to other reactions as well, i.e $VO+V \rightarrow V_2O$, $VO+V_2 \rightarrow V_3O$, etc. The fact now that the remaining VO defects, after the conversion of VO to VO_2, are not the same for all samples could be generally related to the effect of HTHP treatment. It indicates that the existed precipitated oxygen in the samples affects differently the conversion of VO to VO_2. Generally hydrostatic pressure P, temperature T and time t of anneal have their own special effect on the precipitation of oxygen. However, when all the parameters are combined it is very difficult to separate the contribution of each one and we have to analyze the results considering them acting externally as a whole. At first sight, it is reasonable to refer to the number of the remaining oxygen interstitials after the final stage of the whole procedure. This change is very important in our opinion and affects the behaviour of the VO and the VO_2 defects as it is indicating in fig.2. At least two parameters influence the conversion of the VO to the VO_2: i) the number of oxygen interstitials still available in the samples and ii) the presence of other defects (precipitates, dislocations, stacking faults) after HTHP, which are more numerous for the samples subjected to HTHP treatments with larger amount of oxygen precipitates (i. e. treatments at 957°C). Notice that after HTHP treatments with T=1027°C the induced oxygen precipitation is much less pronounced.

4. CONCLUSIONS

Cz-grown silicon samples of the same initial oxygen content have been subjected to various HTHP treatments and then irradiated by fast neutrons for the purpose of investigating the effect of these treatments on the conversion of the VO centers to the VO_2 defects. We have found that the HTHP pre-treatment affects the amount of the VO defects converted to the VO_2 defects. The phenomenon is attributed to the production of oxygen precipitates affecting the available oxygen interstitials participating in the formation reaction of VO_2 defect and also to the creation of various defects due to the HTHP treatment, as for example dislocation and stacking faults, which have also an impact on the above reaction.

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