Below-band-gap electroluminescence related to doping spikes in boron-implanted silicon *pn* diodes

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The origin of two luminescence bands with maxima around 1.05 eV and 0.95 eV is studied in silicon *pn* diodes prepared by boron implantation. The two peaks are related to the formation of *p*-type doping spikes on a nanometer scale. These doping spikes are generated by long-time thermal activation of preformed boron clusters. The peak with a larger binding energy stems from spatially indirect excitons bound to doping spikes in a strained environment, while the peak with a lower binding energy is related to doping spikes without strain. The doping spikes are able to capture spatially indirect bound excitons with a low recombination rate, thus effectively suppressing the fast nonradiative recombination at defects. This effect leads to an efficient room temperature electroluminescence in silicon light-emitting diodes prepared by boron implantation.

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I. INTRODUCTION

The combination of silicon-based electronic circuits with optoelectronic functionality is one of the key challenges for future semiconductor technology.¹ As the packaging density of CMOS transistors becomes higher and higher, a severe interconnect bottleneck for intrachip and interchip connections is foreseen. One possible solution could be optical interconnects integrated with standard silicon technology.² However, since silicon is an indirect semiconductor, it is an inherently bad light emitter for usage in optical communication. Recently, several approaches for gaining light from silicon-based systems have been reported with the prospect of sufficient electroluminescence (EL) efficiency. The prominent systems are porous silicon,³ silicon nanocrystals in SiO₂,⁴ Ge⁺ implanted SiO₂,⁵ Er-doped SiO₂ sensitized with silicon nanocrystals,⁶ surface textured silicon diodes,⁷ and dislocation-rich silicon *pn* diodes.^{8,9} The latter systems are especially attractive, since they are fully compatible with standard silicon processing technology and low-voltage operation. Recently, concepts for increasing the EL efficiency of silicon *pn* diodes have been focused on reducing the fast nonradiative recombination, such as using high purity float-zone silicon with good surface passivation⁷ or carrier confinement by strain induced potentials around dislocation loops. In this paper, we present a detailed study on the origin of the two luminescence peaks observed at low lattice temperatures from bound excitons in silicon, which are relevant for the efficient EL from silicon *pn* diodes produced by ion implantation.¹⁰ A close relationship between the bound-exciton luminescence and the formation of locally enhanced boron doping spikes is observed. This relationship is supported by results of cross-sectional transmission electron microscopy (XTEM), by introducing excess defects with Si⁺ implantation, as well as by changing the boron doses and annealing times. A model is proposed which relates the two EL peaks below the band gap of silicon to excitons bound to *p*-type doping spikes with a locally enhanced boron doping on a nanometer scale. These doping spikes arise from activation of preformed boron clusters by long-time and high-

temperature annealing. They produce a stronger three-dimensional (3D) confinement of holes in real space compared to the one-dimensional (1D) confinement in silicon δ -doping quantum wells.^{11,12} The doping spikes capture spatially indirect bound excitons which have a low recombination rate. Thus the faster nonradiative recombination arising from the exciton diffusion to defects and surface states is effectively suppressed. The doping spikes significantly contribute to the efficient EL from band edge recombination via the release of free electron-hole pairs at elevated temperatures, thus playing an important role for the efficiency of the diodes at room temperature as observed in our previous work.¹⁰

This paper is organized as follows: In Sec. II we summarize the fabrication steps of the *pn* diodes and the experimental methods applied. Section III contains the experimental results concerning the microstructure of the diodes, the influence of the implanted boron dose, the influence of extended defects, the EL dependence on injection current, and the temperature dependence of the EL. In Sec. III the experimental results are discussed and the consistency with the proposed model is checked with emphasis on the evidence for the formation of doping spikes, the blueshift of the EL peaks with increasing current, and the temperature dependence of the EL.

II. EXPERIMENTAL METHODS

The silicon *pn* diodes were prepared by boron implantation into {100} oriented Sb-doped *n*-type (0.1 Ω cm) silicon substrates at a tilt angle of 7° through a 50 nm thermally grown SiO₂ layer. Boron doses from 2×10^{13} to 3×10^{17} cm⁻² were implanted at an energy of 25 keV, corresponding to a projected range of $R_p=60$ nm (with respect to the Si surface) and a range straggling of 33 nm. Two reference diodes were prepared using boron doses of 5×10^{14} and 2×10^{13} cm⁻² and preamorphized by Si⁺ implantation at 50 keV with doses of 1×10^{15} and 1.5×10^{15} cm⁻², which is above the dose for amorphization of silicon (approximately 5×10^{14} cm⁻², Ref. 13). For these Si⁺

ions the projected and straggling range with respect to the Si surface are 30 nm and 29 nm, respectively, as obtained from a TRIM calculation. The purpose of these preamorphized reference samples is to introduce a density of defects overlapping the boron projected range after regrowth of the preamorphized layer by annealing, similar to the samples prepared by high dose B⁺ implantation. This allows us to disentangle features in the microstructure and EL spectra related to boron cluster formation and defects. For 25 keV implantation of boron only, no amorphization of silicon is observed (by TEM) except in a thin layer of less than 10 nm close to the Si surface for extremely high boron doses above $3 \times 10^{16} \text{ cm}^{-2}$.

