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STUDY OF THE 1096.9 meV PHOTOLUMINESCENT OXYGEN-RELATED CENTRE IN NEUTRON-IRRADIATED CZ–Si: FORMATION AND STRUCTURE

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The creation process and the structure of an oxygen-associated centre in Si are investigated by means of photoluminescence (PL). The centre is formed after annealing between 250°C; and 450°C in neutron-irradiated CZ–Si and is photoluminescent with a bound exciton emission at 1096.9 meV. We show that this PL line as well as the I1 PL line (1018.2 meV) are the major features of the PL spectra for samples annealed in this temperature range. The comparison of the PL spectra obtained in CZ–Si and FZ–Si crystals indicates that the 1096.9 meV PL line is formed at expenses of I1, thus suggesting the associated centre is presumably created by complexing the trigonal I1 centre with one (or more) interstitial oxygen. Uniaxial stress measurements and the observed oxygen isotopic shift (0.037 meV) show that the PL line is associated with an oxygen centre of monoclinic I symmetry. The thermal activation energy of the binding exciton deduced from the intensity decay, $\Delta E = 5.1$ meV, together with the stress behaviour suggest that the centre probably corresponds to an iso-electronic centre.

Keywords: Neutron irradiation; Oxygen centres in silicon; Isotopic shift

1 INTRODUCTION

Oxygen-related centres formed in Czochralski (CZ) silicon have been the object of intense investigation since the discovery of thermal donors

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(TD) [1] arising after thermal treatments of annealing at about 450°C. The interest in understanding the structure and the formation processes of such centres of marked technological interest has increased the activity in the research field of radiation damage by neutron, electron or ion bombardment as an efficient way of creating new defect centres in silicon [2]. The study of simple centres created after annealing irradiated crystals during the first stages of the TD formation can provide useful information to reveal the structure of these centres.

In this paper we investigate a new photoluminescent oxygen centre formed in neutron-irradiated CZ–Si after thermal annealing at 350–400°C. The bound exciton emission of this centre with a Zero Phonon Line (ZPL) at 1096.9 meV is the major feature observed in the photoluminescence (PL) spectrum. Although PL lines at 1097 meV have already been reported as minor PL lines in H [3], P or B [4] ion bombardment Si and in In-implanted Si [5], the relevance of this centre as one of the more important PL centres in neutron-irradiated CZ–Si annealed between 300°C and 400°C and the fact that it can be formed in CZ–Si independent of the type of impurity H, C or Li present in the crystal has not been so far reported [2,6,7]. We show that this PL centre is monoclinic I involving at least one oxygen. The centre can be formed after annealing in either electron- or neutron-irradiated Si. The oxygen concentration provided by CZ–Si seems to be the unique requirement for the creation of this centre. It is likely that the centre presumably corresponds to an intrinsic defect complexed with oxygen since its formation is not affected by the presence of common impurities such as H, Li, P, or B. In contrast to other Si PL defects this centre is not passivated by Li even for $[Li] \approx 10^{17}\,cm^{-3}$ [6].

2 EXPERIMENTAL

The three series of Li doped silicon crystals employed in this work were used elsewhere [6]. The isotopic studies were performed on FZ–Si with $[C] = 7 \times 10^{15}$ and $2.1 \times 10^{17}\,cm^{-3}$ as starting materials. The ^{18}O was introduced into the crystal by indiffusion at 1300°C in the presence of ^{18}O H_2O vapour at atmospheric pressure for seven days. The oxygen concentration determined from optical absorption was 4.1×10^{17} and $1.7 \times 10^{17}\,cm^{-3}$ for ^{18}O and ^{16}O, respectively. ^{16}O was indiffused from the quartz tube. All samples were doped with $[Li] = 2 \times 10^{16}\,cm^{-3}$ since this impurity is very efficient to passivate minor PL centres with ZPL near 1100 meV thus clearing up the PL spectrum from unwanted PL lines [6]. Three sets of X-ray oriented crystals along ⟨100⟩, ⟨111⟩ and ⟨110⟩ with dimensions of $15 \times 2 \times 2\,mm^3$ were treated and polished for uniaxial stress experiments.

PL spectra were obtained using a Nicolet 60XS and a Bomem DA3 Fourier Transform spectrometers fitted with North Coast Ge diode detectors. Most of the experiments were done with samples immersed in liquid helium at 4.2 K, and with excitation by a 514 nm argon laser. An Oxford flow cryostat was used for temperature variation and stress experiments. Special care was paid for obtaining the PL spectra under the same experimental conditions for intensity analysis.

