

# Time-resolved measurements of dislocation-related photoluminescence bands in silicon

E A Steinman<sup>1</sup>, A J Kenyon<sup>2</sup> and A N Tereshchenko<sup>1</sup>

<sup>1</sup> Institute of Solid State Physics, RAS, Chernogolovka, Moscow Distr. 142432, Russia

<sup>2</sup> Department of Electronic and Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, UK

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## Abstract

Time decay measurements of dislocation-related PL have been performed for plastically deformed Si samples. Dislocation structures with different spectra were realized by deformation and subsequent thermal treatment. In all cases the decay time of the D1 band is less than that of the D2 band. Intrinsic properties of dislocations may therefore define the difference in decay times between the two bands. We compare this observation with previous results and propose a model of recombination between shallow and deep levels for D1/D2 bands. Different decay times are attributed to different spatial separation of shallow traps from a common deep trap.

## 1. Introduction

Dislocation-related luminescence (DRL) in Si, consisting of the four luminescence bands labelled D1, D2, D3 and D4, attracts considerable attention due to its possible application in light emitting diodes (LEDs) based on silicon technology. The most promising emission from this point of view is that from the long-wave band D1, as this has the highest temperature stability and the most appropriate spectral position [1] for communication applications. In spite of intensive investigation, the exact origin of the D1/D2 bands is still unknown. The solution of this question is of great importance for proper generation of centres responsible for high temperature DRL and further increases in the efficiency of silicon LEDs.

Whilst the D4 line originates from carrier recombination on straight dislocation segments of 60° dislocations, the D1/D2 lines more probably arise from recombination on some point defects on dislocation lines [2, 3]. A phenomenological model of recombination on dislocations has been suggested in [2], in which different recombination centres, responsible for dislocation-related PL lines, are assigned to one dislocation. In this case, a competition between different recombination centres is realized due to diffusion of captured carriers along extended dislocations. A natural barrier to such diffusion occurs due to a fluctuation of potential along dislocations due

to different structural inhomogeneities. To surmount potential barriers the carriers must be excited to above some level—the mobility edge [2] (several meV). Apparently, an increase in the linear density of point defects on dislocations increases the probability of recombination at these points and leads to a relative increase of the intensity of D1/D2 lines with respect to the D4 line [3].

Several experiments have suggested a very close relationship between the centres responsible for the D1 and D2 bands. As an example, we mention similarities in their stress dependence, obtained in piezo-spectroscopic measurements ([3] and references therein). On the basis of these measurements it was concluded that D1/D2 centres are defects with tetragonal symmetry with corresponding tensor elements  $A_1 = -45.94 \text{ meV GPa}^{-1}$  and  $A_2 = 11.25 \text{ meV GPa}^{-1}$ . As the splittings for D1/D2 lines are practically equal, these lines have been attributed to transitions at the same defect, involving one common deep level and different shallow levels. In addition, the observation of equal populations of all equivalent orientations of tetragonal axis of the defect led to the conclusion that they are probably not located in the immediate region of a dislocation core [4] because they do not follow the limited set of directions related to a given dislocation structure. On the other hand, taking into account the unknown structure of the defects, the final conclusion about defect location requires additional proof.

**Table 1.** Samples used for measurements. All samples were deformed by three-point bending at 950 °C in a ceramic furnace under flowing argon. The amount of sample sag was about 0.1 mm with distance between external supports 10 mm. The time of deformation was about 60 min. The third column shows the additional treatment or deviation from standard conditions.

Sample	Type	Treatment
A2d13	FZ, p-type, $n = 3 \times 10^{15} \text{ cm}^{-3}$	Cl gettering at 950 °C for 1 h
A2d16	FZ, p-type, $n = 3 \times 10^{15} \text{ cm}^{-3}$	As deformed, but with larger base (see the text)
B1-1	CZ, p-type, $n = 10^{15} \text{ cm}^{-3}$	Quenched after annealing at 1100 °C for 5 min, 450 °C annealing for 162 h, + passivation in H plasma
B2-1	CZ, p-type, $n = 10^{15} \text{ cm}^{-3}$	Cl gettering at 1000 °C for 1 h + quench

The temperature quenching of dislocation-related PL has been studied by several groups. In [5], the conclusion has been made that two kinds of traps participate in recombination. The shallow traps are in the range 4–12 meV above the valence band, whilst the deep traps are in the range 160–350 meV below the conduction band. Activation energies for D1 thermal quenching that are close to these values have been obtained in [4]. However, the authors put forward a different model for recombination on D1/D2 centres on the basis of a combination of several experimental features for D1/D2 centres, including uniaxial stress dependence. They suggested a trapping of electron–hole pairs on some deep centre, with two slightly different electronic configurations interacting via a potential barrier of some meV, which prevents thermal equilibrium between the states.