All samples were subsequently furnace annealed at 1050 °C for 10 to 40 minutes and processed into 1 mm diameter diodes with metallic ring contacts as top electrodes. For low-temperature EL studies, the diodes were mounted on the cold finger of a closed-cycle cryostat with silver paste. All EL spectra at low temperature were measured at 12 K at a constant current supplied by a sourcemeter (Keithley 2410). The EL signals were recorded with a monochromator (Triax320) and a liquid nitrogen cooled InGaAs detector. The microstructure of the diodes was analyzed by XTEM using a Philips CM300 microscope. The local boron concentration was analyzed by energy dispersive x-ray (EDX) spectroscopy using a focused electron beam with a beam diameter of approximately 70 nm.

III. EXPERIMENTAL RESULTS

A. Microstructure

The diodes analyzed by XTEM were produced by boron implantation at an energy of 25 keV with different doses ranging from 2.0×10^{13} to $1.0 \times 10^{16} \text{ cm}^{-2}$. The reference sample was implanted by boron at 25 keV with a low dose of $2.0 \times 10^{13} \text{ cm}^{-2}$, sufficient for creating a *pn* junction, and then preamorphized by Si⁺ implantation at 50 keV with a dose of $1.5 \times 10^{15} \text{ cm}^{-2}$. No visible large residual extended defects were observed for the diodes implanted with boron only at dose levels less than $2 \times 10^{14} \text{ cm}^{-2}$ after annealing at 1050 °C for 20 minutes (not shown). For higher boron doses above $5 \times 10^{14} \text{ cm}^{-2}$, visible extended defects were observed in the *pn* junction region, while no extended defects were observed in the silicon substrate outside of the *pn* junction.

The XTEM images of four diodes are shown in Figs. 1(a)–1(e) after annealing at 1050 °C for 20 minutes. Figure 1(a) is the XTEM image of the reference sample, which was implanted with a low boron dose and preamorphized by Si⁺ implantation before annealing. Since the boron dose is far below the limit for creating visible residual extended defects after annealing, the extended defects observed in the reference sample are mainly created by the regrowth of the preamorphized silicon layer formed via Si⁺ implantation.

Figure 1(b) is the XTEM image of the sample created by implantation of boron only with a higher dose of $1 \times 10^{15} \text{ cm}^{-2}$. After annealing at 1050 °C for 20 minutes, the defects in Fig. 1(b) extend to a range of 110–130 nm (i.e., around the end of the boron implanted region). The *pn* junction is assumed to be located 85 nm deeper than directly

FIG. 1. XTEM images of the silicon *pn* diodes prepared by B⁺ implantation at 25 keV with different doses of 2.0×10^{13} (a), 1.0×10^{15} (b), 4.0×10^{15} (c), and $1 \times 10^{16} \text{ cm}^{-2}$ (e). The extended defects in image (a) of the reference sample are produced by preamorphization via Si⁺ implantation at 50 keV with a dose of $1.5 \times 10^{15} \text{ cm}^{-2}$. (d) is a close-up view of strained clusters formed at the end of an extended defect taken from the same sample as in (c). All analyzed samples were annealed at 1050 °C for 20 minutes.

after implantation (60 nm projected plus 33 nm straggling range), i.e., at about 180 nm ($\approx 85 + 60 + 33$ nm). This is due to the diffusion-induced boron displacement during annealing.¹⁴

Figure 1(c) is the XTEM image of the sample created by boron-only implantation at 25 keV with a dose of $4 \times 10^{15} \text{ cm}^{-2}$. The defects extend down to 180 nm below the surface with a morphology similar to that in Fig. 1(b). Some individual dark spots (diameter ~ 10 –20 nm) are observed at the end of the dislocation lines close to the *pn* junction after annealing. The origin of the contrast of these dark spots is

FIG. 2. Energy dispersive spectra from a silicon *pn* diode prepared by B^+ implantation at 25 keV with a dose of $4.0 \times 10^{15} \text{ cm}^{-2}$. The spectrum (a) was measured with a focused electron beam of 70 nm diameter on a dark strained spot at the end of an extended defect; the spectrum (b) was taken in the same depth region but without visible defects.

attributed to high strain in an area of locally high density of Si-B interstitial clusters, Si interstitials, or it is induced by the strain field around extended defects, as will be discussed later. Figure 1(d) shows a close-up view of the strained dark spots at the end of an extended defect taken from the same sample as in Fig. 1(c). Two large strained spots with diameters of 10–20 nm are formed at the ends of the dislocation lines close to the *pn* junction. As will be discussed later, these dark spots are attributed to boron doping spikes surrounded by a strain field. Smaller dark spots of 1–2 nanometers are mainly observed between the surface and the projected range. The morphology of the extended defects in Fig. 1(a) created by preamorphization Si^+ implantation is different compared to those created by high dose boron implantation in Figs. 1(b) and 1(c). The preamorphized samples exhibit mainly $\{111\}$ threading dislocations which grow from the *a*-Si/*c*-Si interface associated with a strain field; most of the boron-only implanted samples have curved dislocation lines. After annealing, individual large strained clusters develop at the ends of some of the dislocation lines, as shown in Fig. 1(d).

