Vol 14 No 9, September 2005
1009-1963/2005/14(09)/1882-04

Chinese Physics

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Accelerated oxygen precipitation in fast neutron irradiated Czochralski silicon*

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(Received 23 March 2005)

Annealing effect of the oxygen precipitation and the induced defects have been investigated on the fast neutron irradiated Czochralski silicon (CZ-Si) by infrared absorption spectrum and the optical microscopy. It is found that the fast neutron irradiation greatly accelerates the oxygen precipitation that leads to a sharp decrease of the interstitial oxygen with the annealing time. At room temperature (RT), the 1107cm^{-1} infrared absorption band of interstitial oxygen becomes weak and broadens to low energy side. At low temperature, the infrared absorption peaks appear at 1078cm^{-1}, 1096cm^{-1}, and 1182cm^{-1}, related to different shapes of the oxygen precipitates. The bulk microdefects, including stacking faults, dislocations and dislocation loops, were observed by the optical microscopy. New or large stacking faults grow up when the silicon self-interstitial atoms are created and aggregate with oxygen precipitation.

Keywords: oxygen precipitation, neutron irradiation, defects, CZ-Si
PACC: 7280C, 3220F, 6180, 8130M

1. Introduction

Oxygen is a main impurity in Czochralski silicon (CZ-Si) and usually exists in a supersaturated state. The supersaturated interstitial oxygen will diffuse and form oxygen precipitates during the thermal annealing process.[1] The concentration and characteristics of oxygen precipitates affect the local electrical and mechanical properties of the CZ-Si wafers. The control of oxygen precipitation in CZ-Si is, therefore, very important. It is well known that the formation of oxygen precipitate mainly depends on the concentration of interstitial oxygen ($[O_i]$), the thermal treatment condition and the gas ambient. A lot of defects will be introduced into CZ-Si by neutron irradiation.[2] These defects, including vacancy (V) and silicon self-interstitial atom (I), can form different defect complexes with interstitial oxygen and/or other impurity atoms in some case, while to a large extent they are annihilated by the reaction V+I. Some stable interstitial oxygen related defects such as vacancy-dioxygen (VO_2) and the aggregation of silicon self-interstitial atoms can be considered as nuclei for the growth of oxygen precipitates, dispensing with the nucleation stage at low temperature.[3−5] Furthermore, supersaturated vacancies induced by neutron irradiation can decrease the crucial nucleation radius and can release misfit stress generated during oxygen precipitation.[5] In other words, the processes of oxygen precipitation can be accelerated greatly by neutron irradiation.

Some of the present authors have investigated the effect of annealing temperature on oxygen precipitation in neutron irradiated CZ-Si.[6] In this work, Fourier transform infrared absorption spectrometer (FTIR) and optical microscopy were employed to study the oxygen precipitate shapes and the evolution of defects in the fast neutron irradiated CZ-Si.

*Project supported by the National Natural Science Foundation of China (Grant Nos 50032010 and 50472034) and the Natural Science Foundation of Hebei Province, China (Grant Nos 601047 and E2005000048).
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2. Experiment

The sample used was a n-type, < 111 >-oriented and dislocation-free CZ-Si crystal with 40–60Ω·cm in resistivity and 104mm in diameter. The sample was cut into wafers, polished chemically with the polishing solution of the composition HNO_3/HF (8:1). One section of the crystal, named G1, was irradiated with 0.1–500MeV fast neutrons at China Institute of Atomic Energy. The irradiation temperature and the irradiation dose were 45°C and 1.17×10^{19}n·cm^{-2}, respectively. The unirradiated section, named G0, was left for comparison. The samples were divided into two groups and all of them were subjected to one-step annealing at 1100°C for different time from 0.5 to 20h in argon atmosphere. After annealing, the samples were immersed in hydrofluoric acid for 2–3 min to remove the oxidized layer. [O_i] was determined at RT by WQF-410 FTIR with a calibrated coefficient of 3.14×10^{17}cm^{-2}. The initial [O_i] in the CZ-Si crystal was about 1.08×10^{18}/cm^3. IR absorption spectra were also obtained by WQF-410 FTIR. For each spectrum, 256 scans were accumulated to improve the ratio of signal to noise and the low temperature measurement was carried out at 10K. Bulk microdefects (BMDs) in the cleavage plane were observed by optical microscopy after a 15 min Wright corrosion.

3. Results and discussion

Figure 1 shows the dependence of [O_i] as a function of annealing time for the samples of G0 and G1. After annealing for 0.5h, [O_i] in G1 increases to a maximum because of decompounding of the complex of vacancy and interstitial oxygen (VO). With the increase of annealing time, [O_i] in G0 and G1 decreases due to the generation of oxygen precipitates. The decrease of [O_i] in irradiated samples is much faster than that in unirradiated samples. During the thermal treatment for 2–8h, [O_i] in G1 decreased sharply. When the annealing time is longer than 10h, [O_i] has no evident change because most of the supersaturated interstitial oxygen atoms have precipitated. After annealing for 20h, [O_i] in G1 is 3.6×10^{17} /cm^3, much smaller than that in G0. These phenomena imply that neutron irradiation accelerates oxygen precipitation.

