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Infrared studies of oxygen-related complexes in electron-irradiated Cz-Si*

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This paper investigates the infrared absorption spectra of oxygen-related complexes in silicon crystals irradiated with electron (1.5 MeV) at 360 K. Two groups of samples with low $[O_i] = 6.9 \times 10^{17}$ cm^{-3} and high $[O_i] = 1.06 \times 10^{18}$ cm^{-3} were used. We found that the concentration of the VO pairs have different behaviour to the annealing temperature in different concentration of oxygen specimen, it is hardly changed in the higher concentration of oxygen specimen. It was also found that the concentration of VO_2 in lower concentration of oxygen specimen gets to maximum at 450 °C and then dissapears at 500 °C, accompanied with the appearing of VO_3. For both kinds of specimens, the concentration of VO_3 reachs to maximum at 550 °C and does not disappear completely at 600 °C.

Keywords: electron irradiation, Cz-Si, defect complex, annealing processes
PACC: 7280C, 6180F, 6170, 6170A

1. Introduction

Oxygen is a very common and important impurity in silicon materials.[1−3] In as-grown crystals oxygen is mainly present in the form of an electrically inactive interstitial defect (O_i), where it binds with two neighbouring Si atoms. Oxygen does not normally occupy a substitutional site, however, in irradiated crystals the mobile vacancy can be trapped at the O_i atom and forms the vacancy-oxygen complex.[4,5] Electron irradiation of Czochralski-grown silicon (Cz-Si) leads to the formation of oxygen-vacancy complexes, so-called A-centres, where a single oxygen atom occupies a vacant site, with a slight off-centre displacement. The A-centre has been studied extensively by many experimental techniques.[6] Upon thermal annealing, these defects are transformed into V_mO_n complexes by successive trapping of oxygen and vacancies.[7] An important class of such complexes represents a family of VO_n defects[7,8] which forms in the course of coalescence of oxygen atoms to the initial VO cores. There is keen interest in understanding their electrical and optical properties for engineering purposes in the fabrication of Si-based electronic devices.

Several articles have been published about the influence of impurities on the concentrations of VO pair and V_2 from optical absorption measurements. Infrared (IR) absorption spectra of vacancy-oxygen-related complexes in silicon have been intensively studied and a number of vibrational bands have been reported.[8−19] Lindström *et al*[20] and Londos *et al*[9] studied the influence of oxygen and germanium on the VO concentration, respectively. Svensson and Lindström[21] studied the influence of phosphorus on the V_2 concentration. In those studies they mainly measured specimens irradiated at a fixed dose of 1×10^{18} cm^{-2} with MeV electrons. Despite this progress, our understanding of the irradiated-defects in silicon is far from being satisfactory. Hence the relation between their results and ours is not clear. Moreover, our specimens were only two kinds with different oxygen concentration to study various point defects generated by electron irradiation of specimens. In the present work the behaviour of oxygen relative defect induced by electron irradiation was investigated in some detail.

2. Experiment

Initial samples were cut from n-Si crystals grown by the Czochralski technique. The concentration

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of oxygen in first group samples which was labeled A is 10.7×10^{17} cm^{-3}. The concentration of oxygen in another group samples which was labeled B is 6.9×10^{17} cm^{-3}. Specimens were irradiated with 1.5 MeV electrons at $T = 360$ K. Irradiations were carried out by using the Dynamitron accelerator at the Tianjin Institute of Technical Physics. The irradiation doses of both group samples were 1.8×10^{18} cm^{-2}. Before irradiation, all the specimens were annealed at 700 °C for 30 minutes in argon ambience. After irradiation, isochronal annealing were carried out on these specimens in the range of 200°C–600°C for 30 minutes in argon atmosphere and subsequently cleaned in hydrofluoric acid to remove surface oxides. After each annealing step, the IR absorption spectra were recorded by means of a Fourier transform infrared (FTIR) spectrometer with a resolution of 1 cm^{-1}.

3. Result and discussion

The vacancy-oxygen complexe is one of the dominant defects in Cz-Si after irradiation with MeV electrons. Figure 1 shows fragments of IR absorption spectra in the region of 800–1150 cm^{-1} of irradiated specimens A and B after an electron irradiation dose of 1.8×10^{18} cm^{-2}. In the cases of specimen A and B, we observed two peaks at 830 and 889 cm^{-1}, which are due to VO and VO_2, respectively. After the irradiation only the VO defect is produced, as usual. But another defect VO_2 is produced too. This important finding can be easily explained by assuming an occurrence of the reaction $VO+O_i \rightarrow VO_2$ in the large dose of electron irradiation. We also can observe a weak band at 877 cm^{-1}[22] in specimen B. This difference in the spectra comes from the negatively charged vacancy oxygen pairs which can be formed via the combination of surface electron with neutral VO in specimen B. This type of defect complex can be seen A-centre of different charged: VO^0 and VO^{-1}.