The above conclusions have been made on the basis of rapid thermal quenching of D1/D2 line intensities. However, the investigation of heavily deformed Si samples revealed no thermal quenching of D1 line up to 100 K while D2 to D4 lines were quenched rapidly. The further quenching of D1 line could be fitted with activation energy of about 170 meV [2]. This controversy has been solved by assuming that different recombination centres are situated on the same dislocation line and redistribution of captured carriers between these centres can be provided by diffusion through a one-dimensional band without excitation to 3D band. The energy necessary to excite carriers from localized states above the mobility edge of the 1D band is much less than the energy necessary to excite the carriers to the 3D band. In order to find consensus between the large spectroscopic difference between the energy of D1 line and band gap ( $\sim 360$  meV) and experimentally obtained activation energy ( $\sim 170$  meV), the symmetrical splitting of defect states from conduction and valence bands has been proposed [2]. On the other hand, the investigation of the nature of the D1 low-energy shoulder led to a model of donor–acceptor (DA) recombination that involved a deep acceptor state in a dislocation interacting with the donor state of a thermal donor (TD) [6, 7]. The replacement of the D1 band by a D–A transition due to generation of TDs and reversible recovery of D1 band after hydrogen passivation of TDs implies that the same dislocation state participates in both transitions. Following this observation we have to locate the deep dislocation level at about 360 meV above the valence band. Then, coming back to the model of deep and shallow levels, related to dislocation centres D1/D2 we should locate the upper state near the conduction band.

The latter conclusion is in agreement with another experimental observation of unusual energy shift of D1 and

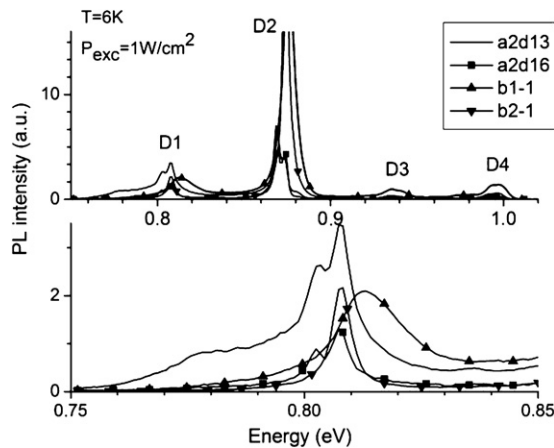
D2 bands with an increase of temperature from 6 to 80 K [8]. The effect was obviously related to concentration of chemical donors and was observed when the concentration of phosphorus donors exceeds the value of  $10^{15} \text{ cm}^{-3}$ . No such phenomenon has been observed with different concentrations of chemical acceptors. Therefore it was concluded that the concentration of free electrons, which increases due to thermal ionization of phosphorus donors, is responsible for the effect.

Finally, a study of the decay time of dislocation-related PL bands at 9 K [9] reveals that the decay curves of D1/D2 bands can be fitted with by two exponents: 200–250 ns at the beginning and 1050–1500 ns at the end. When the temperature increases the decay time decreases showing an increasing contribution of nonradiative channels. The different decay times for D1/D2 and D4 observed in [9] were interpreted as free-to-bound and bound-to-bound transitions, respectively.

The goal of the present paper is to elucidate the energy level scheme providing a whole set of PL bands in DRL by investigation of their decay behaviour. The samples with conditions of dislocation generation excluding a joint generation of point defects and different spectral distribution of intensity have been specially prepared for this purpose.