Figure 1(e) is the XTEM image of the sample implanted with an even higher dose of $1 \times 10^{16} \text{ cm}^{-2}$ (Refs. 13 and 15). The appearance of the boron clusters within the implantation range suggests that the boron concentration reaches the thermal equilibrium solubility limit ($1.53 \times 10^{20} \text{ cm}^{-3}$) at the annealing temperature of 1050 °C. Hence the boron clusters cannot be dissolved during the long-time annealing. This result is consistent with the observation of Solmi *et al.* in silicon implanted with the same boron dose of $1 \times 10^{16} \text{ cm}^{-2}$.^{13,15}

The relative boron concentration at the end of the extended defects was analyzed by EDX using a focused electron beam of 70 nm in diameter for the diode implanted at 25 keV with a boron dose of $4 \times 10^{15} \text{ cm}^{-2}$. Figure 2(a) is the EDX spectrum obtained with the electron beam focused on an individual strained dark spot, which is formed at the

end of an extended defect close to the *pn* junction. The spectrum is compared to a spectrum taken in the same depth region but without visible defects [Fig. 2(b)]. Although we cannot obtain the absolute boron concentration within the dark spot since the area of the electron beam is larger than the dark spot, the EDX spectrum reveals a high boron concentration at the dark spot compared to the region free of defects. Such a localized high boron concentration is attributed to boron gettering during the nucleation of the extended defects, as observed in heavily boron doped silicon wafers preamorphized by Ge^+ and Si^+ .^{16,17}

B. Influence of the boron doses

Under the forward bias, electrons and holes are injected from the *n*-type substrate and boron implanted *p*-type region, respectively. The electrons and holes form free excitons by Coulomb attraction (we note that at the high doping densities and high injection current the excitons are screened and one would have to speak of free electron-hole pairs; however we will use the term exciton in the following for convenience). The free excitons are trapped to defects or impurities, forming bound excitons with lower transition energy. Both free and bound excitons recombine around the *pn* junction and give rise to electroluminescence (EL) by the assistance of phonons. The EL from bound excitons in the *pn* diodes was analyzed at 12 K with a constant current of 50 mA (for the temperature dependence see below). The diodes were prepared by boron-only implantation at 25 keV with different doses followed by annealing at 1050 °C for 20 minutes. The EL spectra taken from four *pn* diodes are shown in Fig. 3(a), where the boron doses were $4 \times 10^{15} \text{ cm}^{-2}$ (A), $1.5 \times 10^{15} \text{ cm}^{-2}$ (B), $5 \times 10^{14} \text{ cm}^{-2}$ (C), and $2 \times 10^{13} \text{ cm}^{-2}$ (D), respectively. The spectrum of the diode (D) implanted with a low boron dose of $2 \times 10^{13} \text{ cm}^{-2}$ shows a very weak peak from trap levels at 1.04 eV, i.e., below the transverse optical (TO) phonon-assisted free exciton peak (FE^{TO}) at 1.1 eV. With increasing the boron dose from 5×10^{14} to $4 \times 10^{15} \text{ cm}^{-2}$ (C)–(A), two asymmetric broad peaks from the (TO) phonon-assisted transitions labeled as P_I^{TO} and P_{II}^{TO} close to 1.05 eV and 0.95 eV, respectively, are observed. Figure 3(b) shows the intensity of the two peaks versus the boron dose. The peak P_I^{TO} appears with increasing boron dose above $1 \times 10^{14} \text{ cm}^{-2}$ (corresponding to a boron concentration at the projected range of $\sim 1 \times 10^{19} \text{ cm}^{-3}$). The peak P_{II}^{TO} increases strongly at a higher boron doses above $5 \times 10^{14} \text{ cm}^{-2}$, 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 $1.53 \times 10^{20} \text{ cm}^{-3}$ at the annealing temperature of 1050 °C. At higher doses above $1 \times 10^{16} \text{ cm}^{-2}$ the EL intensity decreases dramatically. At these doses the boron clusters cannot be dissolved, since the background is saturated with a boron concentration at the solubility limit.¹⁵

C. Influence of the extended defects

The EL spectra of the diode (D) free of extended defects are compared to the reference diode (D*) containing a large

FIG. 3. (a) EL spectra at 12 K from silicon *pn* diodes prepared by B^+ implantation at 25 keV with different doses of 4.0×10^{15} (A), 1.5×10^{15} (B), 5.0×10^{14} (C), and 2.0×10^{13} (D) cm^{-2} . (b) EL intensity of the two bound exciton peaks at 12 K versus boron doses for silicon *pn* diodes prepared by B^+ implantation at 25 keV after annealing at 1050 °C for 20 minutes. The vertical dashed line represents the boron solubility limit at the annealing temperature.

amount of $\{111\}$ extended defects, implanted with the same low boron dose of $2 \times 10^{13} \text{ cm}^{-2}$, as shown in Fig. 4. In this reference diode (D^*) the excess extended defects were created by regrowth of the preamorphized silicon layer, as shown in the image of Fig. 1(a). When the boron concentration is low, the spectra of the defect-rich reference diode (D^*) are different from the defect-free diode (D) implanted with the same low boron dose only. A new peak P_B with a shoulder at low energy and an increase of band P_A were observed with the creation of the highly strained $\{111\}$ planar extended defects in the reference diode (D^*). The peak P_B is similar to the photoluminescence peak observed in the hydrogenated lightly boron-doped silicon containing defects clusters and strained $\{111\}$ planar defects.^{18–20} Due to the low boron concentration, the band-gap shrinkage arising from the *p*-type doping can be neglected in the reference sample (D^*), so the peak energy of P_B below the band gap is mainly related to strain-induced band-gap shrinkage near the planar $\{111\}$ defects of silicon interstitial clusters. The origin of P_A peak is unclear.