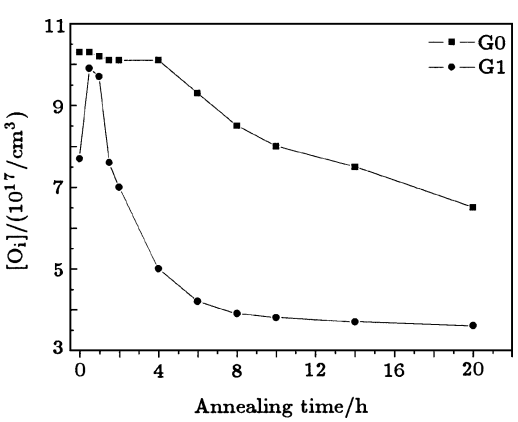


Fig.1. Dependence of [O_i] as a function of annealing time for irradiated and unirradiated samples after annealing at 1100°C.

Figure 2 shows the evolution of the RT infrared absorption spectrums of the G1 samples with annealing time. The vibrational IR absorption band of 1107cm^{-1}, attributed to interstitial oxygen, becomes weak and broadens toward low energy side with increasing annealing time. The weakening means the decrease of [O_i], and the broadening should be caused by the oxygen precipitates which have a few peaks at the low energy side of the 1107cm^{-1} band[7] which the FTIR cannot distinguish out of infrared absorption band related to interstitial oxygen at RT.

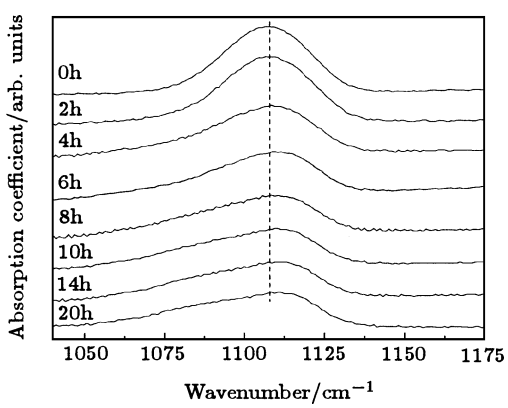


Fig.2. Infrared absorption spectra measured at RT for samples G1 after annealing at 1100°C in argon atmosphere for different time.

In order to obtain the fine structure of the broadened band, the FTIR measurement at low temperature was carried out. Figure 3 shows the absorption spectra measured at 10K on the G1 sample annealed for 10h in comparison with that at 300K. The 1107cm^{-1} absorption band of interstitial oxygen slightly shifts toward the high-energy side, and seven distinguishable peaks appears. The peaks at 1136cm^{-1}, 1122cm^{-1}, 1127cm^{-1} and 1205cm^{-1} are all attributed to interstitial oxygen, and the peaks at 1078cm^{-1} and 1182cm^{-1} are attributed to spherical oxygen precipitates and platelet oxygen precipitates, respectively.[8–10] The 1096cm^{-1} peak was attributed to the thin oxide film on the sample surface by Sasella

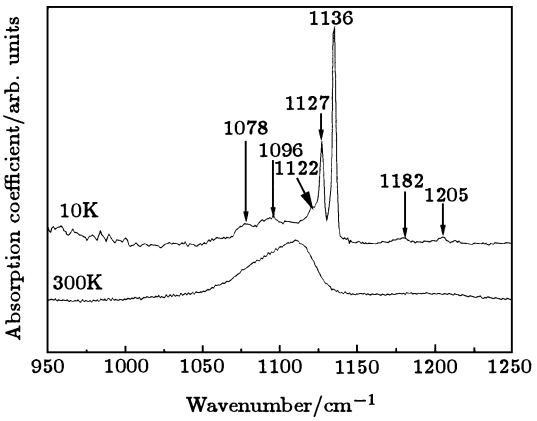


Fig.3. Infrared absorption spectra taken at 10K and 300K for the sample G1 after annealing at 1100°C for 10h.

et al.[11] However, there should be no thin surface oxide in our experiment since the samples have been immersed in hydrofluoric acid. According to the suggestion of Borghesi *et al*[10] the energy of the absorption peak of the oxygen precipitates is strongly dependent on their symmetric shapes: the lower the symmetric shape, the higher the energy of the infrared absorption peak. Therefore, it is reasonable to assume that the octahedral precipitate is responsible for the 1096cm^{-1} peak in our sample. In fact, the octahedral precipitates were also observed by Sasella *et al.*[11]

