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The production of vacancy-oxygen defects in electron-irradiated Cz-Si initially treated at high temperatures and high pressures

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Abstract. We report studies of defects in electron-irradiated Czochralski-grown silicon (Cz-Si) subjected to thermal treatments at 1000°C and 1130°C with or without the application of high hydrostatic pressure of ~ 11 Kbars, prior to irradiation. The work is primarily focused on the impact of the pre-treatments on the production rate of the VO defect and its conversion to the VO_2 defect. To this end, IR spectroscopy measurements were carried out and the amplitudes of the VO band (830 cm^{-1}) and the VO_2 band (888 cm^{-1}) were monitored in the course of an isochronal anneal sequence up to ~ 550°C. Thermal treatments at 1000°C result in a reduction of the production rate of the VO defect. This rate however increases when pressure is applied during the treatment. The opposite behavior is observed for thermal treatments at 1130°C. The production rate of the VO increases slightly in heat treated samples but decreases substantially when high pressure is applied. Similar trends show the conversion of the VO to the VO_2 defect for the corresponding treatments. The results are discussed taking into account the oxygen precipitates formed at the various treatments and their impact on the amount of primary defects available during irradiation which affects the production of the vacancy-oxygen defects.

Introduction

The presence of defects in a material affects mostly in the negative but also in the positive way the technologically related properties and generally the behavior of this material. The study of defects is needed both for understanding the physics of the material but also to enable industry to improve the performance, the reliability and the durability of the corresponding devices. Especially for semiconductors, defect control and defect engineering is an important branch of electronic technology.

Nowadays, silicon is the basic material for modern electronic technology. Its use for certain applications always requires a number of processing stages, among them thermal treatments at characteristic temperatures as well as implantations or irradiations. Both processes generate defects. As regards thermal treatments, depending on the used temperature, they introduce in Si various kinds of thermal defects as for example thermal donors, new thermal donors, oxygen precipitates, etc. We note that in the temperature range 900-1200°C, very important and crucial for technological purposes operations take place, for instance diffusion, oxidation and transmutation doping processes. The main defects formed in Cz-Si at these temperatures are oxygen precipitates, dislocation loops, stacking faults and other structural defects. These defects usually interact with primary defects, that is vacancies and self-interstitials.As a result, the formation of impurity-

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vacancy and impurity-interstitial pairs, their concentration and behavior is affected. Additionally, thermal treatments are extensively used in the course of device fabrications to change the ability of some impurities to capture primary defects, with the scope to control and improve the quality of the material for certain applications.

Besides temperature, pressure is an important parameter in semiconductor technology. For instance since the semiconductor gap can be changed by pressure and temperature, both parameters are used in the so-called field of “band gap engineering” with many applications in the electronic industry. Without doubt pressure is a precious tool for studying various phenomena in Semiconductors and generally in Solid State Physics. Pressure introduces changes in the bond lengths and angles of a squeezed material, induce changes in its electrical, optical, mechanical and structural properties [1].Furthermore, pressure either hydrostatic or uniaxial has a wide range of applications in getting insight into the properties of solids [2,3,4,5]. In Cz-Si, the application of pressure in the course of thermal treatments enhances the formation of thermal donors and oxygen precipitates [6,7,8].

As regards irradiations, the most important defect formed in Cz-Si, besides divacancy, is the vacancy-oxygen pair (VO), the so-called A-center .Oxygen is the main trap for vacancies in Cz-Si. Thus mobile vacancies produced in the course of irradiation and avoided annihilation by self-interstitials, are readily captured by oxygen impurities to form the A-center. The defect introduces a well known acceptor level E_C-0.17eV in the energy gap and therefore affects the behavior of the corresponding devices. In particular affects the carrier lifetime as well as the effective carrier concentration .These parameters are of high interest for the Si-based electronic technology. In the neutral charge state the center give rise to a LVM band in the IR spectra at ~ 830 cm^{-1}.It is stable up to 300°C.At these temperatures the 830 cm^{-1}band begins to decay in the spectra accompanied by the emergence of another band at 888 cm^{-1}attributed to the VO_2 defect. The latter defect forms [9,10] mainly when mobile VO centers are captured by oxygen interstitial atoms (VO+ $O_i \rightarrow VO_2$).The major purpose of this work is to study the impact of high temperature treatments with or without the application of pressure on the production of the VO defect and its conversion to the VO_2 defect.

