

Quantifying boron and phosphorous dopant concentrations in silicon from photoluminescence spectroscopy at 79 K

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Photoluminescence spectroscopy at 79 K is shown to provide an alternative, non-destructive characterisation method for quantifying the boron and phosphorous dopant concentrations in silicon. The dopant concentrations are revealed by the photoluminescence intensity ratios of the dopant-related

features to the band-to-band recombination peaks. The intensity ratio is found to be insensitive to the excitation power in a wide range of 0.3 W cm^{-2} – 100 kW cm^{-2} . Calibration curves for boron and phosphorous in silicon are presented for [B] below $5 \times 10^{17} \text{ cm}^{-3}$ and [P] below $8 \times 10^{16} \text{ cm}^{-3}$.

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1 Introduction The concentration of shallow dopants in crystalline silicon determines the conductivity of the bulk material, and is an important material and device parameter. The commonly used techniques for measuring the dopant concentration in silicon include four-point-probe, conductance measurements, electrochemical capacitance-voltage (ECV) profiling, secondary-ion mass spectrometry (SIMS) and inductively coupled plasma mass spectrometry (ICP-MS). In this work, we show that photoluminescence spectroscopy (PLS) at liquid nitrogen temperature is an alternative method for sensitively measuring the dopant concentration in silicon for certain doping range.

The presence of neutral shallow dopants in silicon provides energy levels from which radiative recombination takes place, in addition to the radiative recombination from the conduction and valence band edges. Tajima [1] first developed the technique for quantifying the boron and phosphorous dopant concentrations in silicon by comparing the luminescence intensity ratios of the dopant bound exciton (BE) to the free exciton (FE) recombination peaks. Other groups applied this technique and reported similar findings [2, 3]. These luminescence spectroscopy measurements were all performed at the liquid helium temperature of 4.2 K, and the technique was limited to dopant concentrations below 10^{15} cm^{-3} . Iwai et al. [4] later extended the dopant concentration range to 10^{17} cm^{-3} by increasing the measurement temperature to 20 K. This technique has also

been successfully applied to the quantification of arsenic and aluminium in silicon, performed at 4.2 K [3, 5] and 15–27 K [6].

In this work, we examine the feasibility of this technique at 79 K, close to the liquid nitrogen temperature, which is more easily achieved in many laboratories. Boron-doped silicon of 10^{14} – $5 \times 10^{17} \text{ cm}^{-3}$ doping, and phosphorous-doped silicon of 7×10^{13} – $8 \times 10^{16} \text{ cm}^{-3}$ doping were examined in this study. We chose samples of dopant concentrations well below the silicon Mott transition concentration of $3 \times 10^{18} \text{ cm}^{-3}$. This is because as the dopant concentration approaches and exceeds the Mott transition, the dopant band starts to overlap with the band tail of the conduction (for n-type silicon) or valence (for p-type silicon) band, making it difficult to clearly distinguish the contribution of the dopant peak from the overall photoluminescence spectrum [7, 8].

2 Experimental Single crystalline float-zone and Czochralski grown silicon wafers of a range of resistivities were used in this work. For the p-type boron-doped silicon samples, the resistivity varied from 0.07 to $90 \Omega \text{ cm}$; and for n-type phosphorous-doped silicon, the resistivity was 0.1– $60 \Omega \text{ cm}$. The resistivity of the wafers was measured using both a four-point-probe and from the dark conductance. ECV analysis was also used to confirm the doping concentration of heavily doped samples. Doping concentrations were

determined from the measured resistivity using Klaassen's mobility model [9, 10] and Altermatt's dopant ionisation model [11, 12]. The silicon wafers were chemically polished, and some were passivated with plasma enhanced chemical vapour deposited (PECVD) silicon nitride films for better signal-to-noise ratios.

Two photoluminescence spectroscopy (PLS) systems were used in this work, as described in more detail elsewhere [13, 14]. The low excitation (LE) system had a laser spot diameter of 2.2 mm, and the high excitation (HE) system, equipped with a confocal microscope, had a spot diameter of only 1.7 μm (both diameters were FWHM of a Gaussian profile). In both cases, excitation was provided by a 785-nm laser source. The on-sample excitation intensity was 0.1–60 W cm^{-2} for the LE and 8–120 kW cm^{-2} for the HE PLS systems. For the LE PLS system, luminescence spectra were captured by a liquid-nitrogen cooled InGaAs detector via a double-grating monochromator, and signal sensitivity was improved by using a mechanical chopper and a lock-in amplifier. The HE PLS system used a liquid-nitrogen cooled InGaAs array detector. The spectral responses of both PLS systems were determined from the same calibrated tungsten-halogen light source. All samples were measured using the HE PLS system. Some samples were also measured using LE PLS, to examine the impact of excitation power. The spectral resolution was 0.25 nm for the HE PLS and 3 nm for the LE PLS measurements.

