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Origin of anomalous temperature dependence and high efficiency of silicon light-emitting diodes

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Efficient electroluminescence with power efficiency up to 0.12% is observed from silicon *pn* diodes prepared by boron implantation with boron concentrations above the solubility limit at the postimplantation annealing temperature. The electroluminescence spectra exhibit a transition from two bound-exciton bands towards the free electron-hole pair recombination with an anomalous increase in the total intensity with increasing temperature. The implantation dose and temperature dependences of the relative peak intensities provide evidence for the relevance of excitonic traps as a supply for free electron-hole pairs and thus for the origin of the enhanced electroluminescence at elevated temperatures.

The implementation of silicon-based optoelectronics requires the realization of light emitters, waveguides, and photodiodes compatible with standard silicon processing technology.[1] Light emitters, such as silicon nanoclusters, Er-doped Si-rich SiO_2, SiGe quantum dots, and silicon *pn* junctions are presently considered as potential light sources.[2] The latter ones are especially attractive, since they are fully compatible with silicon ultralarge-scale integration technology including low operation voltages. Although bulk silicon, being an indirect semiconductor with inefficient radiative recombination, has been neglected for this purpose for a long time, significant improvements in the electroluminescence (EL) efficiency from bulk silicon *pn* diodes have been reported recently.[3,4] The main concept for improving the light emission from silicon is based on a decrease of nonradiative decay channels possibly with carrier confinement in the active region of the device. Green *et al.*[3] employed surface texturing in combination with efficient surface passivation of high-purity float-zone silicon to improve the light extraction from the *pn* junction. Ng *et al.*[4] prepared silicon light-emitting diodes by high boron-dose implantation for the *p*-type doping in silicon *pn* junctions. They explained the increased EL efficiency by carrier confinement introduced by dislocation loops formed during implantation, where the strain-induced potential at dislocations loops prevents carriers from diffusing to nonradiative channels, thus leading to a strong band edge electron-hole recombination. Similar high EL efficiency was also reported in silicon p^+n junctions prepared by thermal diffusion of high boron concentrations (3×10^{19} cm^{-3}) in the surface layer.[5] All these *pn* diodes with highly boron-doped surface layers have in common the interesting feature of an anomalous increase in EL efficiency with temperature, which is in stark contrast to the conventional behavior of photoluminescence from bulk silicon. A study of this anomalous temperature dependence is essential for the understanding of the enhancement of the EL with increased boron doses. However, up to now no detailed experimental investigation has been reported for clarifying the origin of the anomalous temperature dependence and its relation to the high EL efficiency in such *pn* diodes. In a previous study of low temperature EL spectra of silicon *pn* diodes we found two luminescence peaks with maxima around 1.05 and 0.95 eV from excitons bound to traps which are introduced by the high-dose boron implantation and the subsequent annealing.[6] A more detailed study indicates that these peaks can be explained by recombination of spatially indirect excitons (with electrons and holes localized in spatially separated potential minima) which are formed by a locally increased boron concentration in combination with strain-free or highly strained environments surrounding dislocations.[7,8] The strong trapping and detrapping of excitons bound to these traps can strongly influence the conductivity via the free carrier concentration and contribute to an *S*-type current bistability at low temperature.[6] In this report, we concentrate on the dependence of the EL on the boron implantation dose and the lattice temperature. The strong correlation between the temperature dependence of the EL intensity from the band edge recombination and from bound excitons provides strong evidence that the release of electron-hole pairs from the excitonic traps to the valence and conduction band play an important role in the anomalous temperature dependence and high efficiency of the diodes. Efficient RT EL with power efficiency up to 0.12% is observed from such silicon *pn* diodes with further improvements to be expected.

The silicon *pn* diodes were prepared by boron implantation into (001) oriented Sb-doped *n*-type (0.1 Ω cm) silicon substrates at a tilt angle of 7° through a 50 nm thermally grown SiO_2 layer. Boron doses between 2×10^{13} and 3×10^{17} cm^{-2} were implanted at an energy of 25 keV. All samples were subsequently furnace annealed at 1050 °C for 20 min and processed into 1 mm diameter diodes with aluminum metallic ring contacts on top. For low-temperature EL studies, the diodes were mounted on the cold finger of a closed-cycle cryostat with silver paste. EL signals were recorded with a monochromator and a liquid-nitrogen cooled InGaAs detector. All EL spectra were measured at a constant

