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LETTER TO THE EDITOR

Vacancy–oxygen complexes produced by 3.5 GeV Xe ion irradiation and their distribution along ion tracks in single-crystal silicon: an infrared study

X G Diao[1,2]**, Y Yoshida**[2,3]**, K Hayakawa**[3]**, F Shimura**[3]**, T Kambara**[2]**, A Iwase**[4] **and Y Yano**[2]

[1] Department of Applied Physics, School of Science, Tianjin University, Tianjin, 300072, People's Republic of China
[2] The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama, 351-0198, Japan
[3] Shizuoka Institute of Science and Technology, Fukuroi, Shizuoka, 437-8555, Japan
[4] Japan Atomic Energy Research Institute (JAERI), Tsukuba, Japan

Abstract
Irradiation of 3.5 GeV Xe ions was performed at room temperature on Czochralski-grown (CZ) and floating zone Si(100) single crystals with different fluences 1.0×10^{12} and 1.0×10^{13} Xe cm^{-2}. All the irradiated samples were investigated by infrared spectroscopy at room temperature. For the first time, vacancy–oxygen (VO) complexes were found experimentally in CZ-Si during high-energy heavy ion irradiation. A depth profile of the IR spectra, the distribution of VO concentration and the interstitial oxygen were successfully obtained along the irradiation depth. The concentration of VO and interstitial oxygen were quantitatively analysed. The effects of electronic excitation and nuclear collision upon the VO production are also discussed in this letter.

Swift heavy ions passing through materials produce defects and produce some tracks remaining in the materials along their trajectories. Those defects and tracks have been apparently observed in most insulators [1], mica [2], metallic glasses [3] and alloys [4], but not in silicon. Irradiation of electrons and neutrons produces point defects in single-crystal silicon. These defects are mainly divacancies in the floating zone (FZ) Si [5–7], mono-vacancy–oxygen (VO) complex and multi-vacancy–oxygen (V_xO_y) complexes in Czochralski-grown (CZ) Si [8, 9]. Among the various defects, divacancy VO and VO$_2$ were most intensively studied and have been determined by infrared (IR) spectroscopy at wavenumbers 2768, 830 and 887 cm^{-1}, respectively. The VO$_2$ defect usually results from annealing effects after irradiation [10]. Low-energy noble gas ion irradiation may produce some kind of damage to the surface of single-crystal silicon by nuclear collision between incident ions and the target atoms [11]. For high-energy ion irradiation, swift ions lose their energy to the materials by electronic excitation and nuclear collision during irradiation, the former being dominant. Many investigations have

been carried out in recent years on the effects of high-energy ion irradiation in single-crystal silicon [12–17]. The efforts were mainly devoted to clarify whether electronic excitation during irradiation is effective in producing defects in Si or not, and to find or observe latent tracks and defects remaining after irradiation using microscopy. The first question has not been solved yet. Moreover, some researchers insist for a confirmation of defects induced by electronic excitation. The second problem is also formidable due to technical difficulties. The difficulties are:

(1) Traditional heat-treatment methods used to make a clean Si surface cannot be used after irradiation for AFM (atomic force microscopy) or STM (scanning tunnelling microscopy) observation because such a treatment may reduce or eliminate the defects. It is inevitable that the irradiated surface of Si is contaminated during the transportation from irradiation to observation.
(2) The fact that high-energy ion irradiation reaches a very deep position in Si (from several to hundreds of microns) makes it impossible for high-resolution transmission electron microscope (HRTEM) to observe a normally irradiated Si sample without any further preparation.

In this letter, we will report our latest results in the search for defects in single-crystal silicon after an irradiation of 3.5 GeV Xe ions. With IR spectroscopy alone, VO complexes are detected in the irradiated CZ-Si and their distribution below the irradiated surface along the depth is also determined.

