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REVIEW ARTICLE

Highly efficient silicon light emitting diodes produced by doping engineering

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Abstract This paper reviews our recent progress on silicon (Si) pn junction light emitting diodes with locally doping engineered carrier potentials. Boron implanted Si diodes with dislocation loops have electroluminescence (EL) quantum efficiency up to 0.12%, which is two orders of magnitude higher than those without dislocations. Boron gettering along the strained dislocation lines produces locally p-type spike doping at the dislocations, which have potential wells for bounding spatially indirect excitons. Thermal dissociation of the bound excitons releases free carriers, leading to an anomalous increase of the band to band luminescence with increasing temperature. Si light emitting diodes with external quantum efficiency of 0.2% have been also demonstrated by implementation of pnpn modulation doping arrays.

Keywords silicon (Si) light emitting diodes, doping engineering, dislocation, modulation doping

1 Introduction

With the development of the modern ultra-large-scale integrated circuits (ULSICs), there are some challenges on heat dissipation and signal delay due to increased metallic interconnects. Several approaches have been proposed for the next generation of microprocessors, such as quantum, molecular and optical computing. Among different routes, integration of optical connects on silicon (Si) is considered to be the most feasible solution, since many optical elements, such as waveguides, modulators and detectors, are available on Si for optical interconnects using the state of arts Si technology [1]. Recently, with hybrid lasers fabricated by bonding external indium phosphide based semiconductor lasers on Si waveguides, small-scaled integrated optical trans-receiver chips have been demonstrated. However, for large-scale optical integration, efficient Si light emitters (lasers) are still under development by complementary metal-oxide-semiconductor (CMOS) technology.

Crystalline Si is not a good light emitter due to its fundamental indirect electronic band structure. The external quantum efficiency of a Si pn junction light emitting device (LED) is typically less than 10^{-5}. Persistent effort has been made on CMOS compatible Si based light emitters for more than a half century. Among different technologies, ion implantation with appropriate post annealing process has been successfully applied on making different Si based light emitting materials, such as Er-doped crystalline Si [2,3], Si nanocrystals in SiO_2 [4,5], Er-doped Si nanocrystals [6], Ge-implanted SiO_2 [7], rare earth implanted SiO_2 [8], and dislocation engineering Si [9]. Si LEDs with pn junction or MOS structures have been demonstrated from these materials.

In this paper, we reviewed our recent progress on the study of electroluminescence (EL) from Si pn junctions by engineering doping at dislocations [10,11]. Si pn junctions were produced by high-dose boron implantation into n-type Si substrate; During the activation annealing of the implanted boron dopant, a dislocation band was generated between the surface and the pn junction for the implanted boron dose above $5\times10^{14}\,cm^{-2}$. Locally heavy p-type doping spikes were created around dislocations by gettering boron along the dislocation lines. The locally doped dislocations have an energy band gap alignment, which can bound excitons with electron and holes separated in real space (so-called spatially indirect excitons). The bound excitons, with a very low recombination rate, can be thermally dissolved into free electrons and holes at elevated temperature. Therefore, the EL from the band to band recombination shows an anomalous increase with increasing temperature. With the assist of the doping engineered dislocations, the room temperature EL efficiency has been improved up to 0.12%, which is two

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orders of magnitude higher compared to the ones without dislocations. Higher EL efficiency above 0.2% was also achieved by implementation of the doping engineering concept on a Si pn diode with lateral two dimensional pnpn modulation doping arrays.

2 Experimental methods

Si pn diodes were prepared by boron implantation into (100) oriented Sb-doped n-type (0.1 Ω·cm) Si substrates at a tilt angle of 7° through a 50 nm thermally grown SiO_2 screen layer. Boron doses from 2×10^{13} to 3×10^{17} cm^{-2} were implanted at an energy of 25 keV. A reference diode was implanted using a low boron doses of 2×10^{13} cm^{-2} at the same energy, followed by Si^+-implantation at 50 keV with a dose of 1.5×10^{15} cm^{-2}. The purpose of Si^+-implantation in the reference samples is to introduce "clean" strained dislocations overlapping the boron projected range [12], similar to the samples prepared by high-dose B^+ implantation. This allows us to disentangle features in the microstructure and EL spectra related to the dislocations created by high-dose boron implantation and Si^+ implantation. All samples were subsequently furnace annealed at 1050°C for 20 min and processed into 1 mm diameter diodes with aluminium ring contacts as top electrodes. The microstructure of the diodes was analyzed by cross-sectional transmission electron microscopy (XTEM) using a Philips CM300 microscope. The local boron concentration at defects was analyzed by energy dispersive X-ray (EDX) spectroscopy using a focused electron beam with a beam diameter of approximately 70 nm.