Figure 4 shows the optical micrographs of the cross-section of the annealed G1 samples. It can be seen that BMDs form in all samples, mapping out the evolution of dislocation and stacking fault with the annealing time. Stacking faults, dislocations and dislocation loops appear after 2h annealing (Fig.4(a)) in agreement with the previous works.[12,13] In the 10h annealed sample (Fig.4(b)), the defect density is much higher than that in the 2h annealed one, many long stacking faults are observed. With further zooming-in (1000×) as seen in Fig.4(d), the typical Frenkel imperfect dislocation accompanied stacking fault can be found.[14] The stacking fault is induced by oxygen precipitation. With oxygen precipitating, silicon self-interstitial atoms are created continuously due to the change in the volume ratio of Si to SiO_2, which aggregate to produce new stacking faults or to lengthen

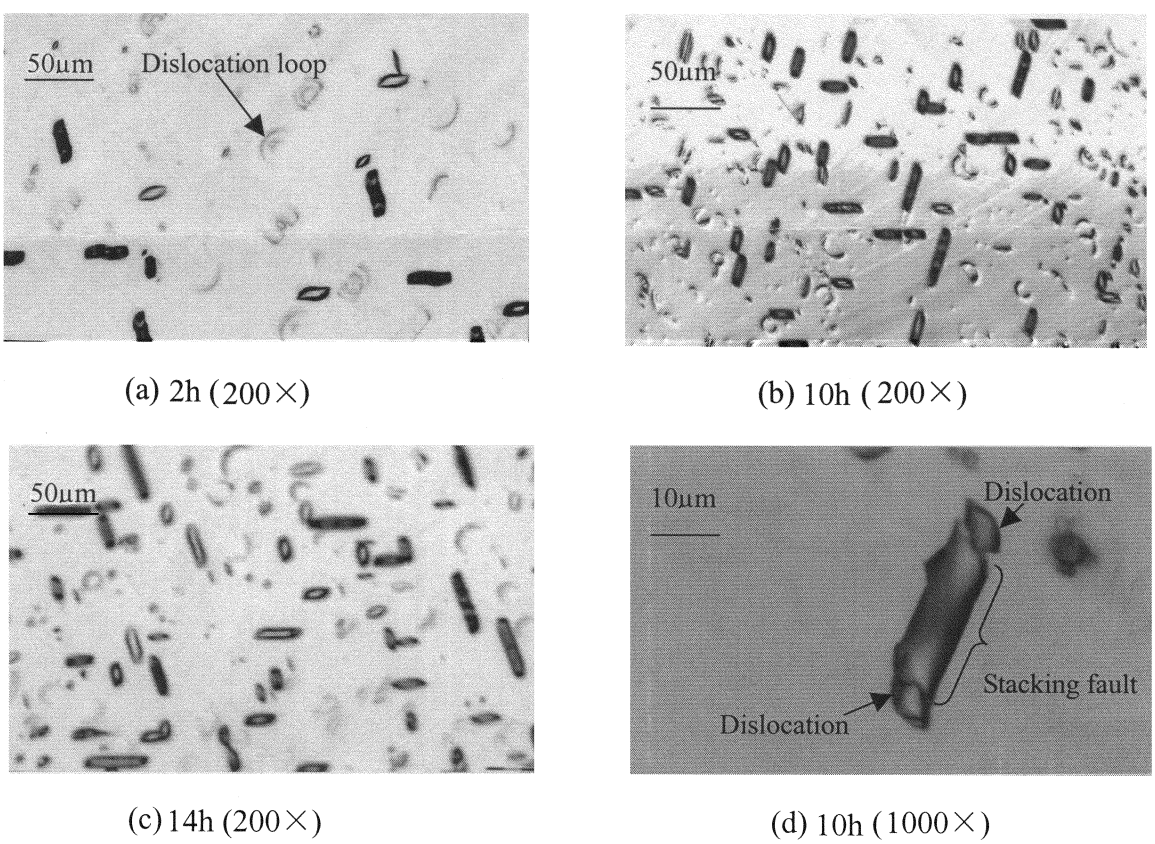


Fig.4. Optical micrographs of BMDs in the sample G1 after annealing at 1100°C.

the old ones. The etching pattern of dislocation loop in Fig.4(b) is semicircular, while that in Fig.4(a) consists of several dislocation lines. Under the condition that silicon self-interstitial atoms are generated continuously, the etching pattern of dislocation loop drives on simply. So those dislocation loops belong to vacancy type.[15] They evolve from vacancies generated during irradiation. The defect density and size in Fig.4(c) are similar to that in Fig.4(b) because almost all the supersaturated interstitial oxygen atoms have been precipitated after 10h annealing. The silicon self-interstitial atoms decrease, and the stacking faults do not grow or be generated any more.

4. Conclusions

The accelerated oxygen precipitation in the neutron irradiated CZ-Si is deduced from the sharp decrease of $[O_i]$ with the annealing time longer than 1h at 1100°C. In addition to the infrared absorption peaks at 1078cm^{-1} and 1182cm^{-1} resulting from the spherical and the platelet oxygen precipitates, the 1096cm^{-1} is assigned to the octahedral oxygen precipitates. From the optical micrographs, we conclude that the stacking faults induced by oxygen precipitate grow with the acceleration of oxygen precipitates, and that the dislocation loop is of vacancy type.

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