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The effects of fast neutron irradiation on oxygen in Czochralski silicon*

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The effects of fast neutron irradiation on oxygen atoms in Czochralski silicon (CZ-Si) are investigated systemically by using Fourier transform infrared (FTIR) spectrometer and positron annihilation technique (PAT). Through isochronal annealing, it is found that the trend of variation in interstitial oxygen concentration ($[O_i]$) in fast neutrons irradiated CZ-Si fluctuates largely with temperature increasing, especially between 500 and 700°C. After the CZ-Si is annealed at 600°C, the V_4 appearing as three-dimensional vacancy clusters causes the formation of the molecule-like oxygen clusters, and more importantly these dimers with small binding energies (0.1–1.0eV) can diffuse into the Si lattices more easily than single oxygen atoms, thereby leading to the strong oxygen agglomerations. When the CZ-Si is annealed at temperature increasing up to 700°C, three-dimensional vacancy clusters disappear and the oxygen agglomerations decompose into single oxygen atoms (O) at interstitial sites. Results from FTIR spectrometer and PAT provide an insight into the nature of the $[O_i]$ at temperatures between 500 and 700°C. It turns out that the large fluctuation of $[O_i]$ after short-time annealing from 500 to 700°C results from the transformation of fast neutron irradiation defects.

Keywords: neutron irradiation, irradiation defects, FTIR spectrometer, positron lifetime
PACC: 7280C, 3220F, 6180, 7870B

1. Introduction

Oxygen is a very common and important impurity in silicon materials.[1] In as-grown crystals oxygen is mainly present in the form of an electrically inactive interstitial defect, where it binds with two neighbouring Si atoms. Oxygen does not normally occupy a substitutional site. However, after neutron irradiation, the interstitial oxygen (O_i) can leave interstitial site, thereby forming all kinds of irradiation defects. In particular, clusters are mainly created in dense displacement regions. The interstitial oxygen diffusion is known to govern the processes of oxygen agglomeration in silicon at high temperatures. And fast neutron irradiation can affect the oxygen clustering significantly. During annealing at a high temperature the oxygen diffusion is enhanced due to the presence of a large number of vacancies near the surface of the wafer.[2]

It is well known that intrinsic point defect related agglomerates or microdefects are formed during the crystal growth. The precipitation of oxygen atoms occurs during the processing of silicon wafers into integrated circuits (ICs), which is closely related to their processes of crystal growth and heat-treatment. Therefore the control of the oxygen atom behaviour in silicon is undeniably one of the most important challenges in semiconductor material engineering. Recent studies have indicated that the neutron irradiation changes the state of defect in Czochralski silicon (CZ-Si), which has a direct influence on the diffusion and precipitation of interstitial oxygen atoms in CZ-Si and is beneficial to the formation of intrinsic gettering structure. In the present paper the effects of fast neutron irradiation on oxygen atoms and oxygen-related defects in CZ-Si are investigated by Fourier transform infrared (FTIR) spectrometer and positron annihilation technique (PAT).

2. Experiment

N-type $<$ 111 $>$ CZ-Si with resistivity in a range of 40–60 $\Omega\cdot$cm was used in the experiment. By using WQF-410 FTIR spectrometer at room temperature (RT), interstitial oxygen and substitutional

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carbon concentrations were monitored by measuring the intensities of the absorption bands at 1107 and 605 cm^{-1} and found to be about 10.3×10^{17} and $< 1.0 \times 10^{16}$ atoms $\cdot$ cm^{-3} respectively. The samples of CZ-Si were irradiated by fast neutrons at an energy of about 500 MeV. The irradiation flux was $6.6 \times 10^{12} n \cdot cm^{-2} \cdot s^{-1}$ at an irradiation temperature of 45°C and irradiation dose of $5.9 \times 10^{18} n \cdot cm^{-3}$. The samples were cut into several pieces and polished. The samples were annealed in an argon atmosphere from 100 to 700°C for 1, 2 and 3h separately. After thermal annealing all samples were treated with hydrofluoric (HF) acid to remove the oxide formed at the surface of samples during thermal treatment and washed in deionized water. Positron annihilation measurements were performed at the Institute of High Energy Physics, Chinese Academy of Sciences, by using a ^{22}Na source sandwiched between two similar samples. Each positron lifetime spectrum contained 10^6 counts and was analysed by using two lifetime components. The last one was used to measure the absorption spectrum of O_i and the defects related to irradiation of all samples by using the FTIR spectrometer.

