Physica B 308–310 (2001) 313–316

PHYSICA B

www.elsevier.com/locate/physb

The effect of high temperature–high pressure treatment on the annealing behavior of VO center in neutron-irradiated Czochralski silicon

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Abstract

It is known that the application of high hydrostatic pressure on Si during heat treatment produces substantial changes in the properties of oxygen precipitates, which in turn, affect the behavior of various defects present in the crystal lattice. In this work, the annealing behavior of the VO complexes in Si samples subjected, before neutron irradiation, to different High Temperature–High Pressure (HT–HP) treatments at temperatures around 900°C and pressures up to 12 kbar, for $t = 5$ h, was investigated using Infrared spectroscopy. We found that (i) the samples pre-treated at $T_1 = 870°C$ and $T_2 = 957°C$, at atmospheric pressure and (ii) the samples pre-treated at $P_1 = 1$ bar and $P_2 = 12$ kbar, at $T_1 = 870°C$, exhibit approximately the same difference in the annealing temperature of the VO complexes. The observed effect is explained by taking into account the impact of the HT–HP pre-treatment on the fraction of the self-interstitials bound at the SiO_x/Si interface of the oxygen precipitates and the Si matrix. We argue that the two regimes of pre-treatments (i) and (ii), see above, produce the similar effects upon self-interstitial aggregation processes in the presence of oxygen precipitates. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silicon; Irradiation; High-pressure anneals

1. Introduction

High temperature (HT) treatment at $T > 400°C$ of silicon crystals leads to the appearance [1] of structural defects such as various kinds of oxygen aggregates and precipitates, rod-like defects, dislocations, stacking faults and so on. These defects, in general, affect the properties and the behavior of the radiation-induced defects. It has been found [2], for instance, that the annealing temperature of the VO defects is considerably changed by variations in the duration of pre-heat treatment at $T = 600°C$ and/or the initial oxygen concentration of the Czochralski silicon (Cz-Si). It was suggested [2] that the annealing of the VO defects takes place through the capture of Si self-interstitials (Si_I's) released from the SiO_x/Si interface of the Si matrix and the oxygen precipitates being formed after the 600°C pre-heat treatment. The Si_I's generated [3,4] during the precipitation process tend to aggregate [5]. They generally form extended structural defects such as stacking faults. Reasonably, it is expected that the annealing process of the A-centers would be affected by the state and the ability of these Si_I's to be released from the aggregates.

In order to understand the phenomenon, it is necessary to consider the effects on the Si_I's due to the different kinds of oxygen aggregates and structural defects formed during pre-HT treatments at different temperatures. As a result of the HT treatment and the consequent formation of precipitates and structural

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PII: S0921-4526(01)00873-0

defects, stress fields are locally created [6] around the precipitates and the extended defects. These elastic fields are anisotropic in general and attract the emitted Si_I's. Concerning now, the annealing of the VO defects, the relation of the self-interstitial aggregates with the precipitates and the structural defects play a very important role, according to our opinion. The grade of binding of the self-interstitial aggregates is very significant, since it is expected to be different for different dominating precipitates and, therefore, for different temperatures of the HT treatments. Evidently, the Si_I's, loosely bound at the interface are responsible for the dependence of the annealing behavior of the A-centers on the temperature of the pre-heat treatment. We assume that the binding force on the Si_I's changes with increasing temperature, due to changes in the oxygen precipitates, i.e. their density, their shape and/or their size upon pre-heating. More specifically, we assume that pre-heating at two temperatures T_1 and T_2 with $T_2 > T_1$, results in a situation that the Si_I's are more tightly bound at the interface in the latter temperature, T_2. In other words, the Si_I's are more effectively released during the course of the isochronal anneal in a material subjected to the lower temperature T_1 of pre-heat treatment.

On the other hand, the application of enhanced hydrostatic pressure during heat treatment has been found [7] to affect a lot of the features of the structural defects and the oxygen aggregates as, for example, the concentration of the dislocations, the density and the size of the precipitates and concentrations of the remaining oxygen interstitials, etc. Thus, pressure is another important parameter, which is expected to affect the behavior of the radiation defects, since every HT–HP pre-treatment establishes a different relation between the self-interstitial aggregates and the precipitates.

