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Phys. Status Solidi A **208**, No. 3, 616–619 (2011) / **DOI** 10.1002/pssa.201000101

physica status solidi a
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applications and materials science

The effect of neutron irradiation on oxygen aggregation processes in Si material treated under hydrostatic pressure

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Received 14 April 2010, revised 20 May 2010, accepted 2 September 2010
Published online 10 December 2010

Keywords neutron irradiation, oxygen, pressure, silicon

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Silicon is the dominant material in electronic industry. Its use for various applications requires processing stages, important among them those involving thermal treatments. Such treatments in Si trigger the mechanisms of oxygen aggregation resulting in the formation of oxygen precipitates which have important influence on the quality of the material. In the present work, we have investigated the effect of thermal treatments, with or without the application of high hydrostatic pressure, on the development of oxygen precipitates. We have particularly studied the effect of neutron irradiation on the formation of the various oxygen agglomerates in the course of the above treatments. To this end, Si samples initially irradiated by neutrons were subjected to high temperature or/and high temperature-high pressure treatments at 1000 and 1130 °C. Afterwards, infrared (IR) measurements were undertaken to study various precipitate morphologies, in particular those giving rise to an IR band around 1080 cm^{-1} related to octahedral-shaped precipitates and an IR band at 1225 cm^{-1} attributed to platelet-shaped precipitates. The obtained results were found to be consistent with reports cited in the literature. It was confirmed that the application of pressure during treatments as well as the irradiation with neutrons before these treatments enhance substantially the oxygen aggregation process. Comparisons of the results between treatments at 1000 and 1130 °C are presented and discussed.

1 Introduction Undoubtedly, silicon is by far the most important semiconductor material, taking into account the manifold of its applications in electronic industry. Since the defects and impurities play an important role in the behavior of materials, reasonably their control is more than necessary. This control however, requires the full understanding of their nature and properties. In this sense, oxygen which is the main impurity in silicon attracts particular interest. An important stage in silicon material processing is thermal treatments. In this process, oxygen atoms begin to aggregate leading to the formation of thermal donors (TDs) at relatively low temperatures in the range of 350–550 °C and to oxygen precipitates at higher temperatures, approximately above 700 °C [1–6]. These oxygen aggregates have mainly detrimental but also beneficial effects in terms of electrical and mechanical properties of silicon wafers [6]. In order to control these defects a full understanding of their properties and behavior is required. The interdependence of material quality and device performance in one hand and the physical understanding on the other has led to considerable advances on the oxygen impurity in Si and especially on issues concerning oxygen agglomeration mechanisms and processes. Nonetheless, some points have not been completely studied and understood.

Pressure besides temperature, is another important parameter used widely not only in semiconductor physics but generally in solid state physics. It has been proven a valuable tool in investigating the complexities arisen in material processing for various applications, but also in assisting researchers to understand various solid state phenomena [7–10]. In the case of silicon, the application of pressure for exploring the properties and behavior of defects is a common procedure. It has been found for example that external hydrostatic pressure enhances TDs formation and oxygen precipitation as well [11, 12], helping in understanding the mechanisms involved in the production of these defects.

Importantly, other stages of silicon material processing employ implantations or/and irradiations. As a result, new defects are introduced which affect the properties of silicon. Even more, they influence the production and behavior of the thermally-induced defects and *vice versa*. Importantly, the irradiation of Cz-Si leads to the formation of the well-known vacancy-oxygen (VO) defect. Upon annealing at higher temperatures various VO_n defects $2 \leq n \leq 6$ form [13, 14]. Members of this family, for example the VO_2 [15] and VO_4 [16] defects have been considered to act as nucleus for the formation of oxygen precipitates.

In some of our previous works [17–19] we have dwelled upon the issue of the interactions between thermal and radiation defects in silicon. In the present paper, as a continuation of those efforts, we explore the effect of neutron irradiation of silicon material on the development of oxygen precipitates produced by thermal treatments with the application of hydrostatic pressure.