All EL spectra were measured at a constant current supplied by a sourcemeter (Keithley 2410). The EL signals were recorded by a monochromator (Triax320) with liquid nitrogen cooled InGaAs detector. For low-temperature EL studies, the diodes were mounted on the cold finger of a closed-cycle cryostat with silver paste. The absolute EL power from the device was measured using a calibrated optical power meters (Newport 818 IR/CM). The external EL power efficiency was calculated by integrating the total EL output power from the front surface of the devices and divided by the total electric input power.

3 Results and discussion

3.1 Microstructures

XTEM images of the dislocations in the Si pn diodes created by high-dose boron implantation and Si^+ implantation are shown in Fig. 1 after annealing at 1050°C for 20 min. The dislocation loops shown in Fig. 1(a) were created by high-dose boron implantation at 25 keV with a dose of 4×10^{15} cm^{-2}. Since the implanted boron dose in the reference sample was only 2×10^{13} cm^{-2}, which was far below the threshold for creation of dislocations, the extended defects in Fig. 1(b) were mainly created by Si^+ implantation at 50 keV with a dose of 1.5×10^{15} cm^{-2}. The morphology of the dislocations created by Si^+ implantation is slightly different from those created by high-dose boron implantation in Fig. 1(a). The dislocations created by Si^+ implantation exhibit mainly {111} threading dislocations, while the dislocations in most of the boron-only implanted samples were dislocation loops. After annealing, individual dark clusters were developed along the dislocation loops in the boron implanted samples. EDX analysis indicated that the dark spots have a higher boron concentration, they are probably boron clusters gettered at the dislocations lines.

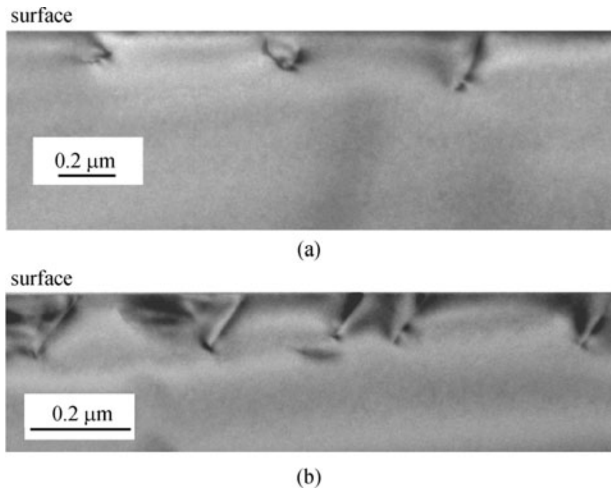

Fig. 1 XTEM images of Si pn diodes prepared by B^+ implantation at 25 keV with doses of (a) 4×10^{15} cm^{-2} and (b) 2.0×10^{13} cm^{-2} plus Si^+ implantation at 50 keV with a dose of 1.5×10^{15} cm^{-2}

3.2 EL spectra

Figure 2 shows the EL spectra at 12 K from the pn diodes under the forward bias with a constant current of 50 mA. The low temperature EL spectra taken from three pn diodes are shown in Fig. 2, where the boron doses are 4×10^{15} cm^{-2} (A) and 2×10^{13} cm^{-2} (B), respectively. The spectrum of the reference sample (B*) is also shown with the dislocations created by Si self-ion implantation. The diode (B) has no observable dislocation due to the low implanted boron dose of only 2×10^{13} cm^{-2}, it exhibits only a weak peak from the transverse optical (TO) phonon assisted free exciton peak (FE^{TO}) at 1.1 eV. Si^+ implantation in sample (B*) produced additional D_2, D_3, D_4 lines and a peak at P_A from the dislocations. With increasing the boron dose to 4×10^{15} cm^{-2}, two asymmetrical broad peaks from the (TO) phonon-assisted transitions labelled as P_I^{TO} and P_{II}^{TO} close to 1.05 and 0.95 eV are observed from the dislocations. The two peaks show different peak energy