3 RESULTS AND DISCUSSION

3.1 Center Formation

Figure 1 shows the PL spectra of neutron-irradiated Si crystals annealed at 250°C and 350°C. Apart from the PL spectra of CZ–Si, the corresponding PL spectra of carbon-lean and carbon-rich FZ–Si crystals are included in Fig. 1 for comparison purposes. The three samples were annealed together in order to get similar thermal treatments. It must be observed that the I1 PL line at 1018.2 meV is dominant in the PL spectra of the annealed samples at 250°C, and its intensity is not significantly affected by the presence of carbon. The annealing at 350°C has however different consequences on the PL spectra depending on the impurity content of the crystal. While the I1 line is still the main feature in the spectrum of the carbon- and oxygen-lean material, it almost disappears in the PL spectra of carbon-rich FZ–Si and CZ–Si. In the C-rich material several C-related PL centres such as M, C and mainly F [2,7,8] spread over the whole spectrum, but in CZ–Si the major contribution to the PL spectrum is due to the 1096.9 meV-line centre. As shown in [6] the increase of the 1096.9 meV-line intensity with the annealing temperature correlates with the decrease of the I1 intensity thus suggesting that the creation of the 1096.9 meV-line centre presumably arises from complexing the trigonal I1 centre with oxygen. Recent studies associate the

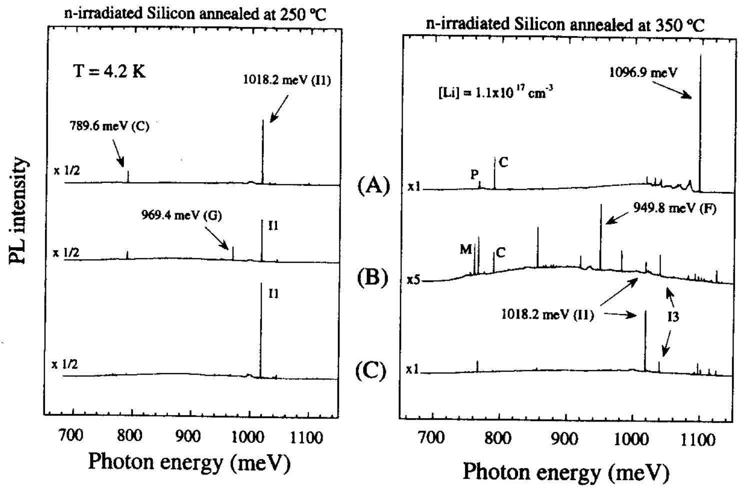

FIGURE 1 PL spectra at 4.2 K corresponding to (A) CZ–Si[O] $= 2 \times 10^{18}\,\mathrm{cm^{-3}}$, (B) FZ–Si with [C] $= 1.6 \times 10^{17}\,\mathrm{cm^{-3}}$, and (C) carbon- and oxygen-lean FZ–Si, neutron-irradiated with a dose of $1 \times 10^{17}\,\mathrm{cm^{-2}}$ and annealed at 250°C and 350°C for 30 min. The Li concentration is $1.1 \times 10^{17}\,\mathrm{cm^{-3}}$ in the three samples. The prominent PL lines are identified by the commonly used labels [2]. Note the different intensity magnifications for each spectrum. Spectral resolution: 0.25 meV.

defect responsible for this 1018.2 meV ZPL with the neutral divacancy [9]. Although a conclusive structural model deserves more experimental evidence the present results support the proposed vacancy-based model rather the $\langle 111 \rangle$ split interstitial model [10], given the weak dependence of the I1 line intensity with [C] (Fig. 1).

3.2 Center Structure

Figure 2 shows the phonon side band associated with the 1096.9 meV PL line. Although Li was intentionally introduced into Si to prevent the creation of unwanted PL impurities we verified that Li is not directly involved in this centre since neither a ^{7}Li : ^{6}Li isotopic shift nor dependence of the centre formation on the Li content as well as on H, C, B or P was detected in these experiments. However, the presence of oxygen as a constituent of the PL centre is clearly evidenced through the isotope shift, $E_{ZPL}(^{18}O) - E_{ZPL}(^{16}O) = +0.037\,\mathrm{meV}$, observed in the high resolution PL spectra of Fig. 3. Although we are not able to elucidate