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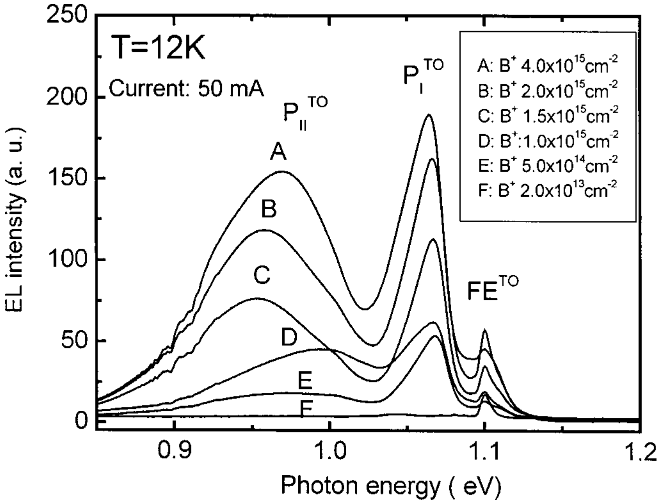

FIG. 1. EL spectra from silicon *pn* diodes prepared by boron implantation at an energy of 25 keV and different doses as given in the figure. All samples are annealed at 1050 °C for 20 min. The spectra are recorded under forward bias at a current of 50 mA.

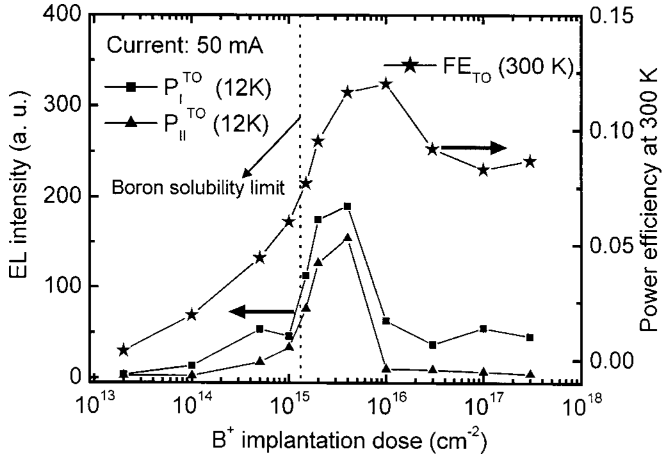

FIG. 2. Boron-dose dependence of the EL intensity from bound-exciton bands at 12 K (full squares and triangles) and the EL power efficiency from the band edge recombination at RT (asterisks). The vertical line represents the boron solubility limit of 1.53×10^{20} cm^{-3} at the annealing temperature of 1050 °C.

current of 50 mA supplied by a sourcemeter (Keithley 2410), with a typical forward bias of 0.85 V at RT. The absolute EL power from the diode at RT was measured using a calibrated large-area optical power meter placed in proximity to the diode. The external EL power efficiency is calculated by dividing the total EL output power from the front plus the back surface by the input electrical power.

Figure 1 shows the EL spectra at 12 K from the silicon *pn* diodes prepared by boron implantation at different doses of 4×10^{15} (A), 2×10^{15} (B), 1.5×10^{15} (C), 1×10^{15} (D), 5×10^{14} (E), and 2×10^{13} cm^{-2} (F). At implantation doses higher than 5×10^{14} cm^{-2}, the spectra show a peak from the TO phonon-assisted free exciton recombination at 1.1 eV (FE^{TO}) and two asymmetric broad EL peaks close to 1.05 and 0.95 eV from TO phonon-assisted recombination of excitons bound to traps (P_I^{TO} and P_{II}^{TO}, respectively). At very low boron implantation doses of 2×10^{13} cm^{-2}, no luminescence from bound excitons is observed in the EL spectrum (F). Above an implantation dose of 5×10^{14} cm^{-2}, the bound-exciton peaks (P_I^{TO},P_{II}^{TO}) increase strongly with increasing the boron doses up to 4×10^{15} cm^{-2}. The photon energy of these peaks also changes with changing boron doses. These results indicate that both peaks are strongly correlated to the traps created by high-dose boron implantation and the subsequent annealing. In Fig. 2 the dependence of the EL intensity at 12 K of the two bound-exciton peaks on the boron doses from 2×10^{13} to 3×10^{17} cm^{-2} is plotted. It is clearly seen that their EL intensities increase strongly up to a boron dose close of 2–3 times the boron solubility limit of 1.53×10^{20} cm^{-3} at the annealing temperature of 1050 °C[9] and then decrease with further increasing the boron doses. Higher boron implantation doses lead to an increased damage of the lattices structure as well as the formation of boron precipitates,[10] therefore a decrease of the EL intensity is observed due to the associated creation of additional nonradiative recombination centers. The correlation in Fig. 2 of the *low-temperature* emission from the excitonic bands with the RT EL *efficiency* from band edge recombination will be discussed later.