The irradiation was carried out at the RIKEN (The Institute of Physical and Chemical Research, Japan) ring cyclotron at room temperature. Four samples taken from different Si wafers, two FZ-Si and two CZ-Si, all p-type, were irradiated using different fluence values of 1.0×10^{13} Xe cm^{-2} and 1.0×10^{12} Xe cm^{-2}, respectively. The thickness of the samples is 0.6 mm. The irradiation direction is perpendicular to the Si(100) surface. According to the TRIM [18] calculation, the irradiation depth is 320 μm, i.e. the incident Xe ions can reach to a depth of 320 μm inside Si. Transmission IR spectra were recorded at room temperature with a Jasco FT/IR 8300 spectrometer. For comparison, both the irradiated sample and non-irradiated sample taken from the same wafer as the irradiated one were measured under the same conditions. The IR spectra were transferred into difference absorption spectra by using FZ-Si as a reference. In order to investigate the defects distribution along the depth below the irradiated surface, one of the four samples, CZ-Si irradiated with 1.0×10^{13} Xe cm^{-2}, was sliced perpendicular to the irradiated surface. The sliced narrow stick was set in resin and two opposite sliced surfaces (cross sections) were finely polished together with the resin. A Jasco WS/IR-8000 Micro IR spectrometer was employed to measure the small slice with the IR light perpendicular to the incident ion direction. This micro-spectrometer supplies an adjustable aperture. We used a narrow aperture of 20×600 μm^2 in the measurement and we shifted the aperture from the irradiated surface to the deeper position, keeping the length direction parallel to the irradiated surface.

Figure 1 displays difference absorption IR spectra of the irradiated and non-irradiated CZ-Si. From the figure we immediately notice that the 830 cm^{-1} line is induced by the irradiation. This line relates to a VO complex (also called an A-centre), which was found and intensively studied in CZ-Si irradiated by electrons or neutrons. To our knowledge, this is the first report of the discovery of the VO complex in single-crystal silicon irradiated by high-energy (GeV) ions. The intensity of the 830 cm^{-1} line decreases dramatically with decreasing irradiation fluence. Extrapolation shows that this line will be undetectable by IR at room temperature when the fluence is below 7.0×10^{11} Xe cm^{-2} for this irradiation. The stronger line at 1107 cm^{-1} is the well known band attributed to the vibration of interstitial
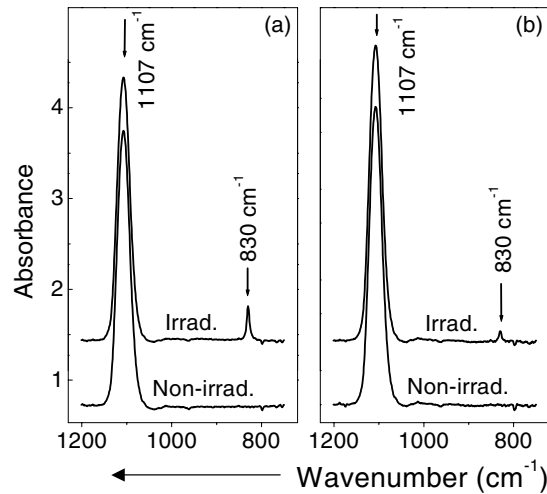
Figure 1. Difference IR absorption spectra of the CZ-Si samples irradiated with 3.5 GeV Xe ions at room temperature with different irradiation fluence. The spectra of non-irradiated sample are also shown for comparison. The total irradiation fluence is (a) 1.0×10^{13} Xe cm^{-2} and (b) 1.0×10^{12} Xe cm^{-2}.

oxygen atoms in CZ-Si. The intensity of this line decreases after irradiation compared to the non-irradiated sample. This indicates that the VO complexes consume part of the interstitial oxygen atoms. By scanning the whole measuring region of the spectra, 400–4600 cm^{-1}, we do not find any other additional lines caused by the irradiation, nor at the position of 2768 cm^{-1} where divacancy (VV) is supposed to be produced. There could exist two possibilities to explain this phenomenon. One is that the irradiation does not induce any other defects except for the VO complex. Second is that some other defects are produced but they are not detectable by room-temperature IR spectroscopy. Low-temperature IR spectroscopy is more sensitive to VV but unfortunately the IR spectrometer we used in this experiment is not equipped with low-temperature apparatus. Probably for the same reason, we do not find any additional lines related to the irradiation in FZ-Si. It is understandable that there is no VO detected in FZ-Si because of its low interstitial oxygen concentration.