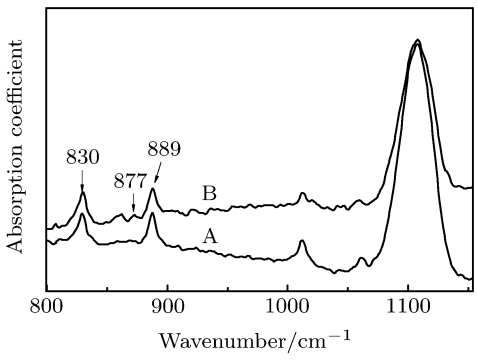


Fig.1. Fragments of IR absorption spectra for specimen A and B subjected to electron irradiation.

Figure 2 shows fragments of IR absorption spectra for specimen B subjected to electron irradiation and subsequent annealing at 300 °C. As we know, the vacancy introduced by electron irradiation can capture interstitial oxygen atoms to form VO (A-centre):

$$V + O_i \rightarrow VO. \quad (1)$$

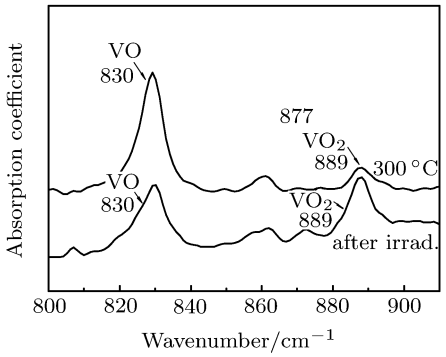


Fig.2. Fragments of IR absorption spectra for specimen B subjected to electron irradiation and subsequent annealing at 300 °C.

The structure of the VO was composed of interstitial oxygen and vacancy, and the oxygen bonded to two silicon neighbours, as shown below in Fig.6(a). At this frame, oxygen atoms and two silicon atoms near the vacancy formed the band of Si–O–Si, and the rest of the two silicon atoms formed the Si–Si. The annealing of the VO defect is a rather complicated process. At first, we observe that the increase of the amplitude of the 830 cm^{-1} band of the VO defect is accompanied by the decrease in the spectra of the 889 cm^{-1} band of VO_2 defect. It is because VO_2 locates at the sub-stability state for the low concentration of the interstitial oxygen at this temperature in the specimen B, in other words, the decrease of VO_2 complex seen after annealing at 300 °C can be related to the dissociation reaction

$$VO_2 \rightarrow VO + O_i. \quad (2)$$

According to the atomic model put forward by Corbett *et al*[13] in their pioneering work during the 1960s, two oxygen atoms saturate four dangling bonds in a vacancy, the oxygen atoms occupy equivalent positions and are each bound to two silicon atoms, as also shown below in Fig.6(b). This defect complex only brings to the local vibration model the peak of the 889 cm^{-1}[23] in the IR absorption spectrum at room temperature origin from this vibration model, and the

concentration of the VO_2 has a linearity relation with the $[O_i]^2$.[24] This phenomenon also conformed to the peak of the 889 cm^{-1} rooting the vibration of the VO_2, so there are two atoms in this configuration.

Figure 3 shows fragments of IR absorption spectra for electron irradiation specimen B annealing at selected temperatures. With the gradual increase of stability of VO_2, VO disappears completely at 400 °C and VO_2 accumulates to the maximum amount at the temperature of 500 °C. More interesting is the fact that the further increase of temperature a part of VO_2 captures diffusing oxygen atoms to form new defects complexes. These defects induce the absorption peak at 904 cm^{-1}, 968 cm^{-1}, 986 cm^{-1}, 1000 cm^{-1} in the IR spectra. In particular, based on the model of the multi-oxygen defect complex put forward by Stein, the peak of 968 cm^{-1} originates from the vibration of VO_3 complex.

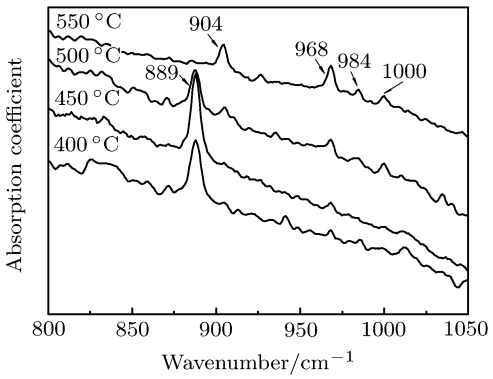


Fig.3. Fragments of IR absorption spectra for electron-irradiated specimen B annealing at 400, 450, 500, and 550 °C, respectively.

