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ELECTRONIC AND OPTICAL PROPERTIES OF SEMICONDUCTORS

IR Luminescence in Thermally Treated Silicon

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Abstract—Near-edge IR luminescence with peak emission at E = 1.084 eV has been studied in n- and p-type silicon samples with different contents of interstitial oxygen under excitation with a Nd:YAG laser diode. Thermal treatments of the samples demonstrated that the luminescence nearly completely disappears upon thermal treatments at T = 1050°C and is partly restored in two stages in subsequent thermal treatments in the temperature range 550–800°C. The temperature intervals of luminescence quenching and restoration (500–600 and 700–800°C) correlate with the temperature ranges of dissolution for shallow oxygen precipitates (1000°C) and the generation of oxygen-containing thermal defects, the so-called thermal donors of types I and II. The data obtained suggest that the electronic states related to thermal donors are traps for nonequilibrium carriers and the emptying of these traps contributes to the near-edge emission.

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Thermal treatments that accompany the growth of silicon crystals and films yield electrically active thermal defects: oxygen precipitates [1–6] and dislocations [7–9]. Electron-microscopic, optical (absorption, IR photoluminescence), electrical (deep-level transient spectroscopy DLTS, Hall effect), and other methods are widely used to study thermal defects [1–6, 10, 11]. For example, detailed studies by DLTS and methods of IR absorption and low-temperature (12 K) photoluminescence (PL) of silicon crystals subjected to prolonged thermal treatments that produce dislocations (PL bands at 0.807 and 0.87 eV) and oxygen precipitates of various sizes (PL bands in the range 0.802–0.929 eV) have been reported [6–9].

In this study, the effects of thermal defects and additional thermal treatments on the near-edge PL [12, 13] were examined. The IR PL was excited by the light of a Nd:YAG pulsed laser diode with an emission wavelength λ_{max} = 1.06 μm and average power of 10–1500 mW. The PL spectra were recorded with a Bruker RFS-100S Fourier spectrometer in the temperature range 77–300 K. Silicon crystals of n- and p-types with resistivities of 7.5, 0.01, 0.005, and 0.001 Ω cm and different oxygen concentrations (2×10^{17}–7×10^{17} cm^{-3}) were studied. The thermal treatments were performed in the atmosphere of dry argon in the temperature range 500–1100°C. Silicon crystals were subjected to grinding, polishing, and etching in an SR-4A polishing etchant. To preclude contamination with impurities during the thermal treatments, the silicon crystals were covered with a protective oxide layer removed before PL measurements.

All the starting crystals exhibit, irrespective of the conduction type, an oxygen content, and growth technique (Czochralski method, crucibleless floating zone melting, monosilane decomposition), broad near-edge PL bands with different intensities, peaked at E = 1.084 eV (Fig. 1). The PL intensity was determined either as the area under the PL band at 1.084 eV or as the intensity at the peak of the emission band. Upon raising the doping level of the silicon crystals, the PL band at 1.084 eV is broadened and extended to the

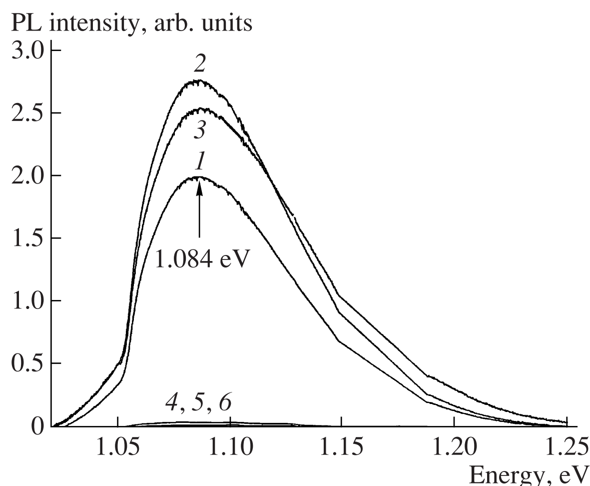


Fig. 1. Typical PL spectra of various silicon samples (T_{expt} = 300 K): (*1*, *4*) KDB-7.5 (p-Si:B with a resistivity of 7.5 Ω cm), (*2*, *5*) KÉF-7.5 (n-Si:P, 7.5 Ω cm), and (*3*, *6*) BKDB-7.5 (dislocation-free p-Si:B, 7.5 Ω cm). Spectra *4* and *6* measured after an annealing at 1050°C.