## 2. Experimental details

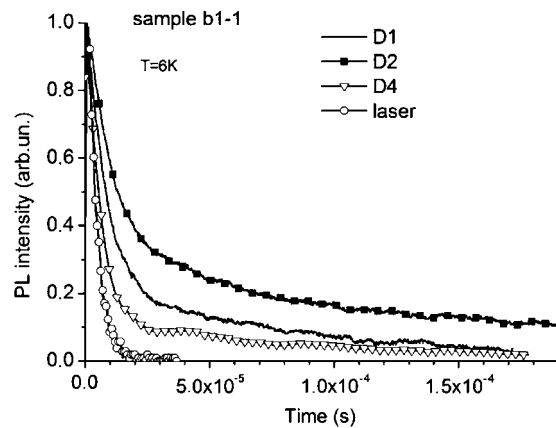
Samples of p-type Fz and Cz silicon were plastically deformed by three-point bending at a temperature of 950 °C. Taking into account the strong dependence of D1/D2 luminescence on the local impurity environment, the samples were prepared in different ways to produce different characteristic luminescence distributions in the vicinity of D1/D2 bands. In spite of precautions to avoid unintentional contamination of the samples during plastic deformation, two of them have been subjected to a gettering in Cl atmosphere to remove residual metallic impurities. A comparative investigation of Fz and Cz grown samples was stimulated by strong dependence of D1 band on the condition and concentration of oxygen in the vicinity of dislocation core [10]. Details of the samples are presented in table 1. PL was recorded using a conventional lock-in technique with a cooled germanium photoresistor as a detector. The samples were placed in variable temperature He cryostat. PL was excited with GaAs laser operating at wavelength 920 nm and penetration depth about 60  $\mu\text{m}$ . The time-resolved measurements were performed with Ar ion laser excitation at 488 nm modulated with a Pockel's cell modulator and Hamamatsu PMT as a detector. No change in DRL spectra has been observed in the same samples due to different excitation wavelengths.



**Figure 1.** (Lower) the dislocation-related luminescence (DRL) spectra in the region of the D1 band for the samples used for time-resolved measurement. The upper graph shows the full range of DRL spectra.

### 3. Results and discussion

The DRL spectra in the region of D1 band for the samples listed in table 1 are shown in figure 1. The top figure shows the full DRL spectrum region, from which it is clear that the main changes in the spectral distribution of intensity due to different histories of the samples happen in the vicinity of D1 band [10]. Samples A2d13 and b2-1 should be free of metal impurities due to gettering in a chlorine atmosphere. Special PL measurements confirmed the reduction of copper impurities below the detection level after Cl gettering, while it was measured in as received samples [11]. Other impurities were not checked. Sample a2d16 is as-deformed and has a more ordered dislocation structure due to the larger base between outer supports during deformation, and a smaller stress gradient. The last two samples are Czochralski grown and differ from the first two by having much larger oxygen concentrations. Therefore, applying a special thermal treatment we were able to prepare dislocations with large concentration and different conditions of oxygen impurities near the dislocation core, which is unachievable in Fz samples. Sample b1-1 has been treated at 450 °C, which is known to produce a high concentration of TDs. In contrast, sample b2-1 has been Cl gettered and quenched in water. The latter procedure is thought to leave dislocations in a pure condition (oxygen and other impurities must be dissolved in the lattice). The corresponding difference in the DRL spectra reflects the difference in contamination of dislocations by impurities. If we compare the spectra of the first two Fz samples, we see that except for the different intensities, which is probably a result of different dislocation density, the same doublet structure is observed in the D1 band. Furthermore, sample a2d13 exhibits an intense low-energy shoulder attributed previously to donor-acceptor recombination [6]. Clearly, this shoulder is caused by additional annealing at 950 °C during the gettering procedure. Sample b1-1 demonstrates a typical spectral distribution of DRL intensity for Cz grown samples [10]. However, it is not



**Figure 2.** The decay curves in the regions of the dislocation-related bands D1, D2 and D4. The laser decay trace illustrates the system time response.

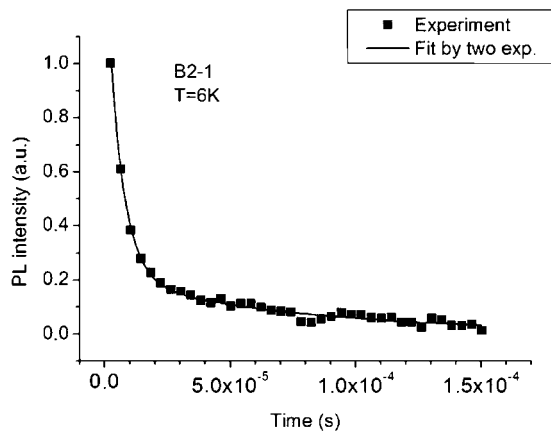
the standard D1 line with energy position 807 meV, but a wide band with a maximum around 813 meV. The position of this band is not fixed, but varies due to the particular parameters of the thermal treatment [10]. This point is well illustrated by the spectrum of sample b2-1 obtained after quenching of the as-deformed sample in water. The D1 line appears in its typical position at 807 meV. It should be noted that the preceding chlorine gettering does not change the result of quenching.