2 Experimental details Three groups of samples with initial oxygen concentration of $[O_i] = 1.1 \times 10^{18}\,cm^{-3}$ and carbon concentration $[C_s] < 1 \times 10^{16}\,cm^{-3}$ were used. All the samples were boron-doped (p-type) with initial carrier concentration (holes) $\sim 3 \times 10^{14}\,cm^{-3}$. The first group contains two samples (T_{21}, T_{31}) subjected to thermal treatments at 1000 and 1130 °C correspondingly, at atmospheric pressure (HT). The second group of samples (T_{22}, T_{32}) was subjected to thermal treatments at 1000 and 1130 °C correspondingly, with the application of high hydrostatic pressure of ~11 Kbars (HTHP). The third group (T_{23}, T_{33}) of samples was initially irradiated by 5 MeV fast neutrons at ~50 °C and then the samples were subjected to the same HTHP treatment as those of the second group, correspondingly. Another sample (T_{24}) initially irradiated by neutrons was subjected to treatment at 1000 °C at atmospheric pressure (HT). All the information about treatments is cited in Table 1. The samples were investigated by infrared (IR) spectroscopy. After the treatments the IR spectra of the samples were recorded at room temperature by means of an FT-IR spectrometer.

Table 1 Amplitudes of the oxygen precipitate peaks at 1080 and 1225 cm^{-1} for the used samples.

samples	treatment T (°C), t (h), P (kbar)	1080 cm^{-1} Abs. (a.u.)	1225 cm^{-1} Abs. (a.u.)
T_{21}	1000, 5, 10^{-3}	0.073	–
T_{22}	1000, 5, 11	0.035	0.014
T_{23}	n.irr. + 1000, 5, 11	0.042	0.029
T_{24}	n.irr. + 1000, 5, 10^{-3}	0.091	0.019
T_{31}	1130, 5, 10^{-3}	0.026	–
T_{32}	1130, 5, 11	0.047	–
T_{33}	n.irr + 1130, 5, 10.7	0.055	–

3 Experimental results and discussion Figure 1 shows IR spectra in the region around the 1107 cm^{-1} band of oxygen interstitial (O_i) [1, 2] for the sample (T_{21}) treated at 1000 °C at atmospheric pressure (a), for the sample T_{22} treated at 1000 °C under hydrostatic pressure (b), as well as for samples initially irradiated by fast neutrons and then submitted to thermal treatment at 1000 °C either under high hydrostatic pressure, sample T_{23} (c), or at atmospheric pressure, sample T_{24} (d). As a consequence of the thermal treatments the shape of the O_i band is distorted due to the appearance in the spectra, in the same frequency range, of other bands related to oxygen precipitates. The contribution of each constituent band could be revealed by computer deconvolution using Lorentzian profiles [5]. Deconvolution shows the existence of two subbands at ~1080 and 1225 cm^{-1} in the spectra. (We notice at this point that while