Another set of IR spectra recorded at a different depth from the irradiated surface of CZ-Si (irradiated with 1.0×10^{13} Xe cm^{-2}) by the micro-spectrometer at room temperature is shown in figure 2. Because of the small aperture and the weak IR light passing through the aperture, the measurement had to last a much longer time (12 h) than the above-normal measurement (30 min) in order to improve the signal-to-noise ratio. Even so, the quality of each spectrum becomes poor on the background. Neglecting the background noise, we can still easily identify the VO line at 830 cm^{-1} and the interstitial oxygen at 1107 cm^{-1}. It is remarkable that the VO line exists within a region of depth $d = 0$–375 μm. When $d \geqslant 400$ μm, the 830 cm^{-1} line completely disappears. The intensity of the VO line varies from the depth, appearing as a maximum at $d = 315$ μm. This corresponds to the stopping position of Xe ions predicted by TRIM. Another notable phenomenon is a dramatic decrease of the intensity of the interstitial oxygen peak at 1107 cm^{-1} at the same depth position as the VO maximum.

Now we analyse quantitatively the distribution of the concentration of interstitial oxygen atoms, [O$_i$], and VO complexes, [VO], from the IR spectra presented in figure 2. For [O$_i$], we use a conversion factor of $f = 3.14 \times 10^{17}$ cm^{-2} to determine the concentration [19, 20]. There are few references for [VO], except for [21], which gives an equation to determine the

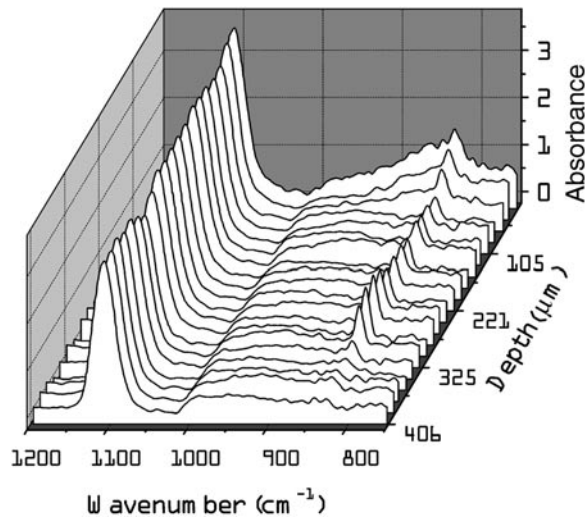**Figure 2.** Difference IR absorption spectra of CZ-Si irradiated with 3.5 GeV Xe ions at room temperature (fluence $= 1.0 \times 10^{13}$ Xe cm^{-2}). The spectra were recorded at room temperature from a slice of the irradiated CZ-Si using an IR micro-spectrometer with a narrow aperture (see text).

concentration of VO complexes from room-temperature IR spectra:

$$[VO] = 6.1 \times 10^{16} \alpha_{830 \text{ cm}^{-1}} (\text{VOs cm}^{-3}) \tag{1}$$

where $\alpha_{830 \text{ cm}^{-1}}$ is the intensity of the 830 cm^{-1} line.