3. Results and discussion

Figures 1 and 2 show a general trend of variation in concentration of interstitial oxygen ($[O_i]$) after isochronal annealing for 1h and isothermal annealing for 1–3 h from 100 to 700°C, respectively. The aim was to ensure the states of O_i in the fast neutron irradiated wafers after annealing at different temperatures and for different times. During neutron irradiation, silicon lattice atoms were displaced, and so the primary CZ-Si defects including silicon interstitials (I) and vacancies (V) appeared.[3] These defects and other impurity formed the impurity defects such as C_i, C_sC_i, C_iO_i, VO_i, etc. Thus the $[O_i]$ atom concentration was observed to decrease greatly from the original 10.3×10^{17} to 7×10^{17} atoms $\cdot$ cm^{-3} after fast neutron irradiation.

From Figs.1 and 2 we can see that the $[O_i]$ atom concentration in fast neutron irradiation CZ-Si fluctuates largely with annealing temperature and time CZ-Si, which means that the oxygen-related irradiation defects are unstable, in other words, the irradiation defects after annealing under different conditions have different states. During annealing a migration of these irradiation defects happens meanwhile the conversion of these defects also takes place. It is well

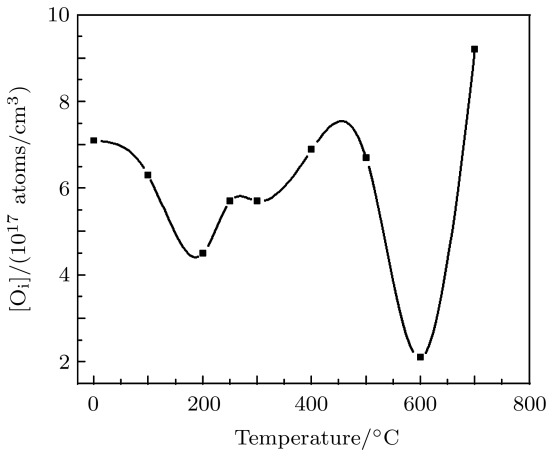


Fig.1. Dependence of $[O_i]$ atom concentration in irradiated sample annealed for 1 h in an argon atmosphere on annealing temperature.

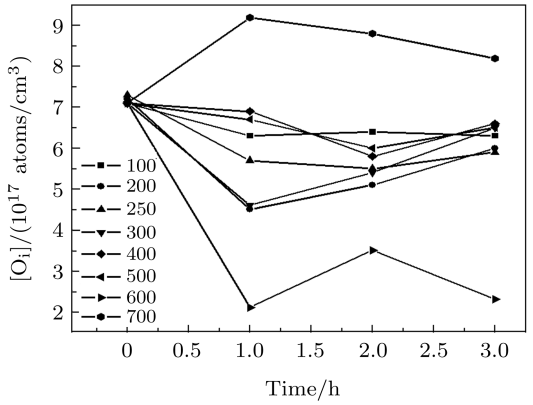


Fig.2. Dependence of $[O_i]$ atom concentration of irradiated samples annealed at 100–700°C on annealing time.

known that the main factor that determines the type of irradiation defect is the irradiation temperature.[4] When the irradiation temperature is low (< 170°C) the main vacancy-type defects are V, V_2 and V_4-type defects, while at higher irradiation temperatures (> 170°C) the main defects are usually multivacancy-type ones such as V_5-type defects. But our results suggest that annealing temperature after irradiation is also important for the type of irradiation defect, especially for the oxygen-related irradiation defects. Figure 2 shows that $[O_i]$ atom concentration remains nearly unchanged during annealing at 100°C for 3 h. It indicates that oxygen-related irradiation defects are stable at this temperature. But during annealing at 200°C, $[O_i]$ atom concentration decreases obviously due to the formation of some oxygen-related irradiation defect complexes such as C_iO_i and VO_i. We can see that the curve for $[O_i]$ atom concentration versus temperature has a peak for the annealing at 250°C

in Fig.1, and that [O_i] atom concentration increases a little with annealing time increasing in Fig.2. Poirier *et al*[5] have reported the variation in [O_i] atom concentration during annealing at 250°C and attributed it to a consequence of some sort of divacancy agglomeration and suggested that chains of vacancies formed at a higher temperature (about 250°C). However, neither the electron paramagnetic resonance (EPR) nor infrared (IR) data are available to support this suggestion until now. The results in Fig.1 give us an appropriate evidence that the formation of divacancy agglomeration leads to the decomposition of oxygen-related vacancy-type defects and consequently causes lots of oxygen atoms to return to interstitial sites. At 300°C, [O_i] atom concentration varies as in the case at 200°C, namely first it decrease and then increases with annealing time. It should be due to the transformation of irradiation defects during heat-treatment. Up to 400°C and 500°C, [O_i] atom concentration almost remains unchanged with the increase of annealing time. In this temperature range the formation and the decomposition of oxygen-related defects have reached a balance. Based on the above discussion, we can draw a conclusion that for the irradiated wafers annealed below 500°C the formation and the decomposition of oxygen-related irradiation defects cause the [O_i] atom concentration to first decrease and then increase.