Experimental details

In this study, Cz-Si material was initially subjected either to high temperature (HT) treatments at 1000°C or 1130°C, or to high temperature-high pressure (HT - HP) treatments at the same temperatures correspondingly, with the application of ~ 11 Kbars. The HT and HT - HP treatments were performed in argon atmosphere and their duration was 5h. Details of the HT and HT-HP treated samples are cited in table 1. The initial oxygen concentration $[O_i]_o$ of all samples was 6.5•$10^{17}$$cm^{-3}$ and it was found by measurements of the 1107 cm^{-1} band using [11] a calibration coefficient of 3.14•10^{17} cm^{-2}. Since carbon impurity, when present, participates in the formation of many radiation defects [12,13] thus complicating the results, we selected samples with initial carbon concentration below 1•$10^{16}$$cm^{-3}$.The material was doped with Ge at ~ 7•$10^{17}$$cm^{-3}$.After the treatments the samples were irradiated with 2 MeV electrons at a dose of 5•$10^{17}$$cm^{-2}$ using the Dynamitron accelerator at Takasaki-JAERI (Japan).The temperature of irradiation was ~ 95°C.Isochronal anneals were carried out after the irradiation up to ~ 550°C, in ~ 10°C steps and 20 min duration. After each annealing step the IR spectra were recorded at room temperature.

Experimental results and discussion

Fig.1 shows the IR spectra of the initially untreated A_0 sample prior to irradiation, after irradiation and at 400°C in the course of the isochronal anneal sequence. Initially only the 1107cm^{-1} band of O_i is present. After the irradiation the well-known band at 830 cm^{-1} of the VO defect appears in the spectra. At 400°C this band has disappeared and a band at 888 cm^{-1} of the VO_2 defect is now present in the spectra. The IR spectra of the other samples are similar to the Fig.1 but with different

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amplitudes of the bands. Fig.2 shows the evolution of the VO and VO_2 defects in the spectra. Fig.3 shows the evolution of the VO and VO_2 defects for the HT and HT-HP treated samples. We shall mainly focus on the production of the VO defect and its conversion to the VO_2 defect. Values of the [VO], the production rate η_{VO} (that is the concentration of the VO defect divided by the irradiation dose) and the $[VO]_2$/[VO] conversion ratio for the various pre-treatments are given in Table 1. The calibration coefficient of the 830 cm^{-1} band of the VO defect was taken [14] as $6.25 \cdot 10^{16}$ cm^{-2}.

Concerning the calibration coefficient of the 888 cm^{-1} band of the VO_2 defect was taken [15] as half of that of the VO defect. Figs. 4 and 5 show the spectral region of the 1107 cm^{-1} band of the oxygen interstitial after the various treatments of the samples at 1000°C and 1130°C correspondingly, as well as after irradiation. As a result of the treatments the band is modified due to the formation of SiOx precipitates [16]. Lorentzian deconvolution -Figs 4 and 5- shows various contributing bands. Their amplitudes are changed and their position in the spectra is shifted depending on the initial treatment. These bands originate from various shapes and morphologies of oxygen precipitates. The band at about 1060 cm^{-1} could be attributed to needle-like precipitates [17]. The band at about 1090 cm^{-1} is generally attributed to spheroidal-like precipitates [18,19], although the band at about 1120 cm^{-1} could be attributed to platelet-like or/and polyhedral-like precipitates [16,20]. It should be noted at this point that the presence of Ge at relative low

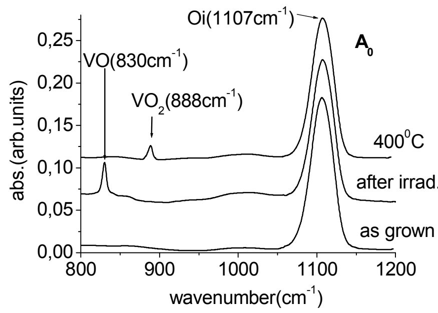

Fig.1 Characteristic IR spectra of A_0 sample.

