The origin of 0.78 eV line of the dislocation related luminescence in silicon

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In this paper, the 0.78 eV line of the dislocation related luminescence in the electron-irradiated silicon has been investigated. It is found that the 0.78 eV line only exists in float zone silicon samples, and its intensity could be largely enhanced by high temperature and long time annealing while no 0.78 eV line was found in Czochralski silicon. The activation energy of 0.78 eV line in floating-zone silicon is ~13 meV, indicating a different nature from that of D1/D2 lines which can be ascribed to specific reconstructed dislocations which could be easily affected by point defects and temperature. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4754825]

I. INTRODUCTION

The dislocation related luminescence (DRL) in silicon consists of four luminescence lines labelled from D1 to D4.[1,2] It has attracted considerable attentions as it is one of the potential candidates for silicon based light sources in silicon photonics. The most promising emission of DRL is the D1 line which has the highest temperature stability and the strongest intensity. Most importantly, the 1.5 μm emission of the D1 line suits well for the appropriate spectral position of the optical communication applications, however, the exact origin of D1/D2 is still unclear.

Usually D1 line consists of several sub-bands or the so called "background". One particular sub-line which lies in the lower energy shoulder of the D1 line at 0.78 eV at low temperature attracts wide attention. This 0.78 eV line was observed in heavily dislocated silicon wafers at 4.2 K without any explanations of its origin.[2,3] Recently, Steinman[4] found the peak at 0.78 eV was greatly enhanced by low-temperature annealing in plastically deformed silicon, attributing the existence of this line to oxygen-related donors. They believed that this line originated from the donor-acceptor recombination was involved in a deep state of a thermal donor coming from oxygen.[4,5] However, these oxygen related models, either thermal donor related or oxygen precipitation related, failed to explain why this line also exists in heavily dislocated floating-zone (FZ) silicon samples[6–8] containing less interstitial oxygen atoms and then few oxygen precipitates.

In this paper, we investigated the 0.78 eV line comparing FZ silicon with Czochralski (CZ) silicon samples with dislocations induced by electron irradiation. This technique allows us to study this line's properties with relatively clean dislocations. The photoluminescence of 0.78 eV line is carefully investigated and its activation energy is newly revealed. The origin of this line is assumed to be associated with some reconstructed dislocation structures or dislocation-defect complex, which is not related to oxygen or oxygen related complex. We hope our result of revealing the nature of this subband at 0.78 eV could help to understand the DRL's nature and allow people to understand its exact luminescence centers and develop proper techniques to increase the intensity and efficiency of DRL based on silicon light emitting diodes.

II. EXPERIMENTS

P-type boron doped FZ-grown silicon and CZ-grown silicon were used in this experiment. The resistivity of both silicon is around 11–25 Ω·cm, and they were both grown in Ar atmosphere. The initial oxygen concentration $[O_i]$ of the CZ-Si samples was $\sim 1.0 \times 10^{18}\,\mathrm{cm}^{-3}$ measured by Fourier transform infrared spectroscope (Bruker 66vs) with the calibration coefficient of $3.14 \times 10^{16}\,\mathrm{cm}^{-2}$. Its carbon concentration $[C_s]$ was below the detection limitation $1.0 \times 10^{16}\,\mathrm{cm}^{-3}$. Both $[O_i]$ and $[C_s]$ in the FZ-Si wafer were also below the detection limitation ($<1.0 \times 10^{16}\,\mathrm{cm}^{-3}$). Then dislocations were induced by electron irradiation.[9] The density of the dislocations was estimated from the etch pits by using an optical microscope, which is $\sim 8 \times 10^{6}\,\mathrm{cm}^{-2}$. For comparison, parts of the samples were annealed at 450 °C for 24 h and 1050 °C for 12 h in nitrogen atmosphere in a clean quartz tube to avoid the undesirable contamination.

The samples were characterised by photoluminescence (PL), double-crystal x-ray diffraction, and transmission electron microscopy (TEM). The PL spectra were recorded by an Edinburgh FLS920P Spectrometer with a nitrogen-cooled near-infrared photomultiplier tube from 15 K to 300 K using a helium flow cryostat (Advanced Research Systems). The light sources were Semiconductor Laser 808 nm and Laser 980 nm. The double-crystal x-ray diffraction was measured by a Philips X'pert MRD instrument using Ge (200) single crystal as the four-crystal monochromator. The copper $K\alpha_1$ radiation was used. The TEM was tested by a TECNAI G^2 20 field emission transmission electron microscope.

