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## Silicon luminescence spectra modelling and the impact of dopants

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### Abstract

This paper presents findings on applying physical models in the literature to describe silicon luminescence spectra at 80 – 300 K. Incorporation of exciton recombination models are shown to disagree with the measured luminescence spectra, whereas a free electron-hole recombination model is shown to match well with the luminescence spectra. However, the lack of consideration for excitons is not justified, as Bludau *et al.* [*J. Appl. Phys.*, vol. 45, p. 1846, 1974] reported that excitons are present even at room temperature. The second part of the paper demonstrates the impact of shallow dopants on the silicon luminescence spectra at 79K. The ratio of the dopant-related peak to the band-to-band peak intensities correlates with the dopant concentration, indicating that luminescence spectroscopy has the potential for quantifying dopant concentrations in silicon in this temperature range.

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**Keywords:** silicon; photoluminescence; spectroscopy; shallow dopant

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### 1. Introduction

The luminescence spectra from silicon contain rich information about the material properties, and has been used extensively in the literature to extract fundamental information such as band-gap narrowing [1], doping levels [2], absorption coefficients [3, 4] and radiative recombination rates [5, 6]. Recently, there has been growing interest in applying spectrally-resolved luminescence techniques to silicon photovoltaics, both for material and defect studies [4, 7-11], and for device characterisation [12-15]. These methods often rely on the analysis of the spectral shape, which is usually modelled using absorption coefficient data, or sometimes with modified Gaussian functions [16]. These approaches, however, do not reveal the underlying physical mechanisms responsible for the structure of the

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luminescence spectra. In this work, we first attempted to model the luminescence spectra using a physical model, for a wide temperature range of 79 – 300 K.

The concentration of shallow dopants in silicon determines the conductivity of the bulk material, and is an important material and device parameter. The presence of neutral shallow dopants in silicon provides energy levels from which radiative recombination can take place, in addition to the radiative recombination from the conduction and valence band edges. In the 1970s, Tajima [2] and other groups [17] utilised this characteristics of doped semiconductors to quantify the concentration of boron and phosphorous in silicon, by comparing the luminescence intensity ratio of dopant bound exciton to free exciton peaks. Their measurements were performed at the liquid helium temperature of 4.2 K, and is applicable to dopant concentrations below  $10^{15} \text{cm}^{-3}$ . Iwai *et al.* [18] later extended the dopant concentration range to  $10^{17} \text{cm}^{-3}$  by increasing the measurement temperature to 20 K. The second part of this paper examines the feasibility of this technique at 80 K, liquid nitrogen temperature, which is a more convenient and achievable temperature for many labs.

## 2. Experiment

For the modelling of luminescence spectra, float-zone phosphorous-doped  $100 \Omega \text{cm}$  silicon wafers were used. The wafers were chemically polished prior to surface passivation with plasma-enhanced chemical vapour deposited (PECVD) silicon nitride films on both sides. The wafer thickness was  $335 \mu\text{m}$ . The minority carrier diffusion length was found to be much larger than the wafer thickness, indicating a uniform carrier distribution at the moderate injection levels used here [4]. The samples were excited using a 785-nm laser diode, with an on-sample average power of 250 mW, and a laser spot diameter of 2.2 mm. The sample temperature was accurately controlled using a liquid-nitrogen cryostat. The luminescence spectra were captured with a liquid-nitrogen cooled InGaAs detector via a double-grating monochromator. Signal sensitivity was improved by using a mechanical chopper for the incoming laser beam and a lock-in amplifier. The effect of photon reabsorption has been corrected for using the absorption data from Ref [4].

For the investigation of the impact of dopants on luminescence spectra, both p- and n-type (boron and phosphorous doped) silicon wafers of a wide range of resistivity were examined. The resistivity of the samples was determined by measurements from four point probe, dark conductance from a quasi-steady-state photoconductance (QSSPC) lifetime tester, and electrochemical capacitance-voltage (ECV). The wafers were chemically polished and some were passivated with PECVD silicon nitride films for better signal-to-noise ratios. A micro-PL spectroscopy system was used, in which the incident laser beam was focused into a spot of less than  $2 \mu\text{m}$ . The on-sample average power was 0.66 mW, and the laser wavelength was 785 nm. The emitted PL signal was collected by a liquid-nitrogen-cooled InGaAs array detector. Sample temperature was controlled at 79 K using a liquid-nitrogen cryostat. Details of the micro-PL setup can be found in Ref [9].

## 3. Results and discussion

### 3.1. Physical modelling of the silicon luminescence spectra at 79 – 300 K

The luminescence spectra of silicon in the temperature range of 79 – 300 K were found to be well fitted by a simple physical model, which is based on the absorption coefficient for the recombination of free electron-hole (e-h) pairs [19], and phonon assignments from Dean *et al.* [20]. Details of this work can be found in Ref [21]. Fig 1 presents the measured and modelled luminescence spectra at 79 and 300 K, demonstrating that the temperature-dependent shapes of silicon luminescence spectra can be well reconstructed by this model.

Given the good agreement between the e-h recombination model and the measured PL spectra, it is tempting to conclude that the effect of exciton recombination is negligible at temperatures above 79 K, and that one may extract the bandgap energy from the spectra using the simple free e-h model. However, Bludau *et al.* [22] presented experimental evidence for the existence of excitons up to 300 K.

