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Production and evolution of defects in neutron-irradiated Si subjected to thermal pre-treatments under hydrostatic pressure

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Abstract
Thermal treatments of Czochralski-grown Si at $T = 450$, 600 and 650 $^\circ$C, under high hydrostatic pressure of $P \approx 11$ kbar, introduce thermal donors and various structural defects, as for example oxygen precipitates. Neutron irradiation of such samples results first in the formation of oxygen–vacancy complexes, mostly VO defects. Upon annealing, the VO defects evolve in larger clusters via the accumulation of oxygen atoms and vacancies in the initial VO core, leading to the formation of $V_m O_n$ defects. We focus on the study of the effect of pre-treatments on the production and evolution of the various $V_m O_n$ defects upon isochronal annealing. The observed changes and variations in the IR spectra and the evolution curves in comparison with the corresponding ones of an initially untreated sample are discussed and some explanations are offered. The most important finding of this work is that the concentrations of the VO$_2$ and the VO$_3$ defects are reduced in the sample pre-treated at 450 $^\circ$C, an indication of interaction between thermal donors and radiation-induced defects.

1. Introduction

The improvement of the functionality of the Si electronic components in various devices requires the control of the defects formed upon processing of the material. The more we know about the defects and their properties, the better we can improve the yield and the performance of the devices. In other words, advances in Si technology require deeper insight into the physics and the behaviour of the defects.
Oxygen is the main, unintentionally added, impurity in Si crystals during growth. Its significance, besides the scientific interest, derives from the technological importance of Cz-grown Si, which is the basic material used as a substrate for the fabrication of integrated circuits. Two kinds of oxygen-related centres are normally observed in Si material. One kind of defects involves complexes formed due to irradiation which leads to the formation of centres containing primary defects (V, SiI), for example the VO and the OiSiI centres, and also pairs with other impurities present in the material. In the case of neutron irradiation it is also possible that more than one vacancy can be trapped by an oxygen atom to form larger clusters. The other kind of defects involves centres formed due to thermal treatments. It is well-known that thermal treatments of the Si material trigger oxygen aggregation processes leading to the formation of thermal donors (TDs), oxygen precipitates and other structural defects.

The Si technology currently used by the industry involves thermal treatment steps of the material at elevated temperatures and also implantations and/or irradiations with various particles. All the above-mentioned processes introduce defects. From the practical point of view, it is therefore very interesting and important to study the basic interactions between the two categories of defects and also to study the impact of the presence of the one kind of defect on the behaviour and the properties of the other. Knowledge of the influence of the oxygen precipitates and accompanying structural defects upon the radiation-induced defects is very important in the case of Si materials being subjected to processes that involve both thermal treatments and irradiations.

Thermal treatments in the temperature range 450–650°C mainly introduce various kinds of TDs [1]. Depending on the duration of the heat treatment with or without the application of high hydrostatic pressure small oxygen precipitates also form [2, 3]. Generally, in the temperature range of our interest in this work, ribbon-like precipitates are expected [4] to form. The effects of these defects in the formation and evolution of radiation-induced defects are still unresolved. There are conflicting reports in the literature. It has been reported [5] that thermal donors can be annihilated by irradiation, but also that primary defects produced by the irradiation do not interact [6] with thermal donors. The main objective of this study is to investigate the effect of the thermal defects, mainly thermal donors and/or small oxygen precipitates formed at the early stages of the oxygen aggregation process on the behaviour of radiation-induced defects in Si, mainly the V\textsubscript{m}\textsubscript{O\textsubscript{n}} defects. The exact knowledge of the thermal stability and generally the annealing behaviour of the oxygen–vacancy-related defects produced by irradiation in Si samples, pre-treated at various temperatures under high hydrostatic pressure, are expected to enable a better understanding of their mutual influence and interactions.