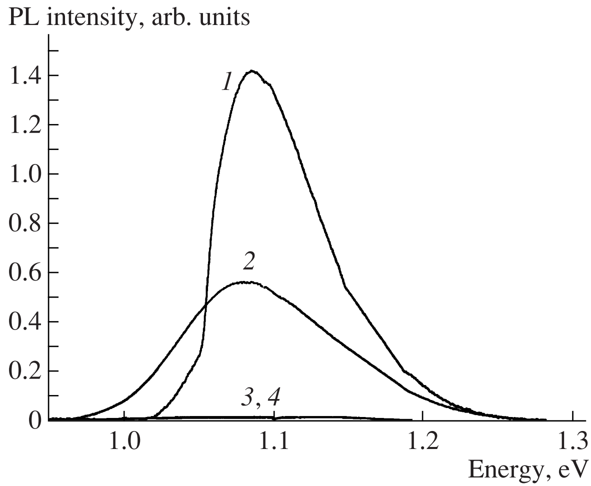
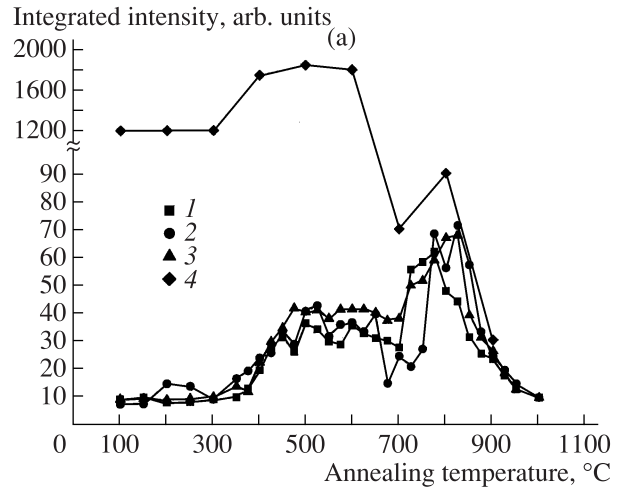


Fig. 2. PL intensity in relation to the doping level of Si crystals: (*1*) KDB-7.5 (*p*-Si:B, ρ = 7.5 Ω cm), (*2*) KDB-0.01 (*p*-Si:B, ρ = 0.01 Ω cm), (*3*) KDB-0.005 (*p*-Si:B, ρ = 0.005 Ω cm), and (*4*) KDB-0.001 (*p*-Si:B, ρ = 0.001 Ω cm).



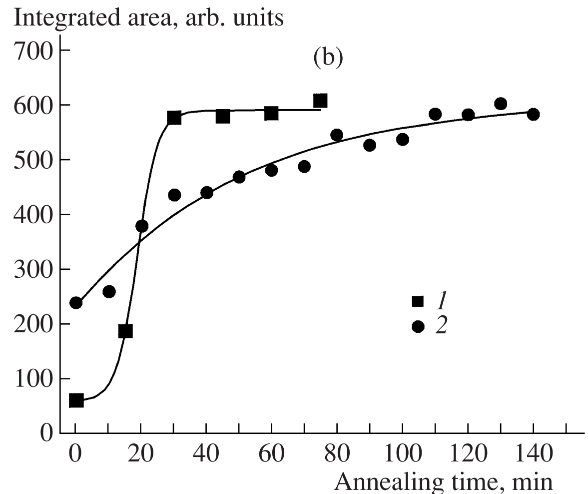


Fig. 3. Integrated PL intensity in relation to the heat treatment type. KDB-7.5 (*p*-Si: B; ρ = 7.5 Ω cm) ample. (a) Isochronal annealing, preliminary thermal treatment at 1050°C for *t*: (*1*) 1, (*2*) 1.5, and (*3*) 2 h; (*4*) starting material. (b) Isothermal annealing: (*1*) starting material and (*2*) preliminary heat treatment at 1050°C for 1.5 h (magnified by a factor of 40 for clarity).

lower energies (Fig. 2; curves *1*, *2*). This may be due to an effective decrease in the energy gap width upon an increase in the dopant concentration.