The most surprising results which we obtained from repeatable experiments come from the sample annealed at 600°C. At this temperature, [O_i] atom concentration falls considerably from 7×10^{17} to 2.1×10^{17} atoms $\cdot$ cm^{-3}. A more interesting point is that [O_i] atom concentration can recover to 9.2×10^{17} atoms $\cdot$ cm^{-3} when the annealing temperature increases to 700°C, and that [O_i] atom concentration is stable with the increase of annealing time. These results indicate that at 600°C O_i atoms may exist in a sample as other states at instance substitutional site that cannot be detected by using the FTIR spectrometer.

Figure 3 shows the dependence of the positron lifetime on annealing temperature of the irradiated samples after isochronal annealing for 1h from 100 to 700°C. Two lifetimes are found from the positron lifetime spectra, labelled as τ_1 and τ_2, and they indicate that they are the positron lifetimes of monovacancy-type defect and multivacancy-type or larger vacancy-type respectively. For annealing at 100°C, τ_1 is 280 ps with an intensity (I_1) of 60%, i.e. $I_1 = 0.6\%$, which can be assigned to VO.[6] And τ_2 is 360 ps and just falls into a lifetime range of V_2 (250–273 ps) and V_4 (390–465 ps). In our experiment the irradiation temperature is 45°C, so the main defects in the fast neutron irradiated CZ-Si are likely to be VO, V_2 and V_4. After annealing at 200°C, τ_1 and I_1 reach 290 ps and 70% respectively. Figure 4 shows the FTIR spectra for neutron irradiated CZ-Si annealed at different temperatures. When the annealing from 200 to 400°C, τ_1 and I_1 are unchanged (see Fig.3). This indicates that monovacancy-type defect and its intensity arrive at steady values in this temperature range. Another noticeable result in Fig.4 is that when the annealing temperature is higher than 250°C, VO disappears and four absorption bands appear at the wavenumbers of 825 cm^{-1}(V_2O_2), 834 cm^{-1}(V_3O_2), 840 cm^{-1} (V_2O), and 919 cm^{-1}(O–V–O).[7,8] Because defect complex such as V_2O_2, V_3O_2 and V_2O cannot contribute to τ_1, the defect-impurity complex O–V–O may play a role in keeping τ_1 unchanged. When the annealing temperature runs up to 500–600°C, the absorption band at 919 cm^{-1} disappears while τ_1 decreases to 220 ps. So it can be concluded that 919 cm^{-1} (O–V–O) should belong to the monovacancy-type defects that have the same positron lifetime as VO.

With temperature increasing form 100 to 200°C, τ_2 increases from 360 to 390 ps ((Fig.3(b)) but I_2 decreases from 40% to 30% ((Fig.3(c)). It is possibly because some of V_2 defects combine either with a vacancy or divacancy to form stable complexes such as V_3 and V_4, or with other wandering interstitials or existing stable interstitial clusters.[5] With the annealing temperature increasing from 200 to 600°C, τ_2 increases from 385 to 415 ps gradually. This result can

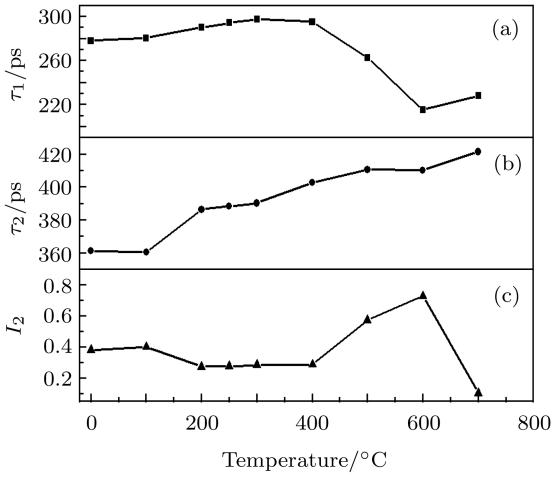


Fig.3. The variations of the positron lifetime of the irradiated CZ-Si with annealing temperature.