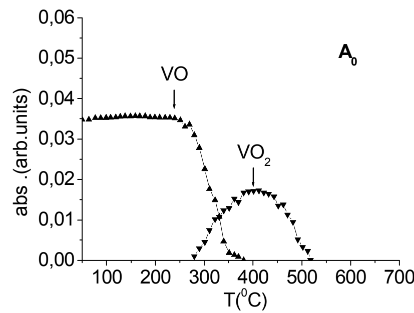

Fig.2 Thermal evolution of VO and VO_2 defects of A_o sample

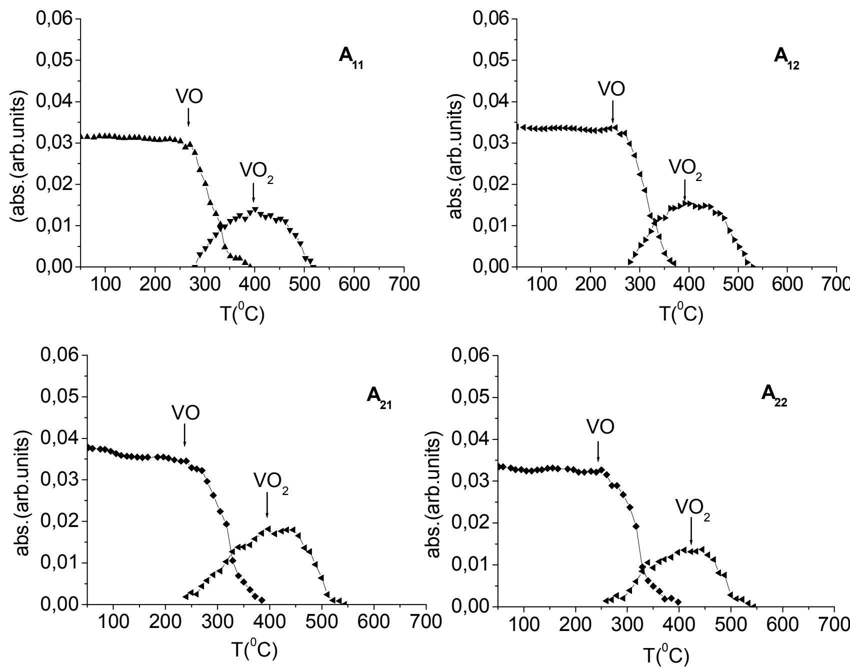

Fig. 3 Thermal evolution of VO and VO_2 defects of the used samples

sample	[VO] $10^{16}(cm^{-3})$	η_{VO} (cm^{-1})	$[VO]_2$ $10^{15}(cm^{-3})$	$\frac{[VO_2]}{[VO]}$
A_0 (as grown)	2,45	0.049	5.88	0.24
A_{11}(1000°C,5h,1bar)	2,30	0.046	4.83	0.21
A_{12}(1000°C,5h,11kbars)	2,43	0.048	5.35	0.22
A_{21}(1130°C,5h,1bar)	2,50	0.050	6.25	0.25
A_{22}(1130°C,5h,11kbars)	2,39	0.048	4.78	0.20

Table 1 Treatments parameters, [VO] and $[VO]_2$/[VO] ratio.

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concentrations, as for instance in our case where [Ge] $=7\cdot10^{17}$ cm^{-3}, does not affect oxygen precipitation. It has been found [21] that for such Ge-doped Cz-Si marerial subjected to HT-HP treatments up to 1130°C with pressures up to 11Kbars for 10h, the oxygen related aggregation processes in Si are quite similar with those in Ge-free Cz-Si, material. Fig.6 exhibits the concentration of the VO defect versus treatments. Fig. 7 exhibits the $[VO]_2/[VO]$ defects ratio versus the various pre-treatments, correspondingly. As it is observed from Fig.5 and the data cited in Table I, the concentration of the defect is decreased in the HT sample at 1000°C in comparison with that of the untreated one, although the concentration of VO increases when pressure is applied taking a value practically equal to that of the untreated sample. However, in the case of heat treatments carried out at 1130°C, the production of the VO defect is different. Its concentration is slightly higher than that of the untreated sample. When high pressure is applied the concentration of the VO defect decreases substantially. It is well-known that the formation of oxygen precipitates in silicon is accompanied by the liberation of self-