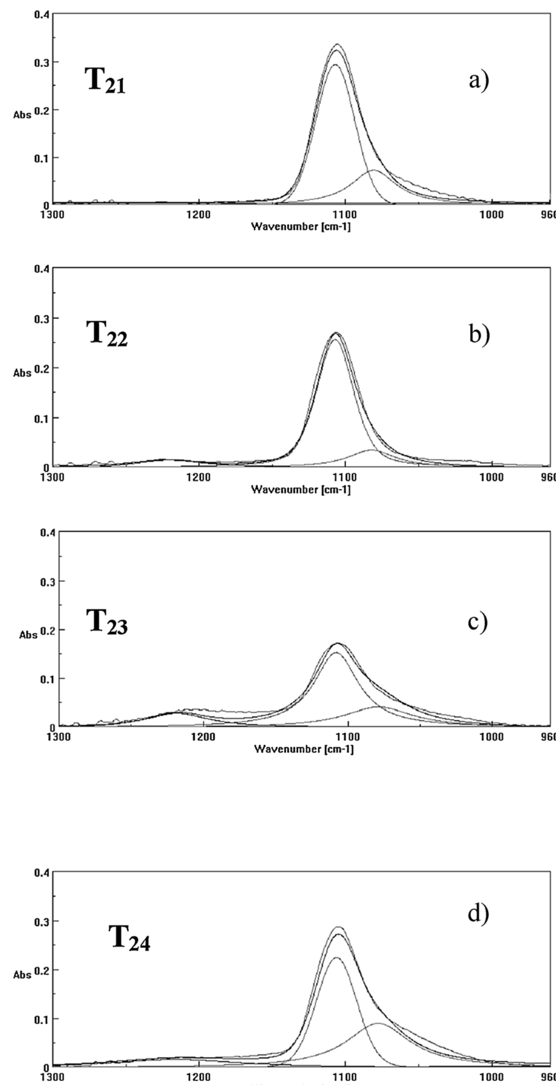

Figure 1 Deconvolution of the oxygen interstitial region IR bands into Lorentzian profiles at 1000 °C HT (a) at atmospheric pressure, (b) at 11 kbar, (c) firstly irradiated and then treated at 11 kbar, and (d) firstly irradiated and then treated at atmospheric pressure.

the deconvolution of the IR absorption spectra in the region of O_i peak can lead to numerous IR subbands [1, 2, 5], in the present work we are dealing with the most intensive ones. Generally, the band centered around 1080 cm^{-1}, is most possibly related to amorphous SiO_x precipitates [2] preferentially in octahedral shape [2, 20], which corresponds to the minimum surface energy of the precipitate structure. The other band, at 1225 cm^{-1}, is most possibly related to platelet-shaped precipitates [21] or more generally to discoidal precipitates [22]). We firstly observe that for the 1000 °C HT at atmospheric pressure only the 1080 cm^{-1} band is present (Fig. 1a). Secondly, we observe that the application of HP at this temperature results in the emergence in the spectra of another band at 1225 cm^{-1} (Fig. 1b) indicating the simultaneous formation at 1000 °C of two different precipitate morphologies. The relative decrease of the amplitude of the 1080 cm^{-1} band related to octahedral precipitates may be taken as an indication that HP favors the precipitation of oxygen in the form of platelets (1225 cm^{-1} band) as well. Additionally, we observe that in samples initially irradiated with neutrons the intensity of both type of precipitates increases (Fig. 1c). This confirms previous conclusions [17] that neutron irradiation produces specific nucleation centers for the subsequent oxygen precipitation. It is important to note that the initial neutron irradiation of samples subsequently subjected to a HT treatment at 1000 °C, but at atmospheric pressure, results in a higher content of octahedral precipitates, although it results to intermediate content of platelets ones (Fig. 1d). Figure 2 is the corresponding of Fig. 1 but for treatments at 1130 °C. An essential difference between the two figures is the absence in Fig. 2 of the 1225 cm^{-1} band related to platelet-shaped precipitates. This behavior may be associated with the tendency of oxygen at higher temperatures to form octahedral precipitates. In fact, thermodynamic arguments and experimental observations [23, 24] suggest that for temperatures above 950 °C the precipitates take the shape with the minimum surface energy and preferentially that of an octahedron. Figure 3 is a schematic representation of our IR results (summarized in Table 1) depicting the intensities of the bands at 1080 and 1225 cm^{-1} after the various treatments at 1000 and 1130 °C, correspondingly. Comparisons of the variations of the intensities of the 1080 cm^{-1} band between the above two treatments show some interesting phenomena. Three salient points are of concern to us. Firstly, we observe that the intensity of octahedral (1080 cm^{-1}) precipitates at 1130 °C is lower in comparison to that at 1000 °C for HT processing, possibly because of the lower supersaturation of interstitial oxygen and even the more pronounced Ostwald ripening effect. Secondly, we observe that the application of pressure at 1130 °C leads to an increase of the intensity of the 1080 cm^{-1} band, indicating that more octahedral precipitates form. This is possibly because more nucleation centers are surviving the Ostwald ripening effect, while some additional nucleation centers are created due to the action of the high pressure. However, in the case of thermal treatments with the application of HP at 1000 °C, the competition between the Ostwald ripening effect and the additional provision of nucleation sites due to the application of pressure leads to a final decrease of the octahedral precipitates. Thus, the temperature of the treatment plays a crucial role in the amount of the octahedral precipitates that form when high pressure is applied. Thirdly, we observe that the irradiation of the samples with neutrons prior to the HTHP processing