III. RESULTS AND DISCUSSION

Fig. 1 shows the DRL spectra at 15 K of FZ silicon and CZ silicon with dislocations induced by electron irradiation. In

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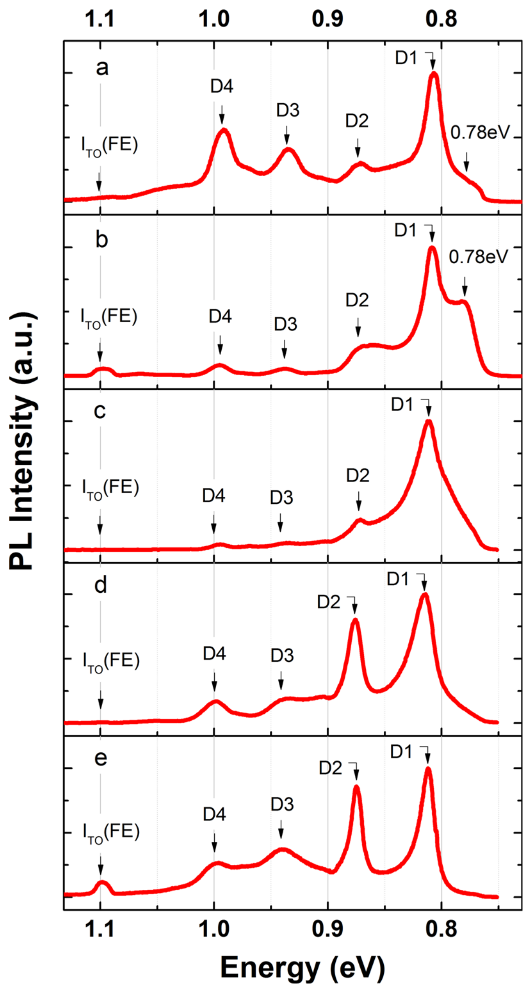

FIG. 1. The photoluminescence spectra at 15 K under the laser 808 nm excitation of (a) FZ silicon sample with dislocations, (b) FZ silicon sample with dislocations after annealing at 1050 °C for 12 h, (c) CZ silicon sample with dislocations, (d) CZ silicon sample with dislocations after annealing at 450 °C for 24 h, and (e) CZ silicon sample with dislocations after the annealing at 1050 °C for 12 h.

the as-prepared FZ silicon sample (Fig. 1(a)), the dislocation related four lines D1–D4 are quite sharp and clear, which is the same as those reported in the previous work.[1,2,7] But there is a noticeable broadened line in the lower energy region of D1 line, which is ascribed to the 0.78 eV line signal. Fig. 1(b) shows a significant intensity growth of 0.78 eV line and D1 line in the FZ silicon after annealing at 1050 °C for 12 h. In the as-prepared CZ silicon (Fig. 1(c)), there is no obvious 0.78 eV line. Furthermore, there are no 0.78 eV line related signals in the CZ silicon samples after annealing at 450 °C for 24 h (Fig. 1(d)) or 1050 °C for 12 h (Fig. 1(e)) neither, which are for introducing thermal donors and oxygen precipitates, respectively. Since the dopant, resistivity, electron irradiation, and thermal treatment of these wafers are the same, the main difference between the CZ silicon and FZ silicon in our experiment condition is the content of interstitial oxygen. Because the [O_i] in FZ silicon is quite small, we ascribe the different behaviours of 0.78 eV line, which exists in FZ silicon and absences from CZ silicon, to the existence of oxygen.