The temperature dependence of the EL spectra was studied at a fixed current of 50 mA for diode (A) prepared by boron implantation with a dose of 4×10^{15} cm^{-2}, which exhibits the highest EL intensity of the bound-exciton peaks at low temperatures. Figure 3 shows a strong increase and broadening of the FE^{TO} peak with increasing temperature. At RT, after the thermal quenching of P_I^{TO} and P_{II}^{TO} peaks, the spectrum resembles the typical band edge recombination spectrum of bulk silicon. The peak height of the bound-exciton peaks P_I^{TO} and P_{II}^{TO} as well as the overall integrated EL intensity of the FE^{TO} peak and its phonon replicas is plotted as a function of temperature in Fig. 4, where the peak height of the P_I^{TO} peak is obtained by subtracting the contributions of the phonon replicas of the free electron-hole recombination. In addition, the temperature dependence of the integrated *photoluminescence* of the FE^{TO} peak of the *n*-doped substrate is shown for comparison. The photoluminescence (PL) spectra are obtained from the substrate of the

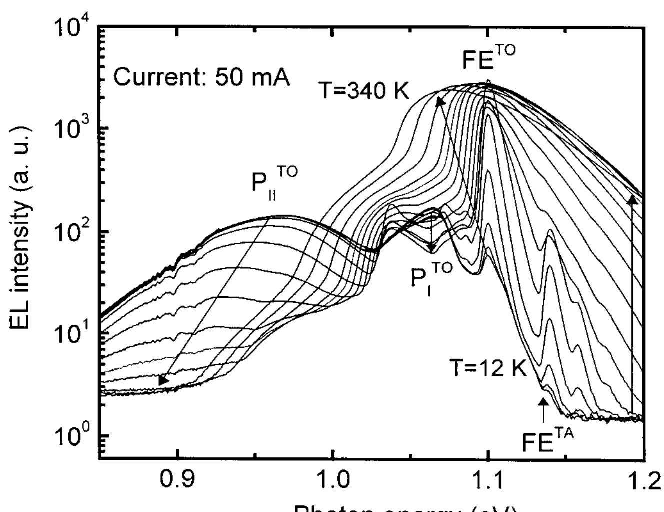

FIG. 3. EL spectra at different temperature from 12 to 340 K from sample (A) implanted with a B$^+$ dose of 4×10^{15} cm^{-2}, the arrows indicate the change of the spectra with increasing temperature.

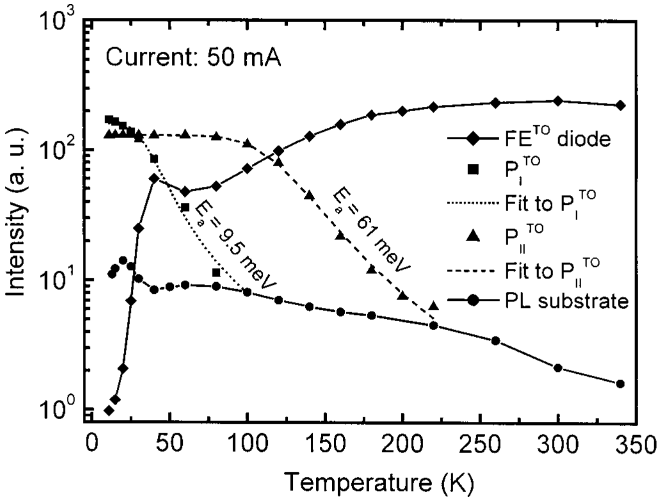

FIG. 4. Dependence of the EL intensity from different bands on the lattice temperature for sample (A). The dotted and dashed lines are theoretical fits to the experimental data of the bound-exciton peaks. The solid lines are guides for the eye. The temperature dependence of the photoluminescence from the band edge recombination of *n*-type silicon substrate is shown for comparison. Note that the relative scale for EL and photoluminescence are arbitrary.

diodes under excitation with a He–Ne laser (power ~10 mW).