For the diodes (C^*) and (C) implanted with a higher boron dose of $5 \times 10^{14} \text{ cm}^{-2}$, the below-band-gap region is

FIG. 4. EL spectra at 12 K from silicon *pn* diodes prepared by B^+ implantation at 25 keV with different doses of 5.0×10^{14} (C), 2.0×10^{13} (D). The reference samples (C^*) and (D^*) were implanted with the same boron doses as samples (C) and (D) and coimplanted with Si^+ at 50 keV with doses of $1.0 \times 10^{15} \text{ cm}^{-2}$ and $1.5 \times 10^{15} \text{ cm}^{-2}$, respectively.

dominated by two broad peaks P_I^{TO} and P_{II}^{TO} which are related to an increase of the boron concentration. The effect of creating excess extended defects on peak P_{II}^{TO} is significant in the reference diode (C^*) with Si^+ co-implantation. The peak P_{II}^{TO} in diode (C^*) increases and shifts to lower energy compared to the diode (C) with fewer extended defects, while the peak P_I^{TO} is not strongly affected. The red-shift of the P_{II}^{TO} peak is attributed to an increase of the strain-induced band-gap shrinkage with increasing the number of extended defects.

The dependence of the peak P_{II}^{TO} on changes of the extended defects can be further confirmed by increasing the annealing time from 10 to 20 or 40 minutes for diodes implanted with a higher boron dose of $1.5 \times 10^{14} \text{ cm}^{-2}$, as shown in Fig. 5. Increasing the annealing time causes a reduction of the defect density by Ostwald ripening,²¹ relax-

FIG. 5. EL spectra at 12 K from silicon *pn* diodes prepared by B^+ implantation at 25 keV with a dose of $1.5 \times 10^{14} \text{ cm}^{-2}$, after annealing at 1050 °C for different times of 10 (solid line), 20 (dashed line), and 40 minutes (dotted line).

ation of strain, and broadening of the locally enhanced doping profiles due to boron diffusion. All these effects lead to a reduction of the potential variations introduced by both the strain and the doping spikes. Therefore the intensity of the peak P_{II}^{TO} associated with extended defects decreases and the peak shifts to higher energy with increasing the annealing time. The peak P_I^{TO} does not show significant changes with annealing time.

To summarize this section, we conclude that the peaks P_I^{TO} and P_{II}^{TO} originate from regions with locally enhanced boron concentration with unstrained and strained environment, respectively, whereas the peaks P_A and P_B are related to defects generated mainly by Si^+ implantation ("preamorphization").

D. Dependence on injection current

The EL spectra of the diode (A) with defects created by high dose boron-only implantation at 25 keV with a dose of $4 \times 10^{15} \text{ cm}^{-2}$ are shown in Fig. 6(a) as a function of the injection current between 1 μA and 200 mA. (This device will be the one mostly discussed in the remainder of the paper, since it exhibits the strongest luminescence.) In addition to the peaks observed in Fig. 3(a), transverse acoustic (TA) phonon assisted transition peaks of free excitons (FE^{TA}) and the P_I band (P_I^{TA}) are observed at high current injection. The intensities of P_I^{TO} and P_{II}^{TO} increase with increasing current and their peak maxima shift to higher energies. Figure 6(b) shows the peak energies of P_I^{TO} and P_{II}^{TO} versus the logarithm of the injection current ($\log I$), for samples implanted with high boron doses of $4 \times 10^{15} \text{ cm}^{-2}$ (A) (solid squares), $1.5 \times 10^{15} \text{ cm}^{-2}$ (B) (up triangles), $5 \times 10^{14} \text{ cm}^{-2}$ (C) (down triangles). The peak energy of P_I^{TO} follows a linear relationship with $\log I$ at low injection current. After the linear regime, i.e., at higher current, the peak energy of P_I^{TO} increases further and approaches a fixed energy around 1.065 eV, which is close to the luminescence peak from heavily doped bulk silicon.^{22,23} The peak energy of P_{II}^{TO} also follows the same linear relationship with $\log I$. A larger blueshift of P_{II}^{TO} up to $\sim 110 \text{ meV}$ is observed as compared to the smaller blueshift of P_I^{TO} of $\sim 20 \text{ meV}$. The large blueshift of the peak P_{II}^{TO} with increasing injection current is in close analogy to the luminescence peak of spatially indirect electron-hole recombination in III-V δ -doping quantum wells, whose potential related to modulation doping is screened upon increasing the excitation power. In the present case, this space charge potential results from the nanometer scale p -type doping spikes, consistent with the observation of locally enhanced boron concentration in the EDX measurements (see Sec. III A and Fig. 2). Contrary to the large blueshift of the peaks P_I^{TO} and P_{II}^{TO} in the diodes (A–C) implanted with high boron doses, no blueshift of the luminescence peaks P_A and P_B (solid dots) is observed in the reference sample (D*) with a very low boron concentration, whose luminescence peak P_B is mainly related to the highly strained defects created by preamorphization via Si^+ implantation (consistent to the observations in Ref. 19).

The above results indicate again that the blueshift of the two peaks P_I^{TO} and P_{II}^{TO} is strongly related to the locally

FIG. 6. (a) EL spectra at 12 K measured at different injection currents from 1 μA to 200 mA for a silicon pn diode (A) produced by boron implantation at 25 keV with a dose of $4 \times 10^{15} \text{ cm}^{-2}$. (b) Dependence of the peak energies of the peaks P_I^{TO} and P_{II}^{TO} on the logarithm of the injection current for three diodes with different boron implantation doses of (A) 4×10^{15} (solid squares), (B) 1.5×10^{15} (up triangles), (C) 5×10^{14} (down triangles), and (D*) $2 \times 10^{13} \text{ cm}^{-2}$ (dots) plus preamorphization via Si^+ implantation at 50 keV with a dose of $1.5 \times 10^{15} \text{ cm}^{-2}$. The solid lines are linear fits to the experimental data. At high injection currents P_I^{TO} shifts to an energy close to the emission of heavily boron doped p -type bulk silicon labeled as "bulk p^+ peak." Note the change of the vertical scale for P_I^{TO} and P_{II}^{TO} .

enhanced boron doping produced by high-dose boron implantation, whereas the absence of any shift for the peaks P_A and P_B relates them to the preamorphization.