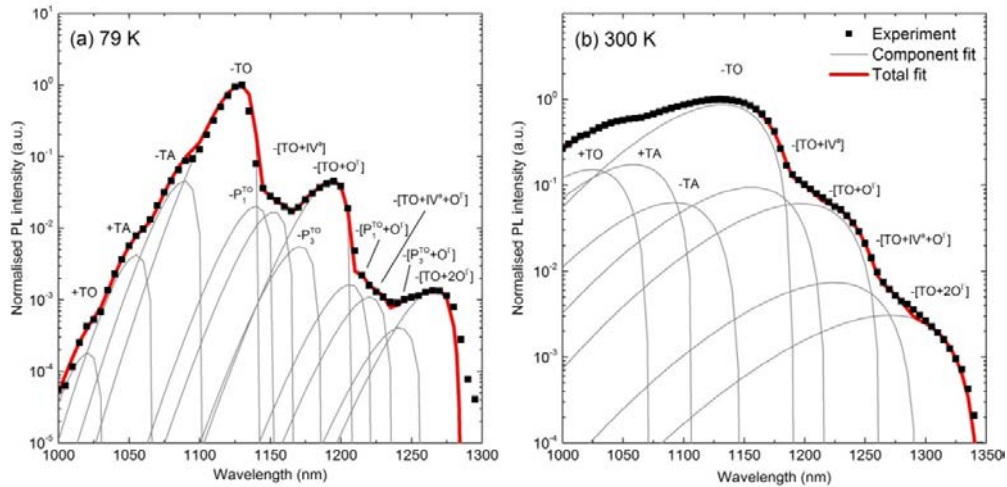


Fig. 1. Measured and modelled luminescence spectra at (a) 79 K and (b) 300 K, using the simple physical model. “+” denotes a photon emission process assisted by phonon absorption, and “-” denotes photon emission assisted by phonon emission. Dopant related peaks are included using the same physical model, for the spectrum at 79 K (a).

Attempts to incorporate the possible impact of excitons were made, using two approaches. One is to combine the physical exciton recombination model [23] with the free e-h model, with the fraction of each component being a fitting parameter. The second approach is to apply a semi-empirical model developed by Macfarlane *et al.* [24], which is also the basis for the works in Refs [25-28]. Both approaches were found to produce modelled peaks that are too sharp on the lower energy side (of each peak) to match with the shape of the measured spectra. This lower energy side corresponds to the application of the exciton recombination model.

The significance of exciton recombination, how to include it in a physical model for luminescence spectra, and its impact on silicon bandgap energy at temperatures above 80 K, remain as open questions at this stage.

### 3.2. Impact of dopants revealed by luminescence spectra at 79 K

In a non-degenerate semiconductor, there is an increasing interaction among the dopant atoms when the dopant concentration increases. This interaction broadens the distribution of the energy states of the dopant atoms, and eventually a dopant band is formed slightly below the conduction band (for n-type dopants) or above the valence band (for p-type dopants) [29, 30]. The density of states of this dopant band increases with increasing dopant concentrations, and thus more free majority carriers can be trapped at this dopant band and then radiatively recombine with free minority carriers. The radiative recombination via the dopant band in doped silicon is manifested in the luminescence spectra, as shown in Fig 2 for both p- and n- types. With increasing doping concentration (i.e. decreasing resistivity), the ratio of the dopant-related peak to the band-to-band (BB) TO peak increases correspondingly, for both boron doped and phosphorous doped silicon samples. This increase is most obvious for samples below  $1 \Omega cm$ . The ratio between the dopant peak and the BB TO peak reflects the dopant concentration of the silicon samples. Further measurements are underway to derive calibration curves for estimating the boron and phosphorous concentrations in silicon from PL spectra at 79 K.

The dopant-related features are found to diminish with increasing temperature, as expected from the ionisation of dopants at higher temperatures [29, 30] and the merging spectral features as shown in Fig 1 (b).

#### 4. Conclusion

In this paper, we present current progress and understanding of modelling the silicon luminescence spectra via a physical approach, and examined the different models in the literature. It was found that the existing exciton

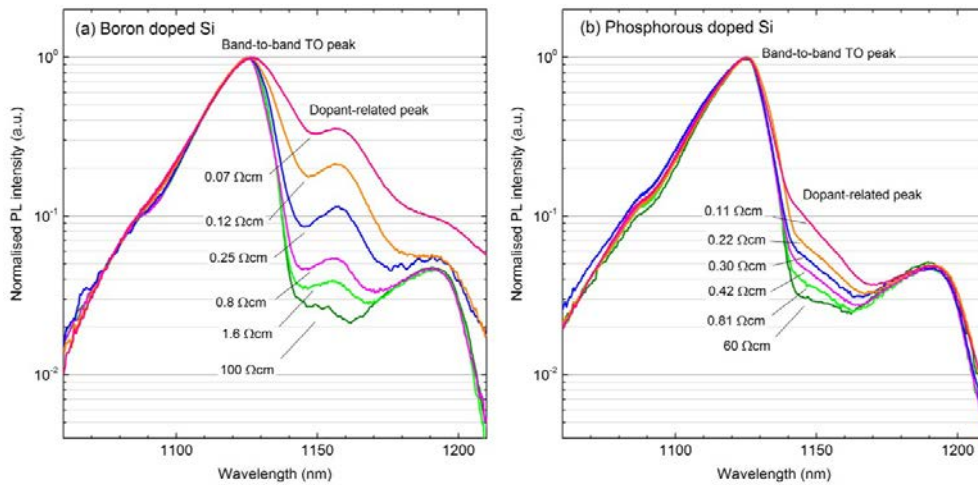


Fig. 2. Photoluminescence spectra of boron doped (a) and phosphorous doped (b) silicon wafers of various doping concentrations, at 79 K.

recombination models do not produce good match with the experimental spectra. Simply applying an electron-hole recombination model agrees with the measured spectra, although its validity requires further investigation.

The second part of the paper presents preliminary results to show that luminescence spectroscopy, at liquid nitrogen temperature, is a promising potential candidate for quantifying the dopant concentrations in silicon.

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