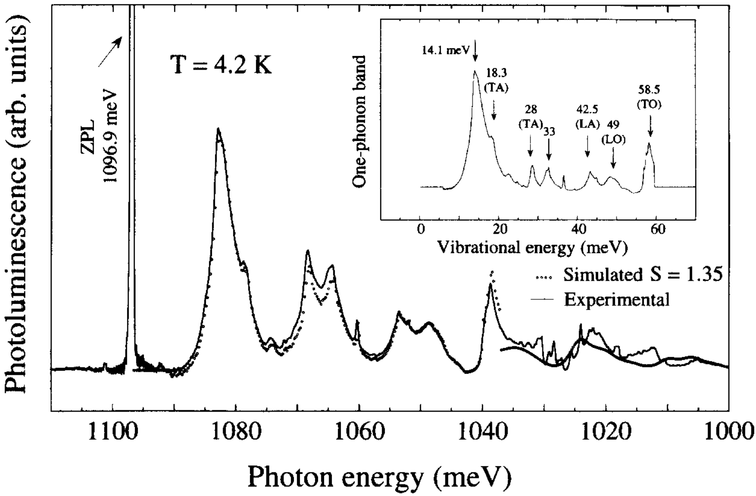

FIGURE 2 PL spectrum of the 1096.9 meV-line at 4.2 K obtained from carbon-lean CZ–Si, neutron-irradiated and annealed at 350°C for 30 min, with a spectral resolution of 0.6 meV. The spectrum has been magnified to analyse the phonon side band. Point data correspond to the calculated phonon side band using the one-phonon spectrum given in the inset for a Huang–Rhys factor, $S = 1.35$. The peaks are labelled with the phonon energy (in meV) of maxima of the phonon state density, and the associated phonon branch.

the number of O involved in the centre with the present data, the observed isotopic shift is similar to 0.04 meV found for the 1060 meV-line [11] or 0.024 meV exhibited by the 789 meV C-line [12].

The thermal dependence of the total intensity (ZPL + phonon side band) shown in the inset of Fig. 3 can be well explained on the basis of thermal activation processes associated with the dissociation of the bound exciton which are described by the equation given in the caption [2]. The activation energy, $\Delta E = 5.1$ meV, is characteristic of exciton binding to shallow donors or acceptors [2]. However, the exciton binding energy derived from the ZPL energy is $E_{BE} = 1154.6 - 1096.9$ meV $= 58$ meV. Therefore it is likely that this centre corresponds to an intermediate deep–shallow donor centre involving oxygen in which one of the bound exciton particles is weakly bound to the centre. Interestingly, the analysis of the phonon side band reveals that like I1, electron–phonon couplings are mainly governed by TA phonons. In fact the one-phonon contribution deduced from the analysis of the PL

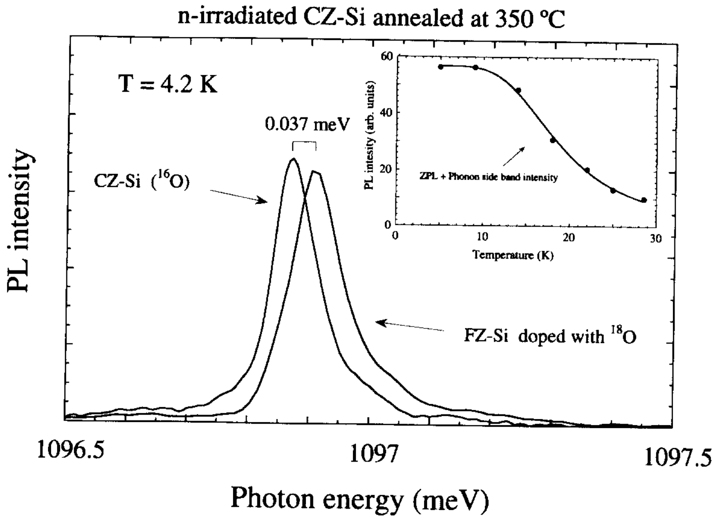

FIGURE 3 Isotope shift of the 1096.9 meV-line at 4.2 K. The high resolution PL spectra correspond to CZ–Si with $[^{16}O]=2\times10^{18}\,cm^{-3}$, and to FZ–Si doped with $[^{18}O]=4.1\times10^{17}\,cm^{-3}$, $[^{16}O]=1.7\times10^{17}\,cm^{-3}$ and $[C]=7\times10^{15}\,cm^{-3}$, neutron-irradiated with a dose of $1\times10^{17}\,cm^{-2}$ and annealed at 390°C for 30 min. $[Li]=2\times10^{16}\,cm^{-3}$. Spectral resolution: 0.012 meV. The inset shows the variation of the PL line intensity with temperature. The curve represents the fit of the data to the equation: $I=I_0/[1+gT^{3/2}\exp(-\Delta E/KT)]$ with $I_0=57$, $g=0.27\,K^{2/3}$ and $\Delta E=5.1$ meV.