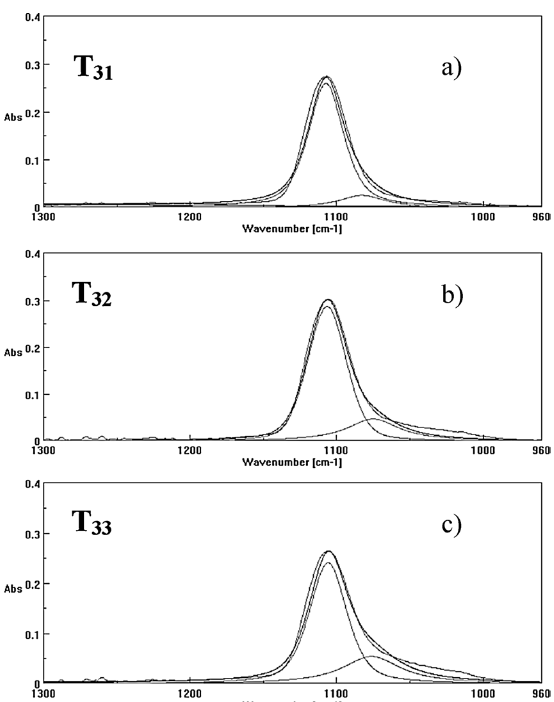

Figure 2 Deconvolution of the oxygen interstitial region IR bands into Lorentzian profiles at 1130 °C HT (a) at atmospheric pressure, (b) at 11 kbar, and (c) firstly irradiated with fast neutrons and then treated at 10.7 kbar.

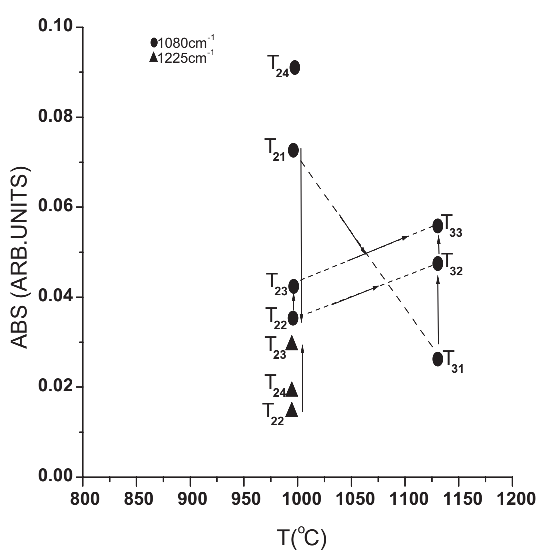

Figure 3 The intensity of the precipitate peaks at 1080 and 1225 cm^{-1} for the samples used.

introduces additional nucleation centers leading to the formation of more octahedral precipitates, a fact which is manifested in the spectra by the higher intensity of 1080 cm^{-1} band, both for the 1000 and 1130 °C treatments.

4 Conclusions We have studied the combining effect of neutron irradiations and thermal treatment with or without the application of high hydrostatic pressure on the formation of oxygen precipitate in silicon. It was found that in non-irradiated silicon thermal treatments at 1000 °C lead to the formation of both octahedral and platelet precipitates. The application of pressure at this temperature leads to a decrease of the octahedral precipitates. Thermal treatments at 1130 °C are not followed by the formation of the platelets precipitates. However, the application of pressure at this temperature leads to an increase of the octahedral precipitates. This behavior is the opposite to that observed for treatments at 1000 °C. The phenomenon was discussed in terms of the (i) effect of pressure on the Ostwald ripening effect and (ii) the provision of additional nucleation centers by the pressure itself, the net result being different between treatments at 1000 and 1130 °C. Importantly, the initial irradiation by neutrons of samples subsequently subjected to HTHP treatments at 1000 and 1130 °C enhances the formation of octahedral precipitates in agreement with previous reports that irradiation provides nucleation sites for oxygen precipitation.

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