The spectroscopic investigation of the above issue, including the study of defect reactions, is substantially facilitated when the concentration of the involved defects increases. To this end, we have carried out neutron irradiations, and the thermal treatments were conducted with the application of high hydrostatic stress. First, it is well-known [7] that in neutron-irradiated material, due to the special separation of the primary defects, more vacancies are available to participate in secondary reactions and therefore the V\textsubscript{m}\textsubscript{O\textsubscript{n}} defects produced by the irradiation and the accompanied thermal treatments are expected to have higher concentrations than those, for example, in the electron-irradiated material. Second, it is known [8–10] that the application of stress increases the total concentration of TDs and enhances the oxygen precipitation process. This behaviour is believed [10] to be due to the enhancement of the diffusivity of single oxygen atoms and small oxygen aggregates. However, the application of stress induces [11–13] changes in the density and the structure of defects, which complicate the reactions. With the application of stress the same concentration of TDs is achieved in shorter time duration than that of the thermal treatment without stress. It may be argued, therefore, that we could have produced the same concentration of TDs by heat-treatments of longer duration.
and thus we could have avoided any complications involved by the application of external stress. However, high pressure is an external parameter, as is the temperature as well, and it is useful to do relative studies. More importantly, defect-engineering of oxygen in silicon wafers is not an isolated process. Other impurities and defects, as well as other parameters, i.e. external pressure, depending on the thermal treatment strategy, are of high importance, and therefore considerable attention has been directed in knowing the details of their influence.

2. Experimental details

In this work we used four Cz-grown Si material samples with initial oxygen concentration of \([O_i] \approx 1.4 \times 10^{18} \text{cm}^{-3}\). The carbon substitutional concentration in our samples was beyond the IR detection limit ([C_s] < 1 \times 10^{16} \text{cm}^{-3}). The as-received sample is labelled \(A_o\), and the three samples subjected to high-temperature–high-pressure (HTHP) treatments are labelled as follows: \(A_2\) (450 °C, 10.7 kbar, 5 h), \(A_5\) (600 °C, 12 kbar, 5 h), \(A_6\) (650 °C, 11 kbar, 5 h). The short time duration of the anneal at these temperatures ensures that only thermal donors of various types and small oxygen precipitates form [2, 3]. Dislocation loops and/or stacking faults, if any, are considered to produce subtle effects. The small variations in the applied hydrostatic pressure (above 10 kbar) among the samples are considered of minor importance. Thus, pressure and time are considered constant and only the temperature of the treatment changes in the range 450–650 °C. The TD concentrations were extracted from Hall-effect measurements and were found to be \(8 \times 10^{15} \text{cm}^{-3}\) for sample \(A_2\), and \(2 \times 10^{14} \text{cm}^{-3}\) for samples \(A_5\) and \(A_6\). After the heat-treatment steps, all samples were irradiated by fast neutrons at a fluence of \(8 \times 10^{16} \text{n cm}^{-2}\). Post-irradiation annealing was carried out up to 600 °C in \(\Delta T = 10^\circ\text{C}\) and \(\Delta t = 30\text{ min}\) steps. The thermal evolution of the various defects was studied by monitoring the amplitudes of the corresponding peaks in the IR spectra, received after each annealing step, with the aid of a Jasco IR-700 spectrometer of dispersive kind.

3. Experimental results and discussion

The most important defect, besides the divacancy (V₂), formed in neutron-irradiated Cz-Si is the VO pair, the well-known A-centre, which in the neutral charge state gives rise [15] to an IR peak at \(\sim 828 \text{ cm}^{-1}\). Upon anneals [15, 16] at \(\sim 300^\circ\text{C}\), the VO defect converts to the VO₃ defect (887 cm⁻¹), which in turn at \(\sim 450^\circ\text{C}\) converts to the VO₃ defect (903, 967 and 1004 cm⁻¹) and so on. A band at 983 cm⁻¹ has been tentatively attributed [17] to a modified VO₃ defect with one more oxygen atom attached. The successive production of VOₙ (\(n = 1, 2, 3, \ldots\)) defects take place via the successive aggregation of oxygen interstitial atoms on the initial formed VO defect. Along with this, another reaction channel leads to the formation of VₙOₘ defects (\(m = 1, 2, 3, \ldots\)), via the successive accumulation of vacancies to the initial VO defects, while VₙOₘ defects are also produced [16, 18] in the course of the annealing process. In a previous work [19], we have correlated the peaks at 839, 833, 824 cm⁻¹ with the V₂O, the V₃O₂ and the V₄O₃ respectively. From their position in the spectra, these defects appear as satellite bands of the much stronger VO band. Note that, due to the pre-treatment steps, the samples are expected [20, 21] to contain thermal donors and small oxygen precipitates.