All measurements were performed at 79 K, using liquid nitrogen cooled cryostats. In order to compare the spectra of different samples, the spectra PL intensity was normalised to the same band-to-band (BB) recombination peak. In this work we chose to normalise to the peak related to the BB photon emission assisted by the emission of a transverse optical (TO) phonon [15], which is the largest peak of the spectrum. The dopant PL intensity therefore refers to the luminescence intensity ratio of the dopant peak to the BB TO peak.

3 Results and discussion Comparison of the normalised PL spectra of samples of different doping clearly reveals features that are related to the dopant concentrations, as shown in Fig. 1. The PL intensity ratio of the dopant peaks is found to increase with increasing doping concentration, for both boron- and phosphorous-doped silicon samples. This effect has also been observed by Daub and Würfel [16] at 90 K, by comparing the PL spectra of two p-type samples of different resistivities. Peaks related to the presence of boron or phosphorous were reported by Dean et al. [15] at 64 and 80 K, respectively, at similar wavelength ranges to what we observed here. Dean et al. [15] suggested that such dopant peaks likely originated from the recombination of free electron–hole pairs through the neutral dopant atoms, rather than through the recombination of excitons bound to dopants (BE), which is commonly observed at temperatures below 20 K, the temperature range used in Refs. [1–6].

In a semiconductor, the interaction among the dopant atoms increases as the dopant concentration increases, and this interaction broadens the distribution of the energy states

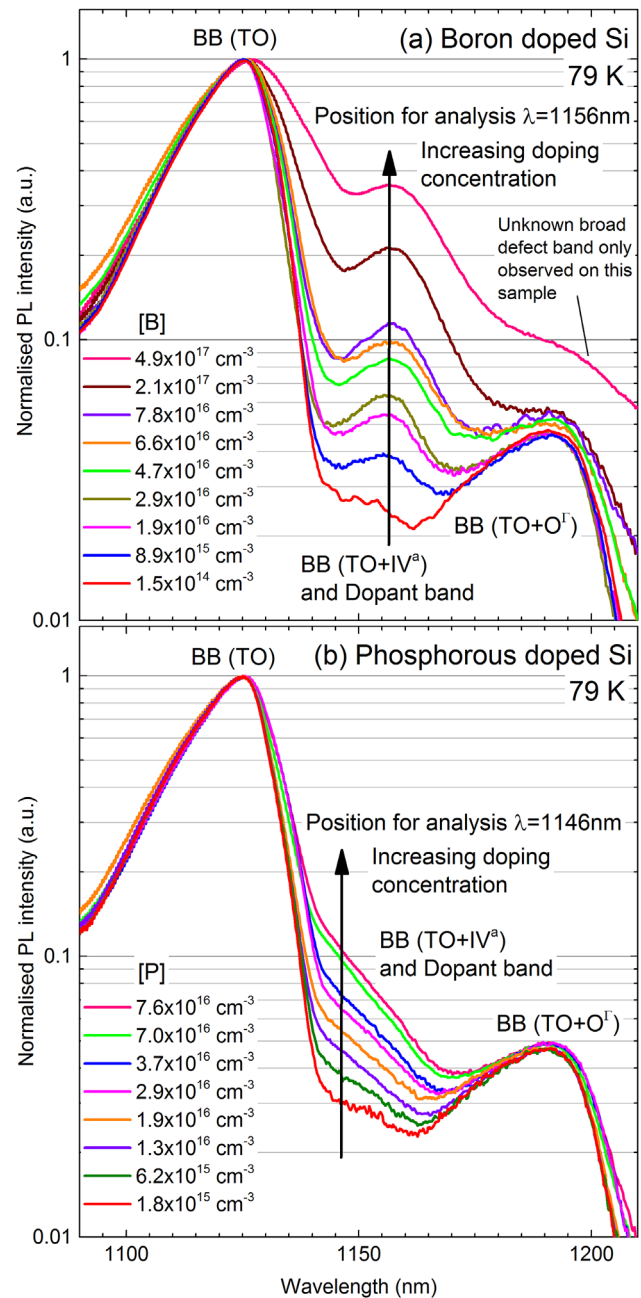


Figure 1 Normalised photoluminescence spectra of (a) boron-doped and (b) phosphorous-doped silicon samples of a wide range of dopant concentrations. Peaks related to the band-to-band recombination assisted by different phonon combinations are also labelled, using Dean's phonon assignments [15].