The P_{I}^{TO} peak starts to decrease from 15 K and is completely thermally quenched at 80 K. The P_{II}^{TO} peak starts to decrease at 80 K, and is thermally quenched at a temperature of 260 K, where the maximum intensity of the FE^{TO} peaks is reached. The increase of band edge EL intensity is in strong contrast to the temperature dependence of the PL from the *n*-type substrate, which exhibits no trap-related luminescence. The EL intensity of the FE^{TO} peak shows a two-step increase with rising temperature in close correlation with the decrease of the two bound-exciton peaks: The first increase of the FE^{TO} peak at low temperature is related to the thermal quenching of the P_{I}^{TO} line with a characteristic activation energy of 9.5 ± 1.5 meV; the second increase is correlated to the thermal quenching of the P_{II}^{TO} line with a characteristic energy of 61 ± 2 meV. The activation energies of the bound excitons to free electron-hole pairs in the continuum states of the valence and conduction bands are obtained by fitting the intensity with the expression $I = I_0/[1+g\cdot T^{3/2}\exp(-E_a/kT)]$,[11] where E_a is the activation energy, I_0 is the EL intensity at low temperature, $g\cdot T^{3/2}$ equals the capture rate of free excitons to excitonic traps times the density of effective states in the valence and conduction bands,[12] and k is the Boltzmann constant. This correlation indicates that the increase of the band edge free electron-hole recombination comes from the thermal dissociation of bound excitons with increasing temperature. Our results also reflect the typical low recombination rate of the spatially indirect bound excitons in the *pn* diodes, which have a recombination rate over 100 times lower than the thermal emission rate at 220 K as calculated by a rate equation model considering the transition between bound excitons and free excitons/electron-hole pairs.[8]

Our interpretation about the relevance of the excitonic traps is corroborated by comparing the electroluminescence efficiency at the FE^{TO} band at RT with the low-temperature emission from the bound excitons—as shown in Fig. 2 as a function of the implantation dose. The RT power efficiency of the diode shows the same strong increase as the low-temperature bound-exciton emission close to a boron concentration around three times the solubility limit of boron at the postimplantation annealing temperature of 1050 °C. This underlines the role of the excitonic traps produced by boron implantation as a source term for free electron-hole pairs at elevated temperatures: They prevent the carriers from decaying in fast nonradiative decay channels at higher temperatures, which govern the usual decreasing photoluminescence intensity as the temperature is increased.

The power efficiency of 0.12% obtained for our diode is comparable to those reported for similar Si:B diodes[4] and also to electrically pumped Er-doped SiO_2 layers. The latter ones have large external quantum efficiencies of 10%, however, considering the larger bias voltage (electric fields) of 43 V (7 MV/cm) necessary for electrical excitation of the Er^{3+} ions, the external power efficiency of 0.18%[13] is comparable to the values reported here.

In summary, efficient EL with power efficiency up to 0.12% was observed from silicon *pn* diodes prepared by boron implantation. The temperature dependence of the electroluminescence from bound excitons and free electron-hole pairs shows that excitonic traps act as a temporary storage of electron-hole pairs, which effectively enhance the band edge radiative recombination in silicon *pn* diodes by supplying free electron-hole pairs at elevated temperature.

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[1] A. Polman, Nat. Mater. **1**, 10 (2002).
[2] L. Pavesi, J. Phys.: Condens. Matter **15**, R1169 (2003).
[3] M. A. Green, J. Zhao, A. Wang, P. J. Reece, and M. Gal, Nature (London) **412**, 805 (2001).
[4] W. L. Ng, M. A. Lourenço, R. M. Gwilliam, S. Ledain, G. Shao, and K. P. Homewood, Nature (London) **410**, 192 (2001).
[5] A. M. Emel'yanov, N. A. Sobolev, T. M. Mel'nikova, and S. Pizzini, Semiconductors **37**, 730 (2003).
[6] J. M. Sun, T. Dekorsy, W. Skorupa, B. Schmidt, and M. Helm, Appl. Phys. Lett. **82**, 2823 (2003).
[7] H. Weman, B. Monemar, G. S. Oehrlein, and S. J. Jeng, Phys. Rev. B **42**, 3109 (1990).
[8] J. M. Sun, T. Dekorsy, W. Skorupa, B. Schmidt, A. Mücklich, and M. Helm (unpublished).
[9] S. Solmi, F. Baruffaldi, and R. Canteri, J. Appl. Phys. **69**, 2135 (1991).
[10] S. Solmi, E. Landi, and F. Baruffaldi, J. Appl. Phys. **68**, 3250 (1990).
[11] G. Davies, Phys. Rep. **176**, 83 (1989).
[12] V. V. Kveder, E. A. Steinman, S. A. Shevchenko, and H. G. Grimmeiss, Phys. Rev. B **51**, 10520 (1995).
[13] M. E. Castagna, S. Coffa, M. Monaco, A. Muscara', L. Caristia, S. Lorenti, and A. Messina, Mater. Res. Soc. Symp. Proc. **770**, I2.1.1 (2003).