Fig. 2 shows the power dependent PL spectra at 15 K of the dislocated FZ silicon sample after annealing at 1050 °C

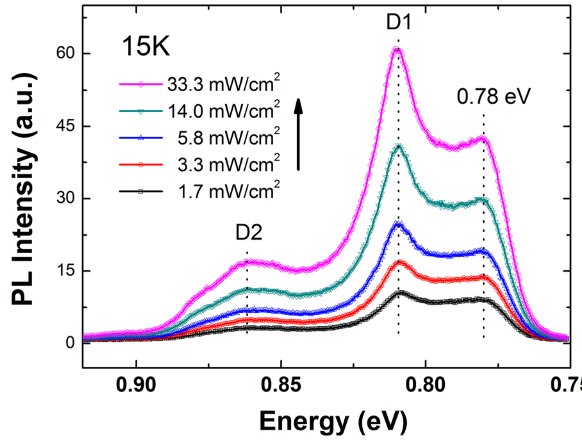

FIG. 2. The power dependent PL spectra at 15 K under the laser 980 nm excitation of FZ silicon sample with dislocations after annealing at 1050 °C for 12 h.

for 12 h. The intensities of 0.78 eV line, D1 line, and D2 line increase with the excitation power homogeneously. Their peak positions remain the same under different excitation powers and under different excitation sources (980 nm and 808 nm). It indicates that the luminescence center of 0.78 eV line is quite stable under different excitation powers and wavelengths.

Fig. 3 shows the intensity dependence of 0.78 eV, D1, and D2 lines on temperatures. With the increase of temperature, the intensity of 0.78 eV line drops much faster than D1 and D2 lines. The dependence of intensities on temperature could be described by an equation[2]

$$I(T)/I(0) = \left[1 + g * \exp\left(\frac{-E}{kT}\right)\right]^{-1}. \tag{1}$$

This formula describes the thermal partition of localized electron-hole pairs between different bound states of the same centers to bound-to-free thermal activation.[2] The total generation rate is balanced by the decay rates from different bound levels under stationary conditions. Then $g*$ incorporates the

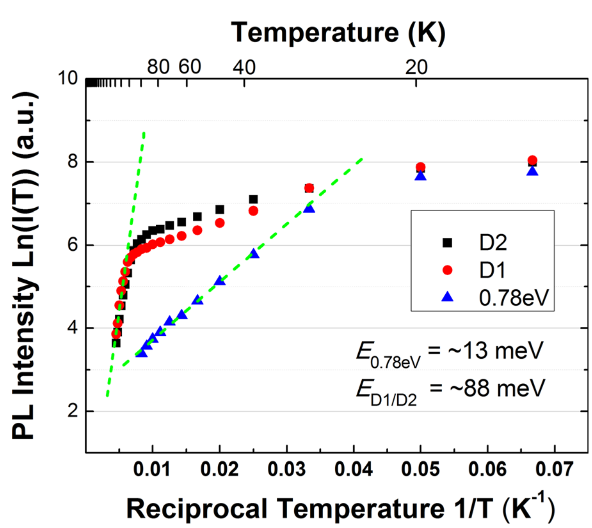

FIG. 3. The dependence of PL intensities of D2, D1, and 0.78 eV lines on the temperature.

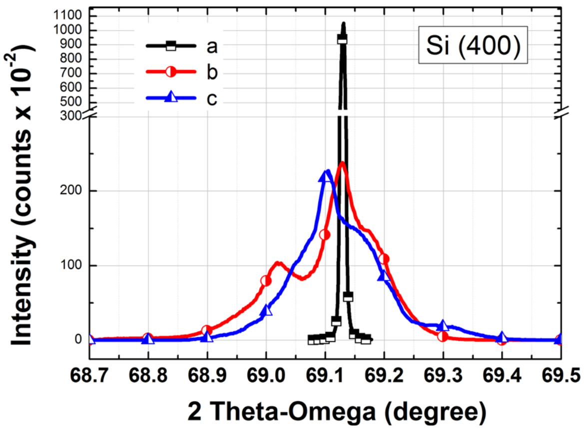

FIG. 4. The double-crystal x-ray diffraction curves of (a) reference FZ silicon wafer, (b) FZ silicon with dislocations, (c) FZ silicon with dislocations after annealing at 1050 °C for 12 h. The silicon (400) plane is detected and the copper $K\alpha_1$ radiation is used.

ratio of the associated degeneracy factors and the inverse ratio of the radiative life times of the involved states.[2,7] This equation fits the temperature dependence of 0.78 eV line quite well with the activation energy (E_a) of ~13 meV. While the D1 and D2 lines activation energy is ~88 meV which agrees with other's results.[2,10] D1 and D2 lines are traditionally considered as the transitions from the same defects since the thermal behaviour is the same, which is also suggested in our experiments. However, the 0.78 eV line has much smaller activation energy and its thermal behaviour is quite different from D1 and D2 lines. It suggests that the transition of 0.78 eV line could be affected by the non-radiative recombination route more effectively which is enhanced by the increase of temperature. It indicates that the origin of 0.78 eV line is different from D1/D2 lines.