In view of the concept that the PL intensity can be governed by some bulk defects acting as nonradiative recombination centers or thermally generated traps for nonequilibrium carriers, the samples were thermally treated in dry nitrogen at temperatures of 300–1100°C (Figs. 3, 4). It was found that the PL intensity increases in the temperature range 400–550°C, then decreases and again slightly increases at a temperature of 700°C, to become insignificant at a heating temperature of 1050°C (Fig. 3a). After the annealing at 1050°C, the samples were again thermally treated at 300–1000°C in order to elucidate the possible involvement of thermal defects in radiative recombination as traps (Fig. 3a). It was found that the intensity of PL at 1.084 eV grows in the temperature ranges 400–550 and 700–800°C, even though it reaches a value lower than that in the starting crystals (before the treatments, Fig. 3a).

A study of the distribution for the PL intensity across the crystal thickness after a heat treatment at T = 1050°C demonstrated (Fig. 5, curves *3* and *4*) that the PL intensity decreases throughout the crystal volume, which may be due both to dissolution of fine oxygen formations (similar to oxygen-related thermal donors) [14] and to formation, as a result of the heat treatment of nonradiative recombination centers uniformly distributed throughout the crystal volume. Similar studies in the stages of increasing PL (450–500 and 700–800°C) also demonstrated the volume nature of the distribution for the trap states involved in radiative recombination.

The results of the study suggest that, both in crystal growth by various methods and in the accompanying heat treatments, thermal defects are formed and give rise to traps for nonequilibrium carriers and, in particular, electrons. The emptying of these traps results in radiative recombination events contributing to the near-edge PL at 1.084 eV. The defects are formed, during the cooling of grown silicon ingots, at a temperature of about 550°C and disintegrate at temperatures higher than 800°C. The concentration of the thermal defects is restored after the high-temperature treatment at 1050–1100°C by a repeated thermal treatment at 450–800°C. This restoration occurs in two stages, at 400–500 and 700–800°C, but it is incomplete due to the formation of the competing channel of nonradiative recombination via thermal defects formed after the high-temperature treatment. The coincidence of the temperature range in which the PL intensity is restored and defects are annealed out with the temperature interval in which oxygen-containing defects, thermal donors of types I

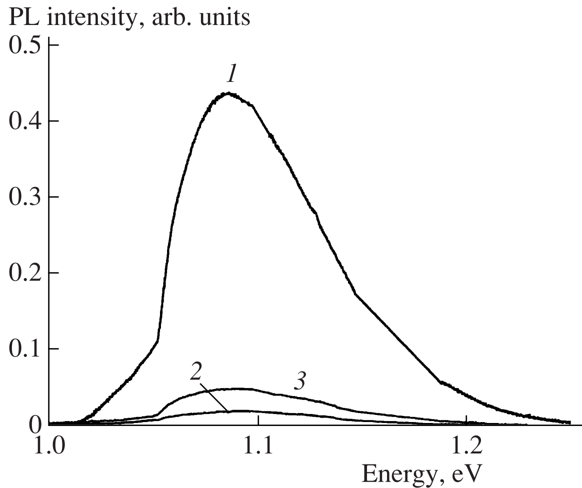


Fig. 4. PL spectra in relation to the type of heat treatment. (*1*) Starting *p*-Si:B (ρ = 7.5 Ω cm), (*2*) heat treatment at 1050°C, and (*3*) heat treatments at 1050°C + 550°C.