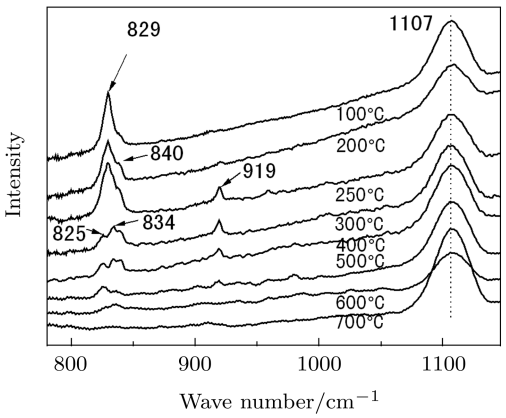


Fig.4. The FTIR spectra for neutron irradiated CZ-Si annealed at different temperatures.

be explained from FTIR spectra in Fig.4, where some multivacancy-type defect complexes appear with the disappearing of 829 cm^{-1}(VO). So we can conclude that the complexes such as V_2O_2(825 cm^{-1}), V_3O_2(834 cm^{-1}) and V_2O (840 cm^{-1}) not only contribute to τ_2 but also have longer positron lifetimes than V_2. Figure 3(b) shows that after annealing at 600°C, τ_2 increases to 415 ps and its intensity I_2 goes up to 70%. It is possibly due to the formation of V_4-type defects. After annealing at 700°C (Fig.3(c)), the decrease in positron trapping rate indicates that the concentration of V_4-type defects decreases rapidly.

The same results can be found in the earlier work by Poirier *et al.*[4] They studied the electron irradiated silicon and found the position lifetime of 295 ps to keep unchanged well beyond 300°C, and suggested the persistence of divacancies in this temperature range. Later, they repeated the PAT measurements through isochronal annealing experiments with temperature increasing up to 500°C by using proton irradiated silicon, and they observed that the position lifetime did increase though only slightly, upon annealing temperature increasing up to 500°C. Thus, vacancy agglomeration does take place, and the small increase in lifetime supports the theoretical calculations[9,10] and suggests that vacancies are stuck together into a chain-like agglomerate. Annealings at temperatures above 500°C show[4] that τ_2 rapidly increases from 300 to 420 ps, which indicates that the string-like vacancy agglomerates become unstable and three-dimensional vacancy clusters are formed.

Figure 4 shows after the CZ-Si is irradiated by neutrons, its main irradiation defect is of A-centre (VO). During annealing at different temperatures the irradiation defects turn into defects in different states. Satellite bands at 825 cm^{-1} (V_2O_2), 834 cm^{-1} (V_3O_2), 840 cm^{-1} (V_2O) and 919 (O–V–O) cm^{-1} are the indication of the appearance of these different defect states. When the temperature increases to 600°C, the IR bands of the irradiation defects almost disappear; meanwhile the 1107 cm^{-1} (O_i) bands become very low. This result means that at this time the vacancy-oxygen defects mostly decompose and turn into V and O defects or others in simple states. As for V-type defects, they mainly form V_4-type defects as three-dimensional vacancy clusters. Oxygen atoms form the molecule-like oxygen clusters rather than return to its interstitial position. In this process, compared with dimer formation rate, the dimer dissociation rate has been neglected. These dimers having small binding energies (0.1–1.0 eV) diffuse more easily into the Silicon lattices because dimers have a lower activation energy (about 1.4 eV) than single oxygen atom.[11] Therefore by combining the infrared spectroscopic measurements and the positron annihilation measurements, a new insight can be gained into the mechanism of oxygen behaviour in the fast neutrons irradiated CZ-Si. The large fluctuations of [O_i] atom concentration after annealing at 600°C and 700°C should be attributed to the formation of molecule-like oxygen clusters due to the V_4 appearing as three-dimensional vacancies clusters. At 600°C, these molecule-like oxygen clusters enhance the diffusion of oxygen atom and accelerate oxygen agglomeration simultaneously; but at 700°C, the decomposition of three-dimensional vacancies clusters frustrates the formation of molecule-like oxygen clusters, stops the oxygen agglomeration at the same time, thereby causing [O_i] atom concentration to increase noticeably. concentration to increase noticeably.

4. Conclusions

Through annealing, it is found that the trend of variation in the concentration of interstitial oxygen atoms ([O_i]) in fast neutron irradiated CZ-Si is fluctuated largely with temperature increasing, especially between 500 and 700°C. In our case the samples are subjected to fast neutron irradiation. So the behaviour of oxygen is mainly affected by states of vacancy generated by fast neutron irradiation. At an annealing temperature of 600°C, V_4 appearing as three-dimensional vacancy clusters leads to the formation of the molecule-like oxygen clusters, and more im-

portantly these dimers having small binding energies (0.1–1.0 eV) diffuse more easily into the Silicon lattices, thereby causing oxygen to agglomerate. When annealing temperature runs up to 700°C, the three-dimensional vacancy clusters disappear, accordingly the oxygen agglomerations are decomposed into single oxygen atoms that can return to the interstitial sites, thereby forcing $[O_i]$ atom concentration to increase obviously. Therefore, the large fluctuation of $[O_i]$ after short time annealing is caused by the transformation of fast neutron irradiation defects.

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