E. Temperature dependence

An interesting feature of the pn diodes with highly boron-doped surface layers is the anomalous increase of the EL from free exciton (or electron-hole-pair) recombination,^{9,10} which is in stark contrast to the conventional decrease of the photoluminescence from bulk silicon with increasing temperature. A study of this anomalous temperature dependence and its relationship to the high EL efficiency in such pn

FIG. 7. (a) The logarithm of the integrated intensity of the FE^{TO} peak (full squares with solid line as a guide for the eye) as well as the peak intensity of P_I^{TO} (solid circles and dotted line) and P_{II}^{TO} (up triangles and dashed line) as a function of the reciprocal temperature from the *pn* diode (A). The dotted and dashed lines are theoretical fits to the temperature dependences of P_I^{TO} and P_{II}^{TO} peaks and the fitted activation energies are indicated. (b) The calculated ratio of thermal emission and recombination (*E/R*) of bound excitons as a function of the reciprocal temperature (squares). The solid lines are theoretical fits using Eq. (4). The activation energies extracted from both fittings [EL peaks (a) and *E/R* ratio (b), respectively] agree very well.

diodes is essential for the understanding of the enhancement of the EL with increased boron doses. Figure 7(a) 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 boron dose of $4 \times 10^{15} \text{ cm}^{-2}$. 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, which grows at the expense of the two others. Thus the EL intensity of the FE^{TO} peak shows a two-step increase with rising temperature corresponding to 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 $9.5 \pm 1.5 \text{ meV}$; the second increase is correlated to the thermal quenching of the P_{II}^{TO} line with a characteristic energy of $61 \pm 2 \text{ meV}$. 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 $I = I_0 / [1 + g \cdot T^{3/2} \exp(-E_a/kT)]$,²⁴ 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,²⁵ 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 to free electron-hole pairs with increasing temperature.

This behavior can be modeled with a set of rate equations for the free and bound excitons (similar to a model put forward in Ref. 26 to describe the luminescence from GaP:N), which are solved under steady-state conditions,

$$\begin{aligned} \frac{dn_0}{dt} &= G + \sum_{i=1}^m e_{i0} \cdot n_i - n_0 \cdot \frac{\sum_{i=1}^m c_{i0}(N_i - n_i)}{\sum_{i=1}^m N_i} - n_0 \cdot W_0 = 0, \\ \sum_{i=1}^m \frac{dn_i}{dt} &= n_0 \cdot \frac{\sum_{i=1}^m c_{i0}(N_i - n_i)}{\sum_{i=1}^m N_i} - \sum_{i=1}^m e_{i0} \cdot n_i - \sum_{i=1}^m W_i \cdot n_i = 0. \end{aligned} \quad (1)$$

(For a simplified version with only one trap level, see Ref. 27). Here G is the areal generation rate of free excitons, m is the number of the bound exciton levels below the free exciton energy, n_0 is the areal density of free exciton states, N_i and n_i are the areal densities of i th bound exciton level ($i = 1, 2$ in the present case), c_{i0} is the capture coefficient of a free exciton to an empty state of the i th bound exciton level, e_{i0} is the thermal emission coefficient of a bound exciton at the i th level to a free exciton level, W_i is the recombination coefficient of bound excitons at the i th level, respectively, W_0 is the recombination coefficient of a free exciton.

The generation rate G of free electron-hole pairs per unit area is assumed to equal the injection current density divided by the unit charge, J/e . The integrated luminescence intensity of FE^{TO}, I_{FE} , is proportional to the free exciton radiative recombination coefficient, W_r , times the areal density of free excitons, n_0 , $I_{\text{FE}} = W_r n_0$. This gives a simple expression for the EL intensity of free electron-hole recombination as a function of the injection current density,

$$I_{\text{FE}} = \frac{W_r J - \alpha - \beta + \sqrt{(J + \alpha + \beta)^2 - 4J\beta}}{W_0} \cdot \frac{1}{2}. \quad (2)$$

The ratio α/β is proportional to the ratio of the recombination coefficient of free excitons divided by the average capture coefficient of the traps,

$$\frac{\alpha}{\beta} = \frac{W_0}{c_{0i}} \cdot \left(1 + \frac{\sum_{i=1}^m n_i e_{i0}}{\sum_{i=1}^m n_i W_i} \right) = \frac{W_0}{c_{0i}} \cdot \left(1 + \frac{E}{R} \right). \quad (3)$$

The second term is the ratio of the total thermal emission rate and the total recombination rate the bound excitons, abbreviated by E/R . The luminescence-current characteristics of the FE^{TO} peaks at different temperature can be very well simulated with Eq. (2) by choosing appropriate values for W_r/W_0 , α and β . The ratio of the recombination coefficient of free electron-hole pairs divided by the capture coefficient, W_0/c_{0i} , can be determined at an extremely low temperature, where the thermal emission coefficient of the bound excitons $e_{i0} \approx 0$, $\alpha/\beta = W_0/c_{0i}$. The ratio of E/R can be calculated by

FIG. 8. EL spectra at 300 K from silicon *pn* diodes prepared by B^+ implantation at 25 keV with different doses of 4.0×10^{15} (A), 1.5×10^{15} (B), 5.0×10^{14} (C), and 2.0×10^{13} (D). Also shown are the spectra of the reference samples C* (dashed line) and D* (dotted line) implanted with the same boron doses as the samples (C) and (D) and coimplanted with Si^+ at 50 keV at doses of $1.0 \times 10^{15} \text{ cm}^{-2}$ and $1.5 \times 10^{15} \text{ cm}^{-2}$, respectively.