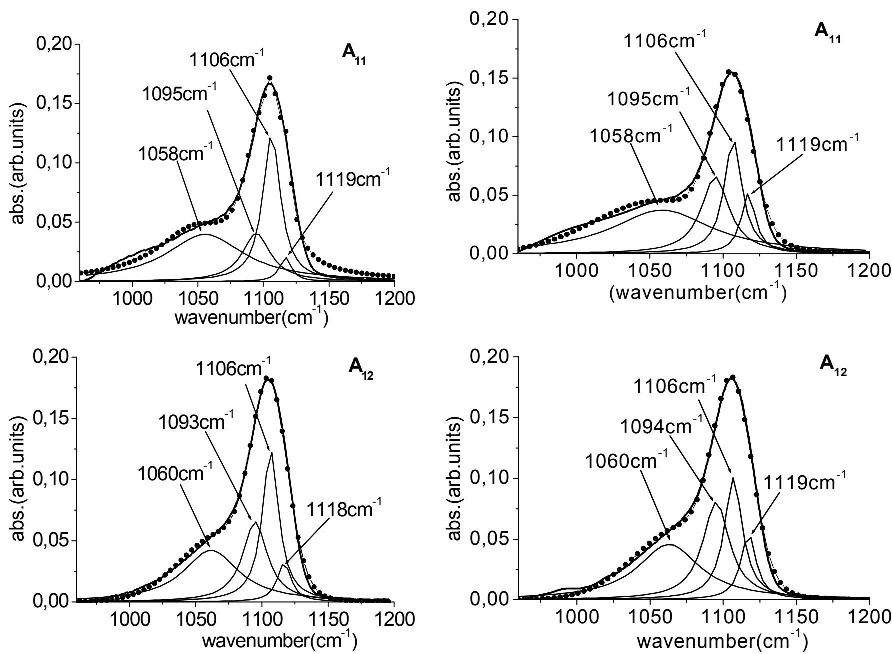

Fig. 4 Deconvolution of the O_i band spectral range after treatments at 1000°C (left column) and after irradiation (right column)

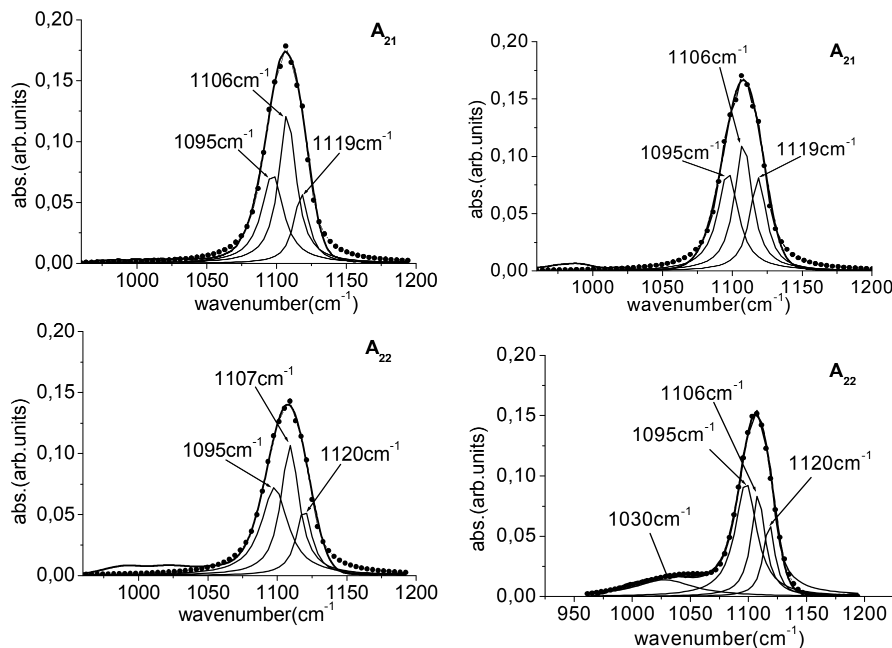

Fig. 5 Deconvolution of the Oi band spectral region after treatments at 1130°C (left column) and after irradiation (right