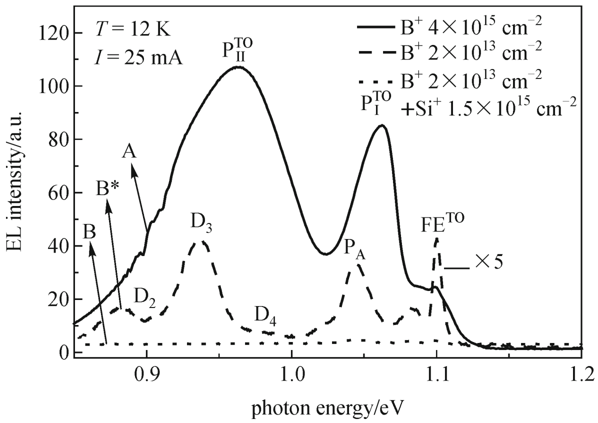

Fig. 2 EL spectra at 12 K of Si pn diodes prepared by B^+ implantation at 25 keV with different doses of 4.0×10^{15} cm^{-2} (A), and 2.0×10^{13} cm^{-2} (B). The reference sample (B*) are produced by B^+ implantation with a small dose of 2.0×10^{13} cm^{-2} plus Si^+ implantation at 50 keV with a dose of 1.5×10^{15} cm^{-2} for creation of dislocations

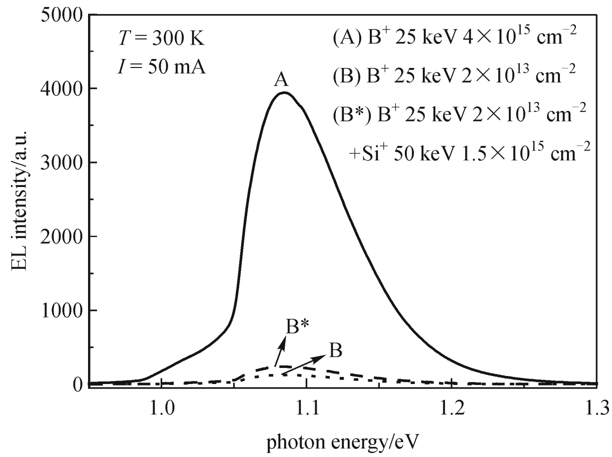

Fig. 3 EL spectra at room temperature from Si pn diodes prepared by B^+ implantation at 25 keV with different doses of 4.0×10^{15} cm^{-2} (A), and 2.0×10^{13} cm^{-2} (B). The reference sample (B*) produced by B^+ implantation with a dose of 2.0×10^{13} cm^{-2} plus Si^+ implantation at 50 keV with a dose of 1.5×10^{15} cm^{-2}

and band width compared to the EL bands from the dislocations created mainly by Si^+ implantation in sample (B*). The peak P_{II}^{TO} increases strongly at a higher boron doses above 5×10^{14} cm^{-2} when the boron concentration is close to the solubility, where visible extended defects are observed in the diodes by XTEM. The intensity of both peaks reaches a maximum at a boron concentration around three times the boron solubility limit of 1.53×10^{20} cm^{-3} at the annealing temperature of 1050°C [11].

EL spectra at room temperature are shown in Fig. 3 for samples (A) and (B) as well as the reference sample (B*) with dislocations created by Si^+ implantation. The spectra of all samples show the same typical band to band emission spectra from bulk Si at room temperature. A strong increase of the EL intensity is observed in the sample with a high density of dislocations created by high-dose boron implantation. In contrast, the sample containing dislocations produced by Si^+ implantation shows a much smaller increase of the EL intensity as compared to the sample (B) without dislocations. This indicates that the defects created by boron implantation have a much stronger contribution to the increase of EL efficiency compared to the "clean" strained dislocations created by Si^+ self-ion implantation [9].

3.3 Dependency on injection current

In order to understand the mechanism of the efficient EL from boron implanted Si diodes, more attention has been paid on searching the difference between the EL peaks from the dislocations generated by boron implantation and Si implantation. Figure 4 shows the dependences of the peak energy versus the logarithm of the injection current density for samples (A) and (B*). Different properties of the EL peaks from the dislocations created by high-dose boron implantation were observed compared to the "clean" dislocations created by Si^+ self-ion implantation. The peak energies of P_I^{TO} and P_{II}^{TO} from the dislocations in the high-dose boron implanted LEDs show blue shifts with increasing the injection current, their peak energies are proportion to the logarithm of the injection current. This behaves similar to luminescence peak from III-V δ-doping superlattices with increasing the excitation density. For the EL bands D_3 and P_A from the dislocations created by Si implantation in the reference sample, no significant blue shifts were observed. Such a different behaviour suggests that a locally heavy p-type δ-doping may exist around the dislocations in the high-dose boron implanted Si diodes. This is consistent with the EDX analysis, which shows a higher boron concentration at the dislocations compared to the region free of defects in the high-dose boron implanted diodes [11].