Eq. (3) from the ratio of α/β calculated at different temperatures, as shown in Fig. 7(b).

The calculated total thermal emission rate of the bound excitons divided by the recombination rate of bound excitons can be easily simulated by the following equation:

$$E/R = A_0 + A_i \cdot T^{3/2} e^{-E_{id}/kT}, \quad (4)$$

where A_0 is the contribution from other bound exciton levels, A_i is a constant related to the product of the density of the i th bound exciton levels and the density of free exciton levels, and E_{id} is the activation energy of the bound excitons at i th level.

The logarithm of E/R as a function of reciprocal temperature in our *pn* diodes shows two linear regimes. Each linear regime can be fitted separately by Eq. (4) with activation energies of 9.5 meV at low temperatures and 63 meV at high temperatures, respectively. Comparing these values to the activation energies of the P_I^{TO} and P_{II}^{TO} peaks, which are determined independently by directly fitting the thermal quenching of the EL from the bound excitons at a constant current in Fig. 7(a), it is concluded that the increase of the EL from band edge FE^{TO} peaks is strongly correlated with the thermal emission of the two bound exciton levels. A small ratio of $W_0/c_{0i} = 0.005$ is calculated at 12 K, and a high ratio of E/R of 3×10^3 is obtained at room temperature. These results reveal that the bound exciton in the *pn* diodes have a unique characteristics of high capture and low recombination rate. *Such a characteristic enables the large thermal emission probability from the bound exciton states to free exciton states at elevated temperatures, thus leading to the anomalous increase of EL from the band edge free excitons with increasing temperature.*

F. Room temperature EL

The EL spectra at room temperature are shown in Fig. 8 for samples (A–C) implanted with different boron doses and

FIG. 9. Current-voltage (*I-V*) and electroluminescence-voltage characteristics at 100 K (a) and 300 K (b) for silicon *pn* diodes prepared by B^+ implantation at 25 keV with different doses of 4.0×10^{15} (A), 1.5×10^{15} (B), 5.0×10^{14} (C), and 2.0×10^{13} (D). The EL intensity is monitored on the maximum of the FE^{TO} peak from the band-edge free electron-hole recombination. The threshold voltages for EL are indicated as the vertical lines.

for two reference samples (C* and D*) with excess extended defects created by the preamorphization Si^+ implantation. The spectra of all samples show the same typical emission spectra of bulk silicon at room temperature after the thermal quenching of the bound exciton peaks. A strong increase of the room temperature EL intensity is observed with increasing the boron concentration only. In contrast, the two reference samples containing excess extended defects due to Si^+ implantation show a much smaller increase of the EL intensity as compared to the samples implanted with the same boron doses only. This indicates that the increase of the locally enhanced boron doping by boron implantation plays a more important role for the increase of EL efficiency than the increase of strained extended defects by Si^+ implantation. The effects of increasing the boron concentration are clearly observed in the current-voltage (*I-V*) and luminescence-voltage (*L-V*) characteristics in Fig. 9(a) at 100 K and Fig. 9(b) at 300 K. The recombination current due to nonradiative recombination below the threshold voltage for band-edge EL is strongly reduced at low temperatures by increasing the boron doping. Thus the diodes exhibit an increasing luminescence efficiency at higher boron doses. This effect is stronger at lower temperature (100 K) due to the stronger trapping of spatially indirect bound excitons; it becomes somewhat weaker at room temperature, as shown by the downward shift of the switch-on voltages of the diodes.

IV. DISCUSSION

A. Formation of doping spikes

There is strong tendency for the formation of locally enhanced doping spikes in ion-implanted silicon. Following the model which was proposed by Pelaz *et al.*,^{28,29} boron clustering occurs at the very early stage of annealing when the supersaturation of silicon interstitials is very high in ion implanted silicon.^{30,31} Boron gathering during the nucleation of the extended defects was also observed by Bonafos and Xia *et al.*^{16,17} The preformed B clusters grow by adding interstitial boron in the presence of a high boron concentration, resulting in boron complexes with a high interstitial content. With increasing annealing time the Si interstitial supersaturation decreases and preformed B-Si interstitial clusters start emitting Si interstitials, leaving more stable boron clusters with a low silicon interstitial content.³² The activation of the stable B clusters produces localized doping spikes, and this involves thermally generated Si interstitials at very high temperatures or long annealing times.