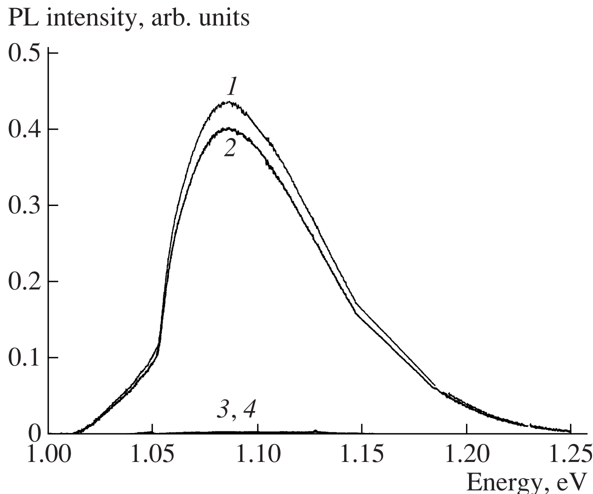


Fig. 5. Distribution of the PL intensity across the silicon wafer thickness. (*1*) Initial surface of *p*-Si:B (ρ = 7.5 Ω cm); (*2*) the same material, 70 μm etched off; (*3*) initial surface of the same material heat treated at 1050°C; and (*4*) the same material heat treated at 1050°C with 70 μm etched off.

and II [1–6, 10, 11] are formed and disintegrated suggests that the trap states are created by oxygen-containing defects and, in particular, by thermal donors of types I and II, whose electronic states lie within the range 0.09–0.15 eV below the conduction band [10]. In terms of this interpretation, the PL observed is a sensitive method for the analysis of silicon crystals being grown for the presence of oxygen-containing thermal defects. The fact that the time dependence of the PL intensity of samples thermally treated at 550°C levels-off after 30 min (Fig. 3b) and there is no noticeable decrease in the concentration of the oxygen impurity, indicates that the concentration of the given thermal defects is comparatively low and they are transformed into more intricate oxygen-containing defect complexes when making the heating duration longer.

REFERENCES

1. W. Kaiser, Phys. Rev. **105**, 1751 (1957).
2. C. S. Fuller, J. A. Ditzenberger, N. B. Hannay, and E. Buehler, Phys. Rev. A **96**, 833 (1955).
3. J. R. Patel, in *Semiconductor Silicon 1981*, Ed. by H. R. Huff, R. J. Kriegler and Y. Takeishi (Electrochemical Society, Pennington, 1981), p. 189.
4. J. R. Patel, K. A. Jackson, and H. Reiss, J. Appl. Phys. **48**, 5279 (1977).
5. Y. Tokuda and N. Kobayashi, J. Appl. Phys. **66**, 3651 (1989).
6. Y. Kamiura, F. Hashimoto, and M. Yoneta, J. Appl. Phys. **66**, 3926 (1989).
7. S. Binetti, S. Pizzini, E. Leoni, et al., J. Appl. Phys. **92**, 2437 (2002).
8. A. Castaldini, D. Cavalcoli, A. Cavallini, and S. Pizzini, Phys. Status Solidi A **202**, 889 (2005).
9. E. Leoni, S. Binetti, B. Pichaud, and S. Pizzini, Eur. Phys. J. Appl. Phys. **27**, 123 (2004).
10. V. S. Vavilov, V. F. Kiselev, and B. N. Mukashev, *Defects in the Bulk and at the Surface of Silicon* (Nauka, Moscow, 1990), p. 28 [in Russian].
11. V. Cazcarra and P. Zunino, J. Appl. Phys. **51**, 4206 (1980).
12. I. P. Varshni, in *Radiative Recombination in Semiconductors*, Ed. by Ya. E. Pokrovsky (Nauka, Moscow, 1972), p. 9 [in Russian].
13. N. A. Sobolev, A. M. Emel'yanov, V. V. Zabrodsky, et al., Fiz. Tekh. Poluprovodn. **41**, 635 (2007) [Semiconductors **41**, 616 (2007)].
14. P. E. Wei, K. F. Kelton, and R. Falster, J. Appl. Phys. **88**, 5062 (2000).

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