We shall first deal with the interaction, if any, between thermal and radiation-induced defects during the irradiation. As is seen from table 1, the amplitudes of the VO defects are about the same in samples \(A_o\) (as-grown) and \(A_2\) (450°C, 10.5 kbar, 5 h), indicating that no interaction occurs between VO and the TDs present in sample \(A_2\). On the other hand, the amplitudes of the VO defects are considerably less in samples \(A_5\) (600°C, 12 kbar, 5 h) and \(A_6\)
Table 1. The [O\textsubscript{1}] after treatment and after irradiation, as well as the VO amplitudes after irradiation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[O\textsubscript{1}] after treatment ($\times 10^{18}$ cm\textsuperscript{-3})</th>
<th>[O\textsubscript{1}] after irr. ($\times 10^{18}$ cm\textsuperscript{-3})</th>
<th>VO (arb. units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A\textsubscript{o} (as received)</td>
<td>1.4</td>
<td>1.37</td>
<td>0.053</td>
</tr>
<tr>
<td>A\textsubscript{2} (450°C, 10.5 kbar, 5 h)</td>
<td>1.38</td>
<td>1.28</td>
<td>0.052</td>
</tr>
<tr>
<td>A\textsubscript{3} (600°C, 12 kbar, 5 h)</td>
<td>1.35</td>
<td>1.33</td>
<td>0.040</td>
</tr>
<tr>
<td>A\textsubscript{6} (650°C, 10.9 kbar, 5 h)</td>
<td>1.4</td>
<td>1.35</td>
<td>0.045</td>
</tr>
</tbody>
</table>

(650 °C, 10.9 kbar, 5 h), compared to that of sample A\textsubscript{o}. Notice that in the A\textsubscript{5} and A\textsubscript{6} samples, besides the presence of TDS, which are much less than in sample A\textsubscript{2}, small oxygen precipitates are expected to form. As a result, Si\textsubscript{I} are injected during the precipitation process, and some of them are trapped at the Si/SiO\textsubscript{x} interface [20]. Thus, the decrease in the VO concentration could be attributed to the destruction of the VO defects by mobile Si\textsubscript{I} liberated from the Si/SiO\textsubscript{x} interface during irradiation (VO + Si\textsubscript{I} $\rightarrow$ O\textsubscript{1}). This is supported by the fact that the difference ([O\textsubscript{1}]\textsubscript{after HTHP} - [O\textsubscript{1}]\textsubscript{after irr.}) is less in samples A\textsubscript{5} and A\textsubscript{6} than in the untreated sample A\textsubscript{o} (see table 1), indicating that some of the oxygen atoms were restored during irradiation at interstitial sites, for pre-treatments at 600 and 650 °C.

We shall secondly deal with the interaction, if any, between thermal defects and radiation-induced defects during thermal anneals. Figure 1 depicts the evolution of the various V\textsubscript{m}O\textsubscript{n} defects in these samples. For comparison purposes the evolution of these defects in an as-received sample is also shown. As is seen from figure 1(a), the maximum intensity of the VO\textsubscript{2} defect in the 450 °C pre-treated sample is significantly lower than that in the as-received sample. This may be taken as an indication that the VO defect participates in additional reactions besides its normal conversion reaction to the VO\textsubscript{2} defect (VO + O\textsubscript{1} $\rightarrow$ VO\textsubscript{2}). Because of the presence of thermal double donors (TDDs) an interaction between them and the VO defects cannot be excluded. Such an interaction has been proposed previously [22], although a direct experimental verification does not exist so far. As a consequence of the lower VO\textsubscript{2} concentration in the 450 °C pre-treated sample, the maximum intensities of the VO\textsubscript{1} LVM bands are also lower than those in the as-received samples. On the other hand, in the 600 and 650 °C pre-treated samples (figure 2(a)) the maximum intensity of the VO\textsubscript{2} signal is approximately equal to that of the as-received samples. It is well-known that heat treatments of short time duration at 650 °C destroy any TDDs present in the material due to the growth process. Moreover, longer time treatments or short time treatments coupled with high hydrostatic pressure (higher than 10 kbar) stimulate [3] the oxygen precipitation process together with the formation of another family of thermal donors, the so-called new thermal donors (NTDs), which have a different structure [21] than that of the TDDs. Our results indicate that any interaction between the VO defects and the thermal defects formed at 600 and 650 °C does not take place. However, it may be argued that since the concentration of the thermal defects induced upon treatments in the latter temperatures is not high enough, it is possible that any complex between them and the radiation defects is not detected in the IR spectra. It is also possible that any such complex that presumably forms may be IR inactive and therefore its presence remains undetected in the IR spectra. One way to resolve this issue is to monitor the intensity of the various defects formed during the isochronal annealing steps in the differently pre-treated samples and compare the results.