According to the above model, the luminescence bands P_I^{TO} and P_{II}^{TO} from the excitons bound to the doping spikes appear above a lower critical boron dose, where the preformed boron clusters were produced in a background boron concentration below the solubility limit. They decrease dramatically when the preformed boron clusters cannot be dissolved into doping spikes above a boron dose, at which the background boron concentration is saturated at the equilibrium boron solubility limit. It has been studied that boron clustering in a high interstitial supersaturating environment occurs within a static boron peak above a critical boron concentration so-called C_{enh} in boron implanted silicon.³³ The values of C_{enh} are nearly equal to the intrinsic carrier concentrations for the annealing temperatures around 700 °C–900 °C, which are one order of magnitude lower than the solubility limit. Taking into account the unavoidable boron clustering during the ramp up of the heating above 700 °C in the very early stage of furnace annealing of our samples, the value of C_{enh} is in the range of $1-2 \times 10^{19} \text{ cm}^{-3}$ at a temperature of 900 °C and then increases close to the boron solubility limit at 1050 °C.^{15,34} This is the same concentration as the threshold boron concentration of $1.0 \times 10^{19} \text{ cm}^{-3}$ for the observation of EL from the bound exciton peaks P_I^{TO} and P_{II}^{TO} in our boron implanted diodes [Fig. 3(b)]. At very high boron implantation doses above $1 \times 10^{16} \text{ cm}^{-2}$, the boron clusters cannot be dissolved into doping spikes due to the saturation of boron at the solubility limit, as shown in Fig. 1(e). Therefore the luminescence from the related bound exciton peaks P_I^{TO} and P_{II}^{TO} from the doping spikes dramatically decreases at very high boron doses above $1 \times 10^{16} \text{ cm}^{-2}$.

B. Blueshift

A large blueshift of the luminescence peaks as well as a linear relationship between the luminescence intensity and the logarithm of the excitation power are observed for the spatially indirect electron-hole recombination in III–V δ -doping superlattices grown by molecular beam epitaxy

FIG. 10. (a) Model for the light emission from a silicon *pn* junction containing *p*-type boron doping spikes. The upper panel shows a real-space cartoon and the lower panel the band diagram under small forward bias. (b) Schematic band diagram and possible transitions at strain-free and strained *p*-type boron doping spikes at low (solid arrows) and high (dotted arrows) injection currents. The spatially indirect character is clearly seen.

(MBE).^{35–37} The blueshift of the peak energy of P_I^{TO} with increasing current in our diodes is also similar to that of the PL peak with increasing excitation power observed in dislocation-free boron δ -doping silicon quantum wells grown by MBE.^{12,38} In Ref. 12, the blueshift of the peak is explained by the screening of space-charge potential around the modulating δ -doping layers.

The strong dependences of the peaks P_I^{TO} and P_{II}^{TO} on changing the boron doses can be interpreted with a model similar to Ref. 12. Figure 10(a) shows a sketch of a model for the light emission from silicon *pn* junctions containing

p-type boron doping spikes. Figure 10(b) is a detailed schematic band diagram for two types of *p*-type doping spikes: one type is unstrained, and one is strained by the presence of a large extended defect in the same area. The locally enhanced boron doping results in a band diagram similar to *p*-type δ -doping quantum wells for both kinds of doping spikes.¹¹ In addition, the strained doping spikes exhibit an excess band-gap shrinkage due to the surrounding strain. Although the strain distribution is not exactly known in the present case, we follow the arguments of Weman *et al.* in Ref. 20, who assume uniaxial compressive strain perpendicular to an extended defect. This leads to a splitting and lowering of the conduction band minimum and a splitting and upward move of the valence band maximum, and thus to a strain-induced confinement for electrons and for holes.³⁹ Thus the total band structure near the *p*-type doping spikes—including strain and space charge contributions—contain a potential well for trapping holes and a repulsive potential for electrons. The resulting bound excitons are indirect in real space with holes confined in the cores of the enhanced *p*-type doping spikes and electrons attracted around their peripheries on a nanometer scale. Therefore the recombination photon energy will reflect both the space-charge potentials around the doping spikes as well as the strain field surrounding them. At low current injection, the EL spectra are dominated by the recombination of the spatially indirect bound excitons trapped around the two type of doping spikes with lower energies, as shown by the solid arrows. At high current injection [see also Fig. 10(b)], the space-charge potential around the doping spikes is screened by an increase of the free carrier concentration; therefore the transition energies increase (blueshift), as shown by the dotted arrows.

The space charge potentials can be clearly distinguished by the blueshifts of peaks P_I^{TO} and P_{II}^{TO} in contrary to the absent blueshifts of the peaks P_A and P_B in the reference sample (D*), which are only related to the strain-induced potentials around defects as shown in Fig. 6(b). At high injection current where the space charge potential is almost screened, the peak P_I^{TO} related to unstrained doping spikes, merges into the fixed emission peak of heavily doped bulk silicon, as shown in Figs. 6(a) and 6(b). Under such conditions, the energy difference between the two peaks P_I^{TO} and P_{II}^{TO} may reflect the strain-induced band-gap shrinkage associated the strained doping spikes. The high strain around the strained doping spike causes a band-gap shrinkage in the range of 75 meV to 215 meV for strain induced changes in the lattice constant between 1% and 3%, respectively, as observed in plasma treated silicon wafers.²⁰ This is in good agreement with the energy difference of 120–130 meV between P_I^{TO} and P_{II}^{TO} in Fig. 6(a) at high current injection. For long-time, high-temperature annealing, the strained doping spikes gradually dissolve and the strain may be relaxed, therefore the intensity of P_{II}^{TO} decreases and blueshifts. The peak energy P_I^{TO} related to unstrained doping spikes is not strongly affected, and shows a slightly increased intensity at the same time, as observed in Fig. 5.