In order to reveal the nature of 0.78 eV line, the structure analyses were applied. Fig. 4 shows the double-crystal x-ray diffraction results of FZ silicon samples with different treatments. The reflection of the silicon (400) plane was detected in order to check the integrity of the crystal. The peak of the reference silicon wafer without dislocations was centered at 69.13°, which was quite sharp with a full width at half maximum (FWHM) of 0.0085° (Fig. 4(a)). After the electron irradiation, the peak became quite broadened and its intensity decreased dramatically (Fig. 4(b)). It was due to the formation of dislocations in the sample. Furthermore, the broadening of the peak was quite unsymmetrical. There were sub-bands around the central peak on the both sides, while one clearly centered at 69.05°. It may be due to the aggregation of point defects around dislocations or the dislocation tangles. After annealing at 1050 °C for 12 h, the width of the reflection peak became narrower but was still much broader than the reference one (Fig. 4(c)). Moreover, the shoulder peak centred at 69.05° disappeared indicating that the excessive self-interstitials and vacancies recombined during the high temperature and long time annealing while the dislocations transformed into lower energy state.

In order to find out what kind of defect change during the annealing, the transmission electron microscopy analysis was applied. Fig. 5(a) shows the TEM image of the as-prepared FZ silicon sample. The dislocations induced by electron irradiation were dispersed randomly and fragmented with mixed dislocations. Some of them even formed dislocation loops. After the high temperature and long time annealing (Fig. 5(b)), lots of cross-slips, kinks, and jogs occurred and the dislocation lines became much longer offering more dislocation intersection sites. The "relaxed" dislocations, dislocation reactions in the intersection sites, together with impurity atmospheres gathering are considered to be the luminescence sources.[2,4,11] When the cross-slip and climb of dislocations occurred, the intensities of D3/D4 lines became rather small and the intensities of D1, D2, and 0.78 eV lines were enhanced in FZ silicon samples. Such dislocation intersections, like kinks, jogs, and nodes, brought by the cross-slip and climb are responsible for the intensity growth of 0.78 eV line.

Formerly, the 0.78 eV line is considered to be originated from oxygen atoms in silicon.[4,5,12] This assumption leads to a model of donor-acceptor (D-A) recombination which is involved in a deep acceptor state in a dislocation interaction together with a donor state of a thermal donor (TD).[8,13] However, it is known that TDs can only form at 300–500 °C and dissolve during annealing at temperatures above 650 °C.[14] In our experiments, the 0.78 eV line could not be found in the CZ silicon sample after annealing at 450 °C for 24 h where the TDs were fully formed (Fig. 1(d)). Furthermore, there was no signal of 0.78 eV line in the CZ silicon sample after annealing at 1050 °C for 12 h neither, where lots of oxygen precipitates were generated according to the FTIR results. This result was contradictive with the idea that the 0.78 eV line is brought by oxygen precipitation.[10,15,16] Moreover, the 0.78 eV line became much stronger in FZ silicon after 1050 °C annealing even there were no TDs formed in the sample which was confirmed by FTIR measurements.