In table 2 the percentage of the VO defects converted to the VO\textsubscript{2} defects is given. Notice that in the A-centre the intensity of the 828 cm\textsuperscript{-1} band corresponds to the vibrations of the single oxygen atom of the defect. However, in the case of the VO\textsubscript{2} defect the intensity of the
887 cm\(^{-1}\) band corresponds to the contribution of the vibrations of the two oxygen atoms that share a common vacancy site and vibrate independently. This means that if all the VO centres were converted to the VO\(_2\) defects the corresponding amplitude of the latter should be twice as that of the former. In other words, the calibration factor of the VO\(_2\) defect is only half that of the VO defect. If \(N_{\text{VO}}\) and \(N_{\text{VO}_2}\) are the concentrations and \(\alpha_{\text{VO}}\) and \(\alpha_{\text{VO}_2}\) the calibration
factors of the VO and the VO₂ defects respectively, then the concentration ratio of the two defects would be

\[
\frac{N_{\text{VO}_2}}{N_{\text{VO}}} = \frac{h_{\text{VO}_2} \cdot a_{\text{VO}_2}}{h_{\text{VO}} \cdot a_{\text{VO}}} = \frac{h_{\text{VO}_2} \cdot a_{\text{VO}}}{2 \cdot h_{\text{VO}}} = \frac{1}{2} \frac{h_{\text{VO}_2}}{h_{\text{VO}}}
\]

(1)

where \( h_{\text{VO}} \) and \( h_{\text{VO}_2} \) are the amplitudes of the VO and the VO₂ peaks in the spectra. In this approximation, the ratio of the integrated intensities of the two bands were taken equal to the ratio of the corresponding amplitudes in the spectra.

Thus, from the evolution curves presented in figures 1(a) and 2(a) it is concluded that the reaction channel \( \text{VO} \xrightarrow{450 \degree C} \text{VO}_2 \xrightarrow{450 \degree C} \text{VO}_3 \) is affected by the HP pre-treatment at 450 °C, where...
Table 2. The maximum amplitudes of the VO and the VO$_2$ defects and the corresponding percentage of the VO $\rightarrow$ VO$_2$ conversion for the HTHP pre-treated Si samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>VO max</th>
<th>VO$_2$ max</th>
<th>VO $\rightarrow$ VO$_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_0$ (as-received)</td>
<td>0.0647</td>
<td>0.0493</td>
<td>38</td>
</tr>
<tr>
<td>$A_2$ (450$^\circ$C, 10.5 kbar, 5 h)</td>
<td>0.0685</td>
<td>0.0374</td>
<td>27.4</td>
</tr>
<tr>
<td>$A_5$ (600$^\circ$C, 12 kbar, 5 h)</td>
<td>0.0586</td>
<td>0.0425</td>
<td>36.3</td>
</tr>
<tr>
<td>$A_6$ (650$^\circ$C, 10.9 kbar, 5 h)</td>
<td>0.0596</td>
<td>0.046</td>
<td>38.6</td>
</tr>
</tbody>
</table>

thermal donors are present in the samples. The evolution curves of the VO$_2$ and VO$_3$ defects for the 600 and 650$^\circ$C HP pre-treated samples have no significant changes in comparison with the untreated sample. The argument presented above about an interaction between TDs and the VO defect holding for the sample pre-treated at 450$^\circ$C, but not for the samples pre-treated at 600 and 650$^\circ$C, is further supported by the fact that in the former case the sample $A_2$ has much higher concentration of TDs ($8 \times 10^{15}$ cm$^{-3}$) than that in the latter case of the samples $A_5$ and $A_6$ where the TDs concentration was $2 \times 10^{14}$ cm$^{-3}$. On the other hand the intensities and generally the evolution of the V$_2$O, V$_2$O$_2$, V$_3$O$_2$ bands (figures 1(b) and 2(b)) are approximately the same in all samples, indicating that these defects seem not to be affected by the pre-treatments at 450, 600 and 650$^\circ$C.