The small blueshift (22 meV) of peak P_I^{TO} might be due to a relatively smaller hole-concentration contrast between the smaller (unstrained) doping spikes and the background concentration. These smaller doping spikes probably arise

from the dissociation of the smaller boron-interstitial clusters, which were performed in the projected range with a higher background hole concentration, as shown by the smaller dark spots in Fig. 1(d). On the contrary, the large blueshift of P_{II}^{TO} peak (~ 110 meV) may arise from the screening of the higher space-charge potential associated with a larger hole concentration contrast between the larger, strained doping spikes and the relative lower background boron concentration. The larger strained doping spikes are probably related to thermal activation dissociation of the larger highly strained boron clusters, which are formed at the end of the extended defects close to the *pn* junction with a relatively lower background boron concentration, as shown by the larger dark spots formed at the ends of extended defects in the image of Fig. 1(d).

C. Temperature dependence

The increase of EL from band-edge free electron-hole recombination up to room temperature can be well understood within our model of the *pn* diodes containing doping spikes produced by boron implantation and subsequent long-time annealing. The doping spikes produce a stronger 3D confinement of holes in real space compared to the 1D confinement in δ -doping quantum wells. The *p*-type doping spikes may have a high capture rate of the indirect bound excitons as calculated from our rate equation model. Due to the spatial separation of the electrons and holes, the wave function overlap of electrons and holes is smaller; therefore these indirect bound excitons have much lower recombination rate than the direct ones. This is also consistent with the high emission and low recombination rate (ratio E/R) of the bound excitons at high temperatures in our *pn* diodes. Since the related spatially indirect bound excitons have a much lower recombination probability, the capture of the spatially indirect bound excitons suppresses the nonradiative recombination current from the fast spatially direct recombination at defects and surface states as shown in Figs. 9(a) and 9(b). On the contrary, without a locally enhanced *p*-type doping, the potential wells produced for holes and electrons by the strain-induced band-gap shrinkage at highly strained defects and dislocation loops are located in the same place. The related spatially direct excitons bound to those defects have a much faster recombination rate. Si^+ implantation could cause in principle an increase of strained boron doping spikes, which is limited by the coimplanted boron dose. However, the Si^+ implantation also creates more highly strained defects of silicon interstitial clusters with strain-induced potentials in the conduction and valence band at the same place, which can trap spatially direct excitons with a much larger nonradiative recombination rate. Therefore, the contribution of the defects created by Si^+ implantation to the increase of band-edge luminescence is much smaller as compared to increasing the density of *p*-type doping spikes by boron implantation, as shown in Fig. 8.

The overlap of the *p*-type locally enhanced doping with the strain field around defects changes the faster, spatially direct bound exciton recombination at the defects to the much slower, indirect exciton recombination as illustrated in

the band structure of the strained doping spikes in Figs. 10(a) and 10(b). The spatially indirect excitons bound to the strained doping spikes have a higher binding energy due to the band-gap shrinkage induced by the strain as compared to the unstrained ones. Therefore, the unstrained spikes contribute to the increase of band edge EL at low temperatures (activation energy $\cong 9.5$ meV), while the strained ones have a strong contribution to the efficient EL at high temperatures (activation energy $\cong 61$ meV).

The sample implanted with a boron dose of $4 \times 10^{15} \text{ cm}^{-2}$ has a room-temperature external power efficiency of 0.12% from the band-edge transitions of silicon. This is comparable to results reported by Ng *et al.*. However, our model presents an alternative interpretation for the high EL efficiency in silicon diodes produced by boron implantation: The boron doping spikes effectively suppress the fast nonradiative recombination channels in silicon by capturing spatially indirect bound excitons which have a very low recombination probability. They are temporary reservoirs of excitons and contribute to the efficient EL from band-edge recombination by release of free electron-hole pairs at elevated temperatures. Our study shows that doping spikes in conjunction with strain fields are the origin of two low-temperature EL bands in silicon *pn* diodes prepared by ion implantation. The model we proposed explains all important aspects, in particular the dependence on the boron dose, the extended defect density, the injection current and the temperature.

Finally we would like to remark that we also have performed investigations of photoluminescence (PL). It turns out that the PL behaves very similar to the here reported EL in most respects; this includes the observed spectra as well as their temperature and excitation power dependence. A more detailed discussion is, however, beyond the scope of the present paper.

V. CONCLUSIONS

For boron-implanted silicon *pn* junctions, the origin of two below-band-edge EL peaks with maxima around 1.05 eV and 0.95 eV is attributed to spatially indirect excitons bound to strained and unstrained *p*-type doping spikes, respectively, which are formed by activation of preformed boron clusters at extended defects. These clusters are produced in a silicon interstitial supersaturation environment during the very early stage of the annealing of the ion-implanted silicon. The EL peaks from excitons bound to the doping spikes show a linear blueshift with the logarithmic current similar to the luminescence from spatially indirect electron-hole recombination in δ -doping semiconductor quantum wells. The doping spikes capture spatially indirect bound excitons with a stronger 3D confinement for holes and a lower recombination rate, thus effectively suppressing the fast spatially direct nonradiative recombination arising from the exciton diffusion to defects and surface states. We like to note that such a behavior is not restricted to the specific material system under study, but may also be found in other materials where charge carriers are trapped at defects, forming a long-lived reservoir by preventing nonradiative recombination. An example may be the GaP:N system (Ref. 26).

On the basis of our model a further improvement of silicon-based light emitting diodes will be possible using standard silicon wafers, thus making silicon *pn* diodes prepared by ion implantation highly attractive for future optoelectronic applications.

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