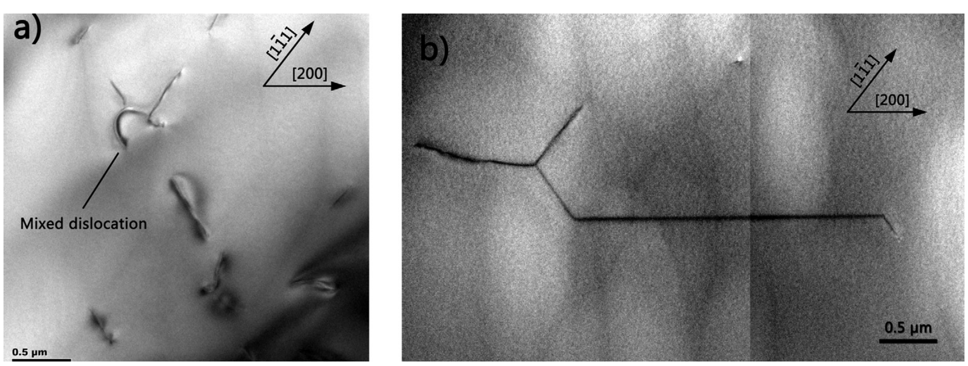

FIG. 5. TEM images of (a) FZ silicon with dislocations and (b) FZ silicon with dislocations after annealing at 1050 °C for 12 h. The bright field image with $\mathbf{B} = \langle 011 \rangle$, $\mathbf{g} = \langle 02\text{-}2 \rangle$.

Even in the as-prepared FZ silicon samples whose $[O_i]$ was too low to form TDs or oxygen precipitates, we still can find the weak 0.78 eV line in the PL spectrum. It means that oxygen related clusters, no matter the TDs nor the oxygen precipitations, are not the critical origins.

In the FZ silicon sample with annealing at 1050 °C for 12 h, there is some transformation of dislocation structure according to the results of double x-ray diffraction and TEM. During the high temperature and long time annealing, the dangling bonds of dislocations will reconstructed. The point defects, such as, self-interstitials could get involved in the dislocations core reconstruction.[17] Such dislocation reconstructions accompanied with point defects during the high temperature annealing could significantly stabilize the 0.78 eV line's luminescence center by giving stronger PL intensity in our experimental case. However, we cannot find the signals of 0.78 eV line in the CZ silicon with dislocations before or after annealing. It leads us to the fact that the existence of oxygen somehow could passivate 0.78 eV line luminescence center. This result indicates that this luminescence center could be affected by point defects and oxygen atoms.

Usually, a dislocation offers an isolated energy state center where electrons could be kept in the excited state.[18] Such energy state center could be a very effective radiative recombination center.[19] In our experimental case, the clean dislocations induced by electron irradiation are the preferable recombination site for carriers.[20] As the dislocation could be considered as a space charge cylinder (shown in Fig. 6), the intensity enhancement of 0.78 eV line after the high temperature and long time annealing is explained as follows: after annealing, the dislocation lines become much longer than the as prepared one's (Fig. 5). The longer dislocation lines are equivalent to the enlargement of the effective area of the space charge cylinder coursed by dislocations, which could highly increases the carrier capture cross section. This effect brings more electrons and holes to recombine at the specific sites of dislocation structures which are related to the 0.78 eV line luminescence center, resulting the enhancement of the luminescence intensity. As the 0.78 eV line luminescence center is directly related to certain dislocation structures, we assume it origins from specific reconstructed dislocation structures.

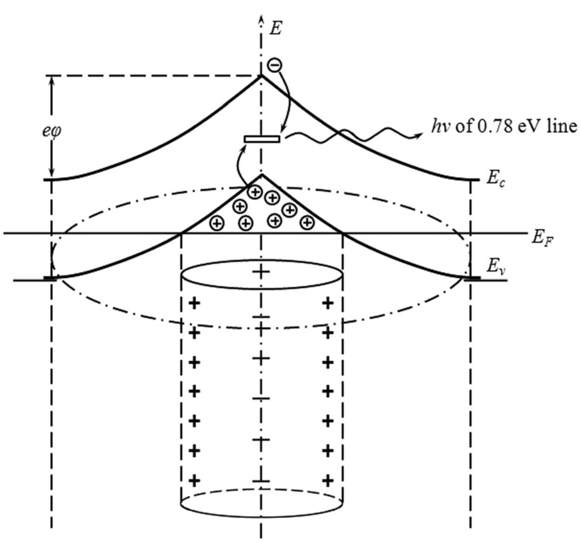

FIG. 6. The space charge cylinder model of dislocation.

IV. CONCLUSIONS

The 0.78 eV line in the silicon samples with dislocations induced by electron irradiation is investigated extensively. The results show a good thermal stability of 0.78 eV line, and its activation energy is ~13 meV, which is much smaller than that of D1/D2 indicating they may have different origins. The 0.78 eV line luminescence center has no relationship with oxygen atom clusters, neither thermal donors nor oxygen precipitations. It is assumed that the 0.78 eV line origins from the specific reconstructed dislocation structures which could be easily affected by point defects and temperature.

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