of the dopant atoms. Eventually, a dopant band is formed slightly below the conduction band (for n-type dopant) or above the valence band (for p-type dopant) [11, 12]. The density of states of the dopant band increases with increasing dopant concentrations, and as a result more free majority carriers can be trapped at this dopant band and then radiatively recombine with free minority carriers. The radiative recombination from the neutral dopant band is

manifested in the photoluminescence spectra, as shown in Fig. 1. At 79 K, there is little reabsorption of the generated photons, and thus the sample optics and excess carrier profiles do not affect the detected PL spectral shape [17]. The relative PL intensity of the dopant peak therefore reflects the dopant concentrations.

As an indirect semiconductor, the radiative recombination through neutral dopants in silicon also requires the participation of phonons to conserve momentum. At temperatures below 20 K, the TO phonon was identified to be involved with the recombination of excitons bound to dopant atoms [1–5]. At 79 K, the features associated with the recombination via neutral boron and phosphorous become much broader, as shown in Fig. 1, and hence the assignment of the TO phonon remains unconfirmed at this stage.

In order to accurately quantify the dopant concentrations from the measured PL intensity ratios, it is important to examine, firstly, the fraction of neutral dopants under the measurement conditions, and secondly, the effect of excitation power on the PL intensity ratio.

The fraction of neutral dopants in silicon was estimated using Altermatt's dopant ionisation model [11, 12], combined with Forster's approach to the calculation of incomplete ionisation [18]. Modelling results show that at 79 K, more than 90% of the dopants remain as neutral for a dopant concentration in the range of 10^{14} – $5 \times 10^{17} \text{ cm}^{-3}$ and an injection level in the range of 2×10^{16} – $8 \times 10^{17} \text{ cm}^{-3}$. The laser excitation power of both LE and HE PLS was controlled such that the injection levels during measurements were kept in this range, although the exact injection level was difficult to determine. However, as shown in the following paragraph, the experimental results in Fig. 2 suggest that the laser power used in this work was unlikely to have caused any significant changes to the dopant ionisation levels.

The BB and dopant band peaks have different recombination mechanisms, and thus the two peaks, in principle, may have different dependencies on the excitation power (see, for example, Ref. [19]). In this work, we experimentally examined the impact of excitation power

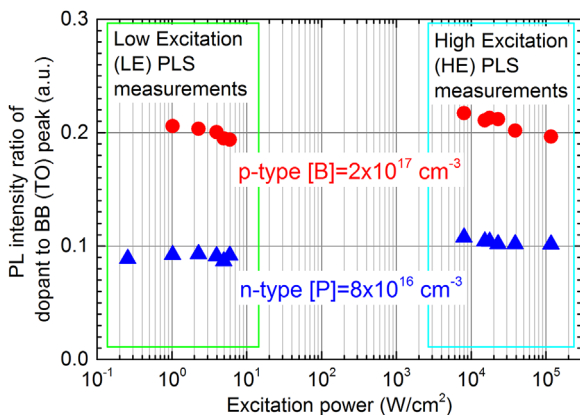


Figure 2 Sensitivity of the dopant peak PL intensity ratio to the excitation power, for boron- and phosphorous-doped silicon, at 79 K.

on the PL intensity ratio for a wide excitation range of 0.3 W cm^{-2} – 120 kW cm^{-2} . The results for one p- and one n-type sample of heavier doping are shown in Fig. 2. The PL intensity ratio is found to vary little with respect to the excitation power for the tested power range. Moreover, the ratios obtained from the two different PLS systems show good agreement. Therefore, for the measurement conditions of 79 K and excitation power of 0.3 W cm^{-2} – 120 kW cm^{-2} , the dopant concentration can be accurately quantified from such PLS measurements.