By inspection of the evolution curves of the VO defect (figures 1(a) and 2(a)) of our samples, it is seen that the annealing temperature of the defect is lower in samples $A_2$, $A_5$ and $A_6$, pre-treated under HP than that of the untreated sample $A_0$. Notice that two main reactions participate [23, 24] in the annealing process of the VO defect, that is VO $+ O_i \rightarrow$ VO$_2$ and VO $+ S_{ii} \rightarrow$ O$_i$. In the case of the untreated sample $A_0$, sources of the $S_{ii}$ are considered [25] large defect clusters. In the case of the pre-treated samples $A_5$ and $A_6$ where precipitates form there is an additional source of Si at the Si/SiO$_x$ interface. In the sample $A_2$ pre-treated at 450$^\circ$C under HP, some small precipitates are also expected to form. It has been reported [26] that pre-heat treatments at 600$^\circ$C cause a decrease in the annealing temperature of the VO defect. The phenomenon was attributed to the agglomeration of $S_{ii}$ at the Si/SiO$_x$ interface, which upon liberation lead to the destruction of the VO defect according to the reaction VO $+ S_{ii} \rightarrow$ O$_i$. We argue, therefore, that in our case the annealing temperature of the VO defect occurs in the HP pre-treated samples at a lower temperature, due to the liberation of the trapped $S_{ii}$ from the Si/SiO$_x$ interface. Understandably, the reaction VO $+ S_{ii} \rightarrow$ O$_i$ is triggered earlier than that in the initially untreated sample, resulting in the decay of the VO band in the spectra at a lower temperature.

Figures 1(c) and 2(c) show computer deconvolution, by using Lorentzian profiles, of the frequency range in the spectra around the A-centre band, for temperatures above 400$^\circ$C. In doing Lorentzian profiles, we have allowed for different values of the half widths in the deconvolution process of the VO band so that the best fit of the corresponding IR spectrum is obtained. As a result, we have obtained different values of the half widths of the same bands in different samples. However, the relative variation of the half widths was not so large as to affect the peak amplitudes of the bands significantly. As is seen from figures 1(c) and 2(c), the total A-centre band contains the contribution of four individual bands. As mentioned above, three of them, that is the 839 cm$^{-1}$ band (V$_2$O), the 833 cm$^{-1}$ band (V$_3$O$_2$) and the 824 cm$^{-1}$ band (V$_2$O$_2$), have been previously detected [19] and studied. In this work, detailed Lorentzian analysis revealed the presence of an additional satellite band at 842 cm$^{-1}$. Its thermal evolution is also presented in figures 1(b) and 2(b). As is seen, the band appears around $\sim$350$^\circ$C and persists in the spectra up to $\sim$450$^\circ$C. The defect is present in the spectra in a temperature
range which is approximately the same with that previously reported [27], from EPR studies, for the V$_3$O$_3$ defect. On the other hand, recent measurements [28] making use of positron lifetime and coincidence Doppler broadening techniques have concluded that when VO centres anneal out they lead to the formation of more stable larger complexes, the V$_3$O and the V$_4$O$_2$ defects. However, the V$_3$O defect has been correlated [29] with another band at 887 cm$^{-1}$. Notice, in addition, that multivacancy–multioxygen centres, such as the V$_3$O$_3$ and the V$_4$O$_2$ structures, are expected to form in heavily irradiated material. Thus, we tentatively correlate the 842 cm$^{-1}$ band with either the V$_3$O$_3$ or the V$_4$O$_2$ structure in neutron-irradiated silicon. More work is needed in order to establish a more definite attribution.

4. Conclusions

The effect of the HTHP pre-treatments on the production and evolution of the radiation-induced oxygen-related defects in Cz-grown Si material was investigated. During irradiation no interaction between thermal donors and VO defects was found, although an indirect interaction between oxygen precipitates and VO defects was inferred. During thermal annealing the reaction channel VO$^{\text{O}_i}$ $\rightarrow$ VO$_2$ $\rightarrow$ VO$_3$ was found to be affected by the HP pre-treatments at 450 $^\circ$C. In that case, the concentrations of the VO$_2$ and the VO$_3$ defects are lower than that of the as-received material. The phenomenon was tentatively attributed to the interaction between thermal donors and VO centres. Interestingly enough, the concentrations of the VO$_2$ and VO$_3$ defects were not affected by the HTHP pre-treatments at 600 and 650 $^\circ$C, where other kinds of donors and thermal defects are produced, which apparently do not interact with the VO centres. Additionally, we found that the thermal evolution of the V$_2$O, V$_3$O$_2$ and V$_3$O$_2$ defects is not affected by any of the above pre-treatments. Furthermore, a band at 842 cm$^{-1}$ was detected and tentatively correlated with either the V$_3$O$_3$ or the V$_4$O$_2$ structure in neutron-irradiated silicon.

Acknowledgment

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References

IR studies of defects in irradiated Si heat-treated under hydrostatic pressure