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interstitials [16]. Moreover for temperature about 850°C dislocations are formed near the precipitates [22].Thus the interface region between the Si matrix and the oxygen precipitate Si/SiOx is a reservoir of self-interstitials. The binding of the Si_I's at this region depends on the size and the morphology of the precipitates which in turn depends on the temperature, the application or not of hydrostatic pressure during the treatments and their duration. In the course of irradiation, vacancies and self-interstitials are produced. Those vacancies that survive annihilation ($V+Si_I \rightarrow Ø$), react mainly with oxygen to form VO defects. However, in the course of irradiation, Si_I's from the Si/SiOx interface region could be liberated. These Si_I's react with vacancies reducing the number of them available for capture by O_i impurity atoms. Thus the production of the VO defects is decreased. Furthermore the production rate of the VO defect may decrease due to the destruction of the VO defects by Si_I's ($VO+Si_I \rightarrow O_i$).Additionally it has been argued [23] that the presence of impurity-defect clusters, which are not specified, can affect the balance of available vacancies and Si_I's in a crystal thus influencing the production of the VO defect. These impurity-defect clusters introduce anisotropic elastic fields in the material which attract vacancies and Si_I's preventing them from participating in other reactions. Thus in the case of a sample subjected to HT at 1000°C the production of the VO defect decreases in comparison with the initially untreated sample (Fig.6). The application of pressure at this temperature seems to reduce the number of available Si_I's from the Si/SiOx region leading to an increase of the VO defects. In the case of a sample subjected to HT at 1130°C the production of the VO defect is practically unaffected by the treatment. Notice that the O_i spectral region is more or less symmetric (Fig.5). It seems that due to the number and shape of the precipitates formed in this case the contribution of Si_I's emanated from the Si/SiOx interface region is less important. Notice, that when the temperature of the HT treatment increases the binding energy of the Si_I's at the interface is expected to be lower [24]. The application of pressure at 1130°C allows conditions at the interface that increase the availability of Si_I's in the course of irradiation, leading to a reduction of the VO production (Fig.6). We should notice that the idea of interaction between thermal and radiation defects has been discussed in the literature [25].Obviously, a reaction between precipitates and VO defects cannot be excluded. However, no additional bands in the spectra appear to indicate the formation of any relevant defects. Annihilation of oxygen precipitates during irradiation and subsequent release of O_i atoms also cannot be excluded, especially for the case of HT at 1130°C.

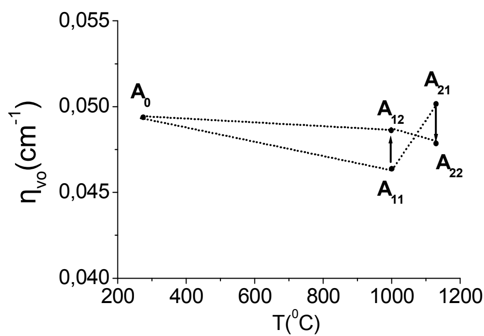

Fig. 6 Production rate of the VO defect versus treatments.

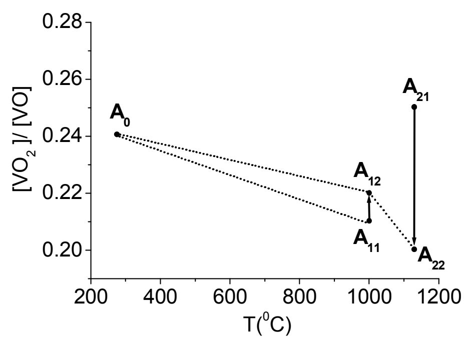

Fig.7 Conversion of the VO to the VO_2 defect versus treatment.

Fig.7 shows the conversion rate of the VO to the VO_2 defect for the various HT and HT-HP pre-treatments. In the course of annealing VO is converted to the VO_2 defect as a result of the reaction $VO+ Oi \rightarrow VO_2$. Previous works [26,27] have verified that the reaction $VO+Si_I \rightarrow O_i$ also occurs in parallel. Evidently the contribution of each of the two reactions in the VO decay determines the concentration of the VO_2 defect. Thus enhancement of the second reaction entails a reduction in the production of the VO_2 defect. In the course of annealing the availability of Si_I's depends on the pre-treatments, as in the course of irradiation. This is in accord with the observation that the VO to the VO_2 conversion versus pre-treatments show similar trends with those of the VO production.

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Summary

Oxygen precipitates introduced in Si by HT and HT-HP treatments have a significant influence on the formation of the VO defect and its conversion to the VO_2 defect. Our data suggest that the release of Si_I's from the Si/SiOx interface affects the production of the VO defect. The amount of these additional self-interstitials depends on the size and morphology of the precipitates which in turn depend on the particular treatment of the material. The conversion of the VO to the VO_2 defect depends on the relative balance of the reactions VO+ Oi→ VO_2 and VO+Si_I→O_i which govern in the annealing of VO defect. The larger the contribution of the latter reaction as a result of release of Si_I's during annealing, the smaller the production of the VO_2 defect due to the former reaction.

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