Higher boron concentration at dislocations may originate from boron gettering during the nucleation of the extended defects, as observed in heavily boron doped Si wafers pre-amorphized by Ge^+ and Si^+ [13]. This happens when the implanted boron concentration exceeds the solubility limits, the initial annealing causes boron gettering at the dislocations, the gettered boron atoms are diffused and electrically activated by prolongation of the annealing time, thus the dislocation lines are decorated with locally nanoscale heavy p-type doping regions. The heavy p-type doping around the dislocations may cause band gap shrinkage around the dislocations for capture free carriers. The proposed schematic band profiles around a locally p-type δ-doping spike have an electron potential similar to that of the p-type δ-doped semiconductors, as shown in Fig. 5. During the forward injection, bound excitons are formed through the coulomb attraction of electrons by the holes located around the dislocations. Due

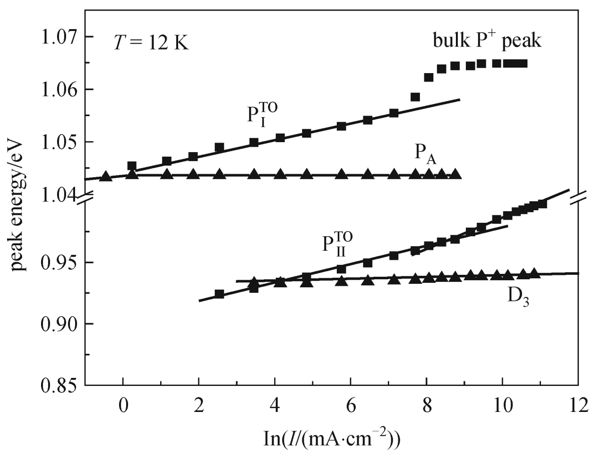

Fig. 4 Dependences of energies of EL peaks from dislocations on logarithm of injection current density at 12 K. EL peaks P_I^{TO} and P_{II}^{TO} are from dislocations in pn diode (A) generated by high dose boron implantation; EL peaks D_3 and P_A are from dislocations in the reference pn diode (B*) created by Si^+ implantation

to the electron potential at the central of the p-type δ-doping doped dislocations, electrons are spatially separated from holes, forming spatially indirect bound exictons. The blue shifts of the peak energy P_I^{TO} and P_{II}^{TO} with increasing the injection current density may be interpreted as in Fig. 5(b): with increasing injection current density, the increased free carrier concentration screens the potentials induced by locally heavy doping around the dislocations, therefore leading to blue shifts of the EL peaks from the spatially indirect excitons trapped around the p-type δ-doping dislocation lines.

3.4 Temperature dependence

Figure 6 shows temperature dependences of the peaks P_I^{TO} and P_{II}^{TO}, as well as the integrated intensity of the FE^{TO} peak from the diode implanted with a high boron dose of $4\times10^{15}\ cm^{-2}$. 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. Thus, the EL intensity of the FE^{TO} peak shows a two-step increase with rising temperature at the expense of the thermal quenching of the two bound exciton peaks. This correlation reveals that the increase of the band edge free electron-hole recombination comes from the thermal dissociation of bound excitons to free electron-hole pairs with increasing temperature. The released free electrons are drifted away from the locally heavy p-type doped dislocations by the electron potentials and recombined with the holes in the defect-free region around the dislocations with a lower hole concentration, where the non-radiative auger recombination is lower. A rate equation model involves interplay of bound exciton and free excitons can give a full description of such anomalous increase of the EL from free exciton (or electron-hole-pair) recombination observed in the boron-implanted Si LEDs, which is in