The purpose of this work was to investigate the annealing behavior of the VO defects and monitor the changes in the annealing temperature in dependence on the conditions of a HT–HP pre-treatment. We shall show that by considering that the binding of the Si_I's at the SiO_x/Si interface depends on the HT–HP pre-treatment, we can explain the obtained experimental results of this study.

2. Experimental details

Five Cz-grown silicon samples with nearly the same initial oxygen concentrations ($O_i = 8.3 \times 10^{17}\,cm^{-3}$), were subjected to different combinations of HT–HP pre-treatments, for the same time, $t = 5\,h$; see Table 1. Then, the samples were irradiated by fast neutrons at $T \approx 50°C$. The fluence was about $10^{17}\,n/cm^2$. Afterwards, 15 min isochronal anneals were performed in steps of $\sim 10°C$. After each annealing step, we employed IR measurements to monitor the annealing behavior of the $828\,cm^{-1}$ LVM band of the VO defect.

3. Experimental results and discussion

In Table 1, the annealing temperature (T_{ann}) of the VO defects is indicated, for each sample. As seen, the beginning of the annealing process, i.e. T_{ann}, was found to be different for the different pre-HT–HP treatment regimes. It is well known that among a number [8] of available reaction paths, two reactions are the most important when the A-centers become mobile: $VO + O_i \rightarrow VO_2$, $VO + Si_I \rightarrow O_i$. These two reactions run in parallel, at least in the temperature range where the VO centers disappear and the VO_2 defects are formed. The emergence of the VO_2 defect in the IR spectra is related to the first reaction. An increase in the $[O_i]$ concentration observed during the VO decay verifies [9] that the second reaction takes place as well.

Let us now compare the behavior of the samples S_1 and S_2, which were annealed at temperatures of $T_1 = 870°C$ and $T_2 = 957°C$, at atmospheric pressure. In these cases, the annealing temperatures of the VO defects are $T_{1\,ann} = 270°C$ and $T_{2\,ann} = 292°C$, respectively ($T_{2\,ann} > T_{1\,ann}$). First of all, we see that the annealing temperature is lower in both cases than the normal annealing temperature of the VO defects (about 300°C) [10] in silicon samples without any pre-heat treatment, a phenomenon being well known and discussed in the literature [2,6]. If the first reaction $VO + O_i \rightarrow VO_2$ is dominating in the annealing process,

Table 1
The annealing temperature T_{ann} of the VO defect for the various pre-HT–HP treated samples

Samples	T (°C)	P (kbar)	t (H)	T_{ann} of the VO (°C)	Comparison of T_{ann} (°C)
S_1	870	10^{-3}	5	270 ± 4	$\Delta T_{12\,ann} = +22$
S_2	957	10^{-3}	5	292 ± 2	$\Delta T_{13\,ann} = +15$
S_3	870	12	5	285 ± 3	$\Delta T_{24\,ann} = +2$
S_4	957	12	5	290 ± 3	$\Delta T_{34\,ann} = +5$
S_5	900	12	5	284 ± 4	$\Delta T_{15\,ann} = +14$

then, one could expect that a larger increase in the oxygen diffusivity (and that of A-centers as well) in the case of pre-heat treatment at the higher temperature, would lead to a faster reaction between VO and O_i, resulting in a lower annealing temperature of the A-centers in the sample S_2 than in the sample S_1. This expectation is opposite to what is observed (see Table 1). Therefore, the first reaction cannot provide a plausible explanation of the experimental data. Other factors should be taken into account, as well. If however, the second reaction $VO + Si_I \rightarrow O_i$ is the prevailing one, then one should consider the sources of the Si_I's. These sources are oxygen aggregates and precipitates, which as we mentioned in the introduction, produce different strains in the lattice due to differences in their forms, as a result of the different pre-heat treatments.