Since each spectrum in the depth profile (figure 2) was measured from a very thin layer (20 μm) parallel to the irradiated surface at a certain depth, both VO and interstitial oxygen are supposed to be homogeneously distributed in this layer. Therefore, the results of [VO] and [O$_i$] obtained from each spectrum can be regarded as the local concentration along the irradiation depth. The results are plotted in figure 3. For comparison, a TRIM-calculated depth dependence of energy losses of 3.5 GeV Xe ions caused by electronic excitation, S$_e$, and nuclear collision, S$_n$, is also plotted in the figure. The figure shows a very good agreement in the depth dependence of [VO], [O$_i$] and the energy loss of ions. From figure 1, we see the formation of VO is accompanied by a decrease of [O$_i$], representing a consumption of O$_i$. However, the consumption of O$_i$ is not quantitatively equivalent to the VO formation presented in figure 3, apparently at the depth of $d = 315$ μm, where [VO] appears maximum but [O$_i$] minimum. At this position, a sharp valley appears in the concentration of interstitial oxygen, indicating a great decrease of [O$_i$]. Although [VO] appears as a maximum at the same position, the decrease of [O$_i$] is obviously larger than [VO]. It is determined that at most 70% of the lost interstitial oxygen atoms have transferred to VO complexes at this position. So the question is: where have the other interstitial oxygen atoms gone? One large possibility is that they have formed other kinds of defects which were undetectable due to our experimental capabilities. TRIM calculation predicts that the irradiated Xe ions have completely stopped at a depth of around 330 μm, but the VO complexes are still obviously detectable until $d = 375$ μm. This is probably because the colliding Si atoms continuously move forward like the tail of the ion trace.

If we compare the distribution of [VO], [O$_i$], S$_n$ and S$_e$ along the depth, we easily see that more VO complexes are produced and more interstitial oxygen atoms have been transferred to other defects or complexes at the position where incident ions stop. It is interesting that the tendency of [VO] distribution resembles the S$_e$ curve but [O$_i$] the S$_n$ curve. This may
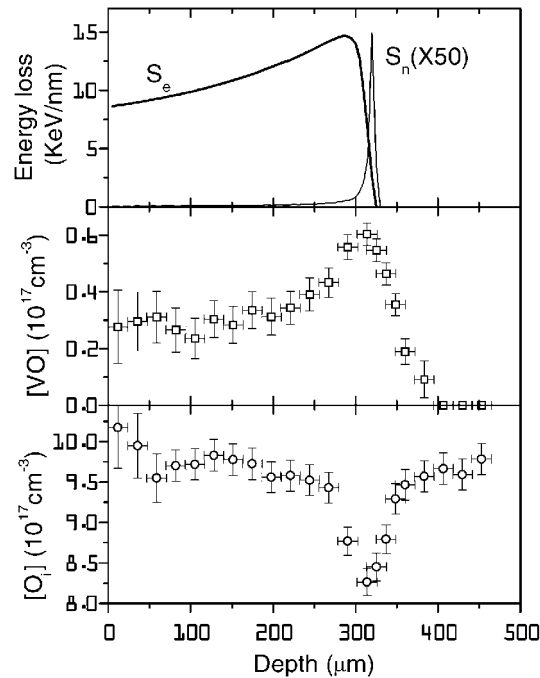
Figure 3. Depth dependence of concentrations of VO complexes, [VO], interstitial oxygen atoms, $[O_i]$, in the irradiated CZ-Si (fluence $= 1.0 \times 10^{13}$ Xe cm^{-2}), and TRIM calculated energy loss of 3.5 GeV Xe ions in CZ-Si by electronic excitation, S_e, and nuclear collision, S_n.

reveal some relationships between [VO], $[O_i]$, S_n and S_e. The number of vacancies produced by nuclear collision can be calculated by TRIM and it is proportional to S_n. Within the whole depth region, this calculated number is about 2–4 orders higher than the number of VO complexes that we have detected at each position. It is clear that most of the vacancies were immediately recovered just after the incident ions have passed through. Only those that are trapped by interstitial oxygen and form complexes can remain. Considering this fact and supposing that the VO production has not reached saturation [22], we may conclude that the VO complexes cannot be produced only by nuclear collision, i.e. S_n. If it were so, [VO] should have been much higher at the position around $d = 315 \, \mu$m than what we have measured. Therefore, the contribution of electronic excitation, S_e, to the VO production has been confirmed from this measurement. We are not yet able to separate how much [VO] is contributed by S_e and how much by S_n. A qualitative conclusion can be that both electronic excitation and nuclear collision have contributed to the VO creation, and each of them becomes dominant within its own dominant region of energy loss.

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