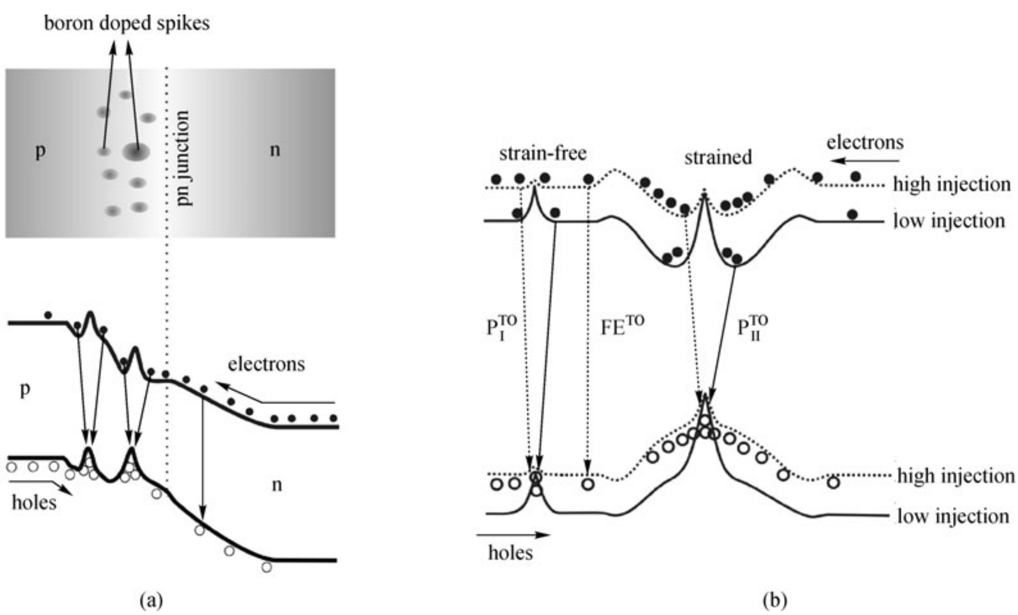

Fig. 5 Energy band diagram and electronic transitions in Si pn diode with heavy p-type doping spikes (a); recombination of spatially indirect bound excitons related to EL peaks P_I^{TO} and P_{II}^{TO} at strained and unstrained dislocations in low and high current injection regimes (b)

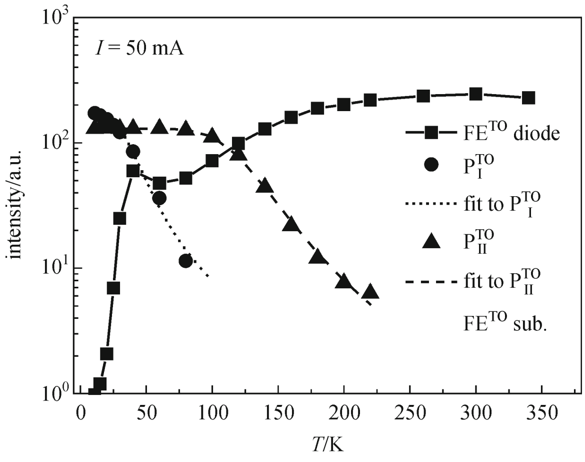

Fig. 6 Integrated EL intensity of FE^{TO} (squares), P_I^{TO} (dots) and P_{II}^{TO} (uptrangles) as a function of temperature from diode implanted with B^+ at 25 keV with a dose of 4×10^{15} cm^{-2}. Solid line: guide to the eyes; dotted and dashed lines: theoretical fitting to temperature dependences of P_I^{TO} and P_{II}^{TO}

stark contrast to the conventional decrease of the photoluminescence from bulk Si with increasing temperature.

3.5 Si pn diodes with modulation doping arrays

High-dose boron implantation creates defects and provides high concentration of boron simultaneously, boron gettering along dislocation lines is a self-organized technique to produce localized p-type doping during the post-annealing. The large amount of dislocations in the boron implanted pn diodes cause reliable problem of the LEDs and may not suitable for integration. For tailoring the band of Si by locally doping with fewer amounts of defects, Si pn diodes with patterned doping arrays are prepared by boron implantation thought a thick SiO_2 mask layer with micro window arrays. Figure 7 is the images of a 0.5 mm $\times$0.5 mm diodes produced by boron implantation thought a 150 nm thick SiO_2 mask layer patterned with micro window arrays, the mask arrays contain 2 μm×2 μm windows with space of 4 μm. Boron ions are implanted at 25 keV with a dose of 4×10^{15} cm^{-2} into the Si below the micro windows. During annealing, boron atoms are diffusing into the n-type Si substrate, creating lateral pnpn interdigital modulation doping arrays, which have a similar localized energy band structure compared to the p-doping spikes along the dislocations. Figure 8 shows the dependences of the room temperature EL intensity on the injection current for the two Si pn diodes with and without patterned doping fabricated on the same chip. Efficient EL intensity with a power close to 1 mW was measured from the diode with patterned micro doping arrays. A further increase of the EL quantum efficiency up to 0.2% was demonstrated compared to the best Si LEDs with an external quantum efficiency of 0.12% produced by B^+ implantation without patterned doping arrays. This suggests that tailoring the band structure of the Si diodes with micro doping engineer may provide a new route for increasing the EL efficiency in Si pn junction light emitting diodes.