spectra (inset of Fig. 2) shows peaks whose vibrational energies chiefly correspond to maxima of the phonon state density. An exception to this behaviour is the 14.1 meV TA resonant mode which exhibits the stronger coupling. From this curve we obtain an average phonon energy of 23 meV. On the other hand, the Huang–Rhys factor derived from the PL spectrum analysis through the ZPL intensity to the total intensity ratio is $S=\ln I/I_0=1.35$. The phonon side band calculated from the one-phonon contribution for $S=1.35$ is shown in Fig. 2. From these values we obtain a mean relaxation energy for the bound exciton of $S\hbar\omega=31$ meV which is about half the exciton binding energy.

Uniaxial stress measurements indicate that the centre possesses a monoclinic I symmetry as shown from the splitting pattern displayed by the singlet to singlet ZPL under axial stress. The characteristic 2, 3 and 4 components shown by the PL spectra of compressed crystals along the ⟨100⟩, ⟨111⟩ and ⟨110⟩ directions, respectively, as well as the

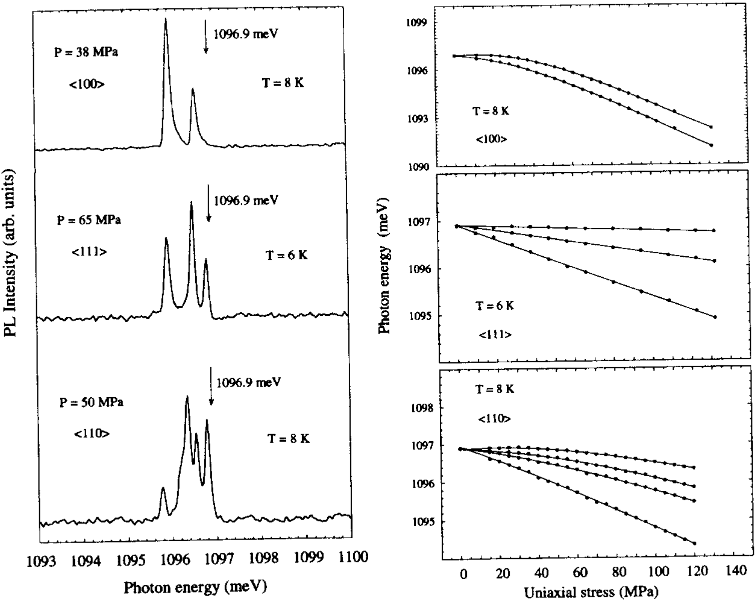

FIGURE 4 Uniaxial stress PL spectra of the 1096.9 meV line and the corresponding stress shifts under axial compressions along ⟨100⟩, ⟨111⟩ and ⟨110⟩. The lines are guides for the eye.

corresponding stress shifts are depicted in Fig. 4. Note that the non-linear shifts observed along ⟨110⟩ and mainly along ⟨100⟩ are the consequences of the stress-induced coupling with excited states located 4 meV above the ZPL such as it is observed in the $T = 21$ K PL spectrum. The observed shifts suggest that the centre is iso-electronic. In the excited state, it traps a hole close to the centre, with the electron part of the exciton orbiting as a shallow particle. An account of the observed variations will be given in a forthcoming publication.

4 CONCLUDING REMARKS

An interesting feature of the present work concerns the correlation between the two major PL lines observed in CZ–Si which associates the anneal out of the I1 line with the formation of the 1096.9 meV-line.

Consequently, the centre responsible for the 1096.9 meV line can presumably be formed either by complexing directly the I1 centre with oxygen or by capturing the species liberated during process where the I1 centre is destroyed by interstitial oxygen. In either case the investigated centre seems to correspond to a vacancy–oxygen complex provided that the divacancy is the centre responsible for the I1 PL line [9].

Further work on this centre is currently in progress.

Acknowledgments

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