Let us consider the sample S_1 subjected to a heat treatment at the lower temperature, $T_1 = 870°C$. Si_I's, if loosely bound to oxygen aggregates can be emitted and interacted with A-centers, (no matter whether A-centers are coming towards the precipitates or Si_I's are emitted from the precipitates), as the temperature increases during the isochronal annealing sequence. This leads to a lower conversion temperature of the VO into the VO_2, $T_{1\,ann} = 270°C$. However, in the case of the sample S_2 subjected to a higher temperature of heat treatment, $T_2 = 957°C$, the dominating oxygen precipitates are different and, therefore, the binding of the Si_I's is also different, compared to the sample S_1. We assume that the Si_I's are more tightly bound in this case. This means that it is more difficult to be emitted from the precipitates or in other words, the reaction $VO + Si_I \rightarrow O_i$, is now more difficult to realise. Alternatively, a higher temperature should be achieved in sample S_2 in order that the reaction $VO + Si_I \rightarrow O_i$ becomes significant. Notice now that this reaction results in the decay of A-centers, i.e. the concentration of A-centers is lowered and from reaction kinetics arguments, it is expected that the lower the concentration of A-centers, the higher the temperature of their conversion into the VO_2 complexes. Indeed, this was found experimentally ($T_{2\,ann} = 292°C$).

We shall now extend our model involving also the application of uniform stress during the pre-heat treatment process. Within the line of our argumentation, we suggest that an increase of stress (from 1 bar to 12 kbars) at a certain low temperature (870°C here) produces equivalent effect on the annealing temperature of the VO defects with an increase of the temperature (from 870°C to 957°C) at certain low stress (1 bar here). In other words, the increase of stress at low temperature ($T = 870°C$) contributes to a change in the kind of the dominating precipitates (and the consequent binding of the Si_I's at the interface), which is equivalent to the increase of temperature at low stress ($P = 1$ bar). Thus, comparing the samples S_1 and S_3 (see Table 1), we actually see an increase of T_{ann} ($\Delta T_{13\,ann} = 15°C$) which is comparable to the increase of T_{ann} in the case of the samples S_1 and S_2 ($\Delta T_{12\,ann} = 22°C$).

Two additional observations should be reported:

(i) Annealing of the samples at high T (957°C here) should have practically no effect in the annealing temperature T_{ann}, irrespectively, of a low ($P = 1$ bar) or a high ($P = 12$ kbars) pressure applied during the anneal, since at high T (957°C), the precipitates have attained their final form and the application of pressure has no further effect on the binding of the Si_i's at the interface. Actually, this is the case concerning the samples S_2 and S_4, for which the annealing temperatures of the VO defects are practically the same; cf. $T_{2\,ann} = 292°C$ and $T_{4\,ann} = 290°C$ (Table 1).

(ii) On the other hand, if high stress (12 kbars here) is applied, the annealing temperature should not depend on the temperature of the pre-treatment (a low one $T_1 = 870°C$ and a high one $T_2 = 957°C$ here) since the oxygen precipitates have attained the final form due to the increase of pressure and that which is not affected by the increase of the temperature of the heat treatment. Actually, this is the case concerning the samples S_3 and S_4 which exhibit approximately equal annealing temperatures, i.e. $T_{3\,ann} = 285°C$, $T_{4\,ann} = 290°C$.

(iii) It is worth also noting that the sample S_5, which has been subjected to a HT–HP treatment at $P = 12$ kbars but at an intermediate temperature $T_3 = 900°C$ ($T_1 < T_3 < T_2$), shows an intermediate increase of $\Delta T_{ann} \approx 14°C$, as one would expect from our model.

4. Conclusions

We have studied the annealing behavior of Cz-grown Si samples subjected to different HT–HP treatments prior to neutron irradiation. We have found that these treatments affect the annealing temperature of the VO center. More specifically, it has been found that (i) pre-treatments on two samples at temperatures $T_1 = 870°C$ and $T_2 = 957°C$, respectively, at $P = 1$ bar, cause the same change in the annealing temperature of the VO defects as (ii) pre-treatments on two samples at pressures $P_1 = 1$ bar and $P_2 = 12$ kbars, respectively, at the low temperature $T_1 = 870°C$. We have explained the results by considering the effects of the HT–HP treatment on the grade of binding of the Si_I's at the SiO_x/Si interface.

Acknowledgements

This work was supported by the NATO HTECH CRG974588 grant.

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