4 Conclusions

In summary, Si light emitting diodes with dislocations created by boron implantation show much stronger band edge EL compared to those with dislocations created by Si self-ion implantation. Our results suggest that the high-dose boron implantation creates dislocation loops. Boron

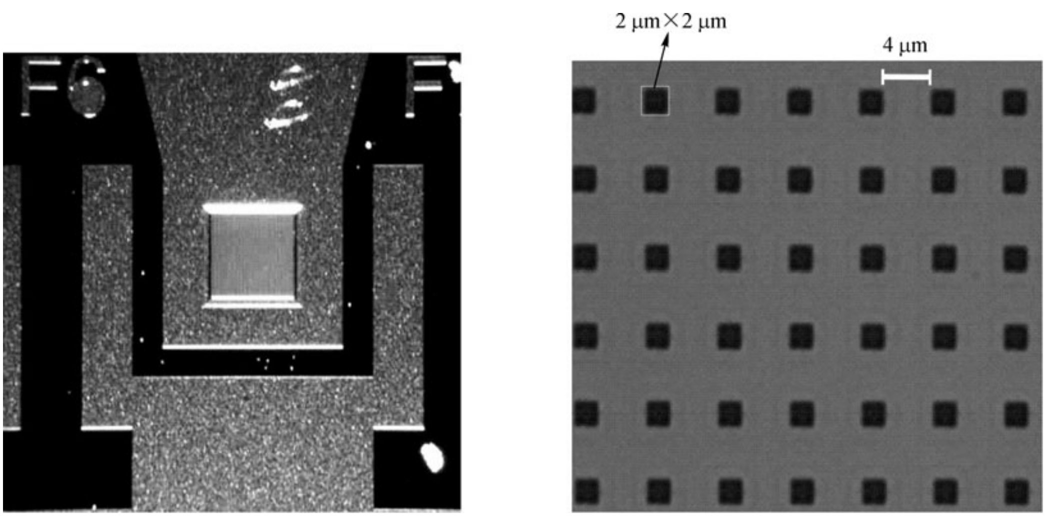

Fig. 7 Images of 0.5 mm×0.5 mm Si light emitting diode containing micro heavy p-doping arrays extended into n-type Si substrate. B^+ ions are implanted into Si at 25 keV with a dose of 4×10^{15} cm^{-2} through micro holes on 150 nm SiO_2 mask layer. Micro windows have an area of 2 μm×2 μm with a space of 4 μm

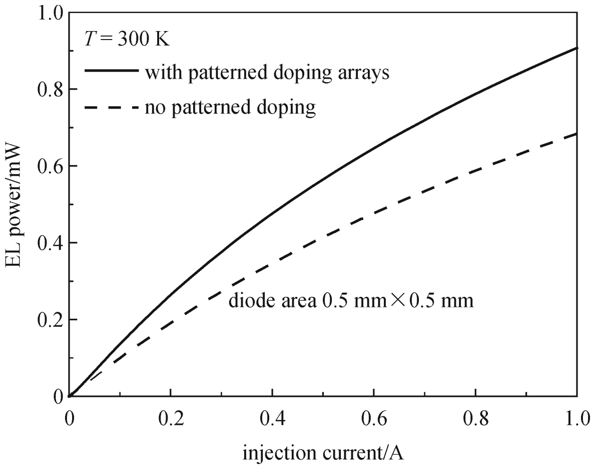

Fig. 8 Dependences of room temperature EL intensity on injection current for two Si pn diodes with and without patterned doping fabricated on the same chip

gettering along the dislocation lines produces locally heavy p-type doping spikes. Spatially indirect excitons with a very low recombination rate are bounded around the dislocations, forming a temporary reservoir of electron and hole pairs. It is the thermal dissociation of the bound excitions that caused an anomalous increase of the light emission from Si band edge free carrier recombination with increasing temperature. With this model, highly efficient Si pn junction light emitting diode with patterned micro doping arrays is produced by the concept of doping engineering.

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