The calibration curves for estimating the boron and phosphorous concentration in silicon from PL spectra at 79 K are presented in Fig. 3. A conservatively estimated 20% uncertainty for both the dopant concentration and the PL intensity ratio has been included. As the dopant band presents as a rather broad feature, as shown in Fig. 1, the wavelength position for the intensity ratio comparison among samples was chosen based on the position of the largest impact of the dopant band on the spectra. For boron-doped silicon, ratios at 1156 nm are plotted in Fig. 3(a), and

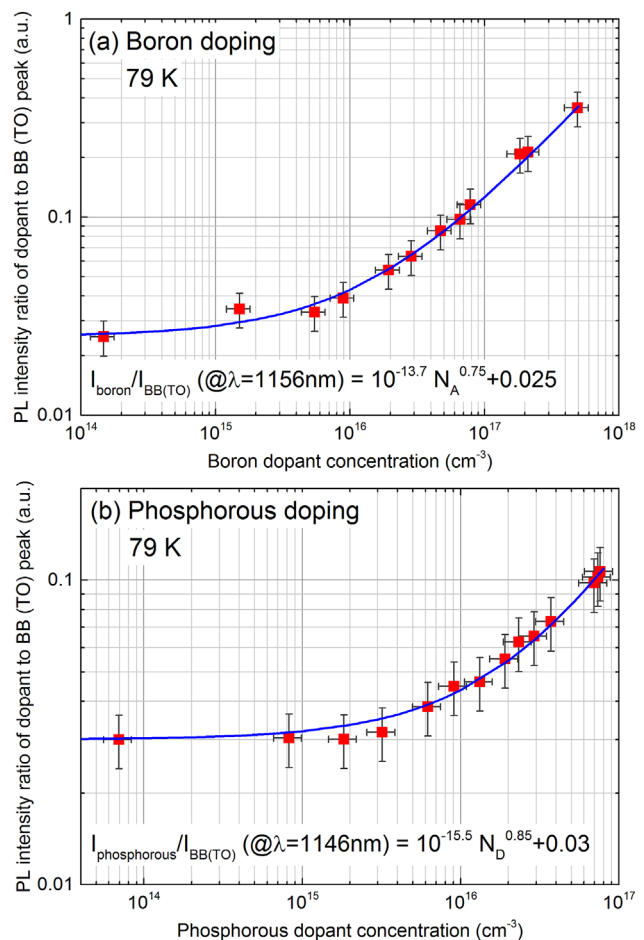


Figure 3 Photoluminescence intensity ratios of the dopant peak to the TO phonon-assisted band-to-band (BB) peak, with respect to the dopant concentrations, for (a) boron-doped and (b) phosphorous-doped silicon.

for phosphorous the wavelength position is at 1146 nm. A simple parameterisation of the measured ratios was performed, yielding the following calibration curves:

– for [B] < $5 \times 10^{17} \text{ cm}^{-3}$,

$$\frac{I_{\text{boron}}}{I_{\text{BB(TO)}}} (@\lambda = 1156 \text{ nm}) = 10^{(-13.7 \pm 2.5)} N_{\text{A}}^{(0.75 \pm 0.15)} + (0.025 \pm 0.005); \quad (1)$$

– for [P] < $8 \times 10^{16} \text{ cm}^{-3}$,

$$\frac{I_{\text{phosphorous}}}{I_{\text{BB(TO)}}} (@\lambda = 1146 \text{ nm}) = 10^{(-15.5 \pm 2.5)} N_{\text{D}}^{(0.85 \pm 0.15)} + (0.03 \pm 0.003). \quad (2)$$

Photoluminescence measurements at 79–300 K were also conducted, and it was found that the dopant-related features diminish with increasing temperature, that the impact of different dopant concentrations on PL spectra becomes undistinguishable at room temperature. This is as expected from the ionisation of dopants [11, 12] and the merging spectral features [13] at higher temperatures. Finally, we note that the application of the technique demonstrated here, in combination with a confocal microscope arrangement, allows micron-scale mapping of dopant concentrations, which may find useful applications in the development of advanced silicon devices.

Preliminary tests of this technique to compensated silicon materials, which are co-doped with boron and phosphorous as a result of cheaper silicon purification processes, show that the dopant-related PL intensity ratios are sensitive to the excitation power, contrary to the findings in non-compensated silicon materials (Fig. 2). This effect, therefore, complicates the applicability of the PL quantification technique to compensated silicon. Detailed analysis on the compensated silicon materials will be reported in a separate publication.

4 Conclusions Photoluminescence spectroscopy at 79 K is shown to allow sensitive quantification of the boron and phosphorous dopant concentrations in silicon, as demonstrated for boron concentrations in the range 5×10^{15} – $5 \times 10^{17} \text{ cm}^{-3}$ and for phosphorous in the range 3×10^{15} – $8 \times 10^{16} \text{ cm}^{-3}$. The dopant concentration is revealed by the photoluminescence intensity ratio of the

dopant peak to the band-to-band TO-assisted recombination peak. Experimental evidence is presented for the insensitivity of the technique to the excitation power for power in the range of 0.3 W cm^{-2} – 100 kW cm^{-2} .

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