Figure 4 shows fragments of IR absorption spectra for the specimen A subjected to electron irradiation and subsequent annealing at 200, 300 °, respectively. Figure 5 shows fragments of infrared absorption spectra for the electron irradiation specimen A annealing at 400, 450, 500, 550 and 600 °, respectively. It can be seen that specimen A has the same thermal behaviour as specimen B at low temperature. However, the concentration of VO_2 complex in the specimen A is hardly changed until the annealing temperature is increased to 300 °C. Another noticeable result is that the bands of 904 cm^{-1} and 968 cm^{-1} in the specimen A start to appear when annealing temperature increases to 450 °. As a consequence, the VO_3 defects are formed due to the reaction:

$$VO_2 + O_i \rightarrow VO_3. \quad (3)$$

Accordingly, we believe that the observed changes are mostly related to the concentration of oxygen in Cz-Si.

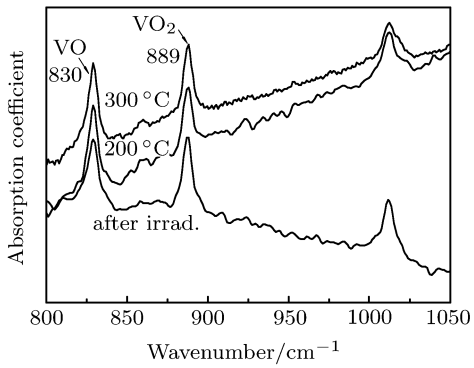


Fig.4. Fragments of IR absorption spectra for the specimen A subjected to electron irradiation and subsequent annealing at 200 °C and 300 °C, respectively.

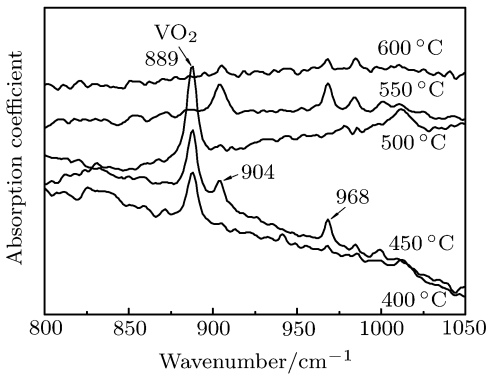
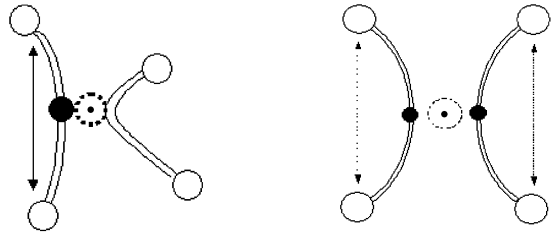
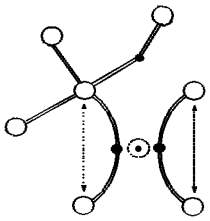


Fig.5. Fragments of IR absorption spectra for the electron irradiation specimen A annealing at 400, 450, 500, 550 and 600 °C, respectively.

The frame of the VO_3 complex is given in Fig.6(c). The VO_3 is not stable at 450 °C, so decomposed to VO_2 again when the temperature rises to 500 °C, at the same time, the concentration of the VO_2 reaches to maximum. At 550 °C, VO_2 disappeares completely, while the concentration of VO_3 gets to maximum. The VO_3 complexes have not disappeared at the annealing temperature of 600 °C. It should be noticed that the concentration of VO_2 in the specimen B reaches to maximum at 450 °C, which is different from the case of the specimen A.



(a)The atomic model of VO. (b)The atomic model of VO_2.



(c) The atomic model of VO_3.

Fig.6. The model of the vacancy-oxygen complexes. ◯-Silicon atoms, •-oxygen atoms, ⊙-vacancy

4. Conclusions

We have studied the oxygen related complexes in Cz-Si subjected to electron irradiation and subsequent annealing. From the FTIR spectra of electron irradiation CZ-Si, a fundamental difference is shown between these samples with different oxygen concentration. It is demonstrated that the annealing processes of oxygen-related complexes as well as such related VO, VO_2 and VO_3 formed in the consecutive reactions VO→VO_2 →VO_3 are markedly sensitive to the concentration of oxygen. As a result, the annealing characteristics cannot be distinctly changed with increasing oxygen concentration.

Acknowledgement

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