The time-resolved measurements were performed on each sample in the different regions of the DRL spectrum. We mainly concentrated on the behaviour of the D1/D2 bands, but the regions of D1 low-energy shoulder, D4 line and transverse optical phonon replica of bound exciton (TO BE) line were also investigated. A distribution of time constants for the same lines has been observed for different samples, but within one sample we always observed the following sequence  $t_{exc} < t_{d4} < t_{D1} < t_{D2}$ , where  $t_{exc}$ ,  $t_{d4}$ ,  $t_{D1}$  and  $t_{D2}$  denote the time decay constants for short decay in TO BE, D4, D1 and D2 lines. Figure 2 shows this difference for sample b1-1. No excitonic line has been observed in this sample.

Typically, the decay of PL can be reasonably described using two exponents. Figure 3 shows an example of such fitting for the D1 line in sample b2-1. The value of the short time decay constant is of the order  $6 \times 10^{-6}$  s. It must be noted that this result is rather different from that obtained in [9], where a much shorter time has been measured for the D1 and D2 bands. This difference can probably be attributed to different techniques of dislocation generation. Reference [9] employed plastic deformation at a relatively low temperature of 560 °C. This is almost the threshold temperature for dislocation nucleation and movement in Si. As is well known [12, 13], a high density of point defects can be expected due to a movement of dislocations at such a low temperature. Therefore, the observed short time constants can be a consequence of intensive recombination via point defects. A further observation of much longer time decays of the D4 band in samples that were relaxed during growth [9], supports the above assumption. In our case, the high deformation temperature and consequent annealing practically

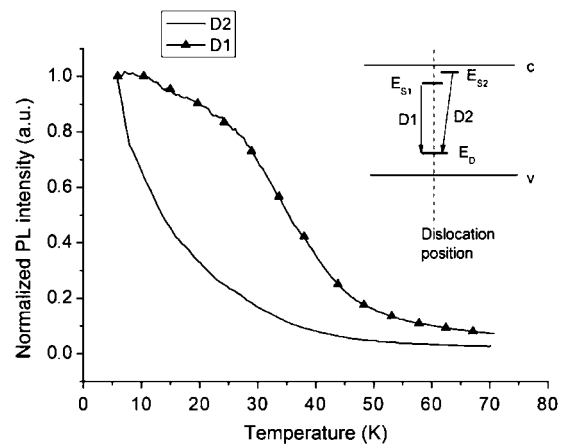
**Table 2.** Time constants obtained for sample listed in table 1 under different measurement conditions.

Sample no.	Region	$t_1$ (short)	$t_2$ (long)	$\chi^2$
a2d13	D1	$6.24 \times 10^{-6} \pm 6 \times 10^{-8}$	$9.7 \times 10^{-4} \pm 2.5 \times 10^{-5}$	$1.2 \times 10^{-8}$
	D1, 780 meV	$5.95 \times 10^{-6} \pm 7 \times 10^{-8}$	$4 \times 10^{-5} \pm 2 \times 10^{-6}$	$5 \times 10^{-10}$
	TO BE	$4.7 \times 10^{-6} \pm 9 \times 10^{-8}$	$5 \times 10^{-5} \pm 2 \times 10^{-5}$	$1.7 \times 10^{-8}$
a2d16	d1	$4.94 \times 10^{-6} \pm 1 \times 10^{-8}$		$2.6 \times 10^{-10}$
	d1		$1.9 \times 10^{-3} \pm 2.4 \times 10^{-4}$	$3.2 \times 10^{-10}$
b1-1	d1, 813 meV	$8.8 \times 10^{-6} \pm 7 \times 10^{-8}$	$1 \times 10^{-4} \pm 1.4 \times 10^{-6}$	$1.7 \times 10^{-9}$
	d2	$1 \times 10^{-5} \pm 1 \times 10^{-7}$	$2.1 \times 10^{-4} \pm 1 \times 10^{-6}$	$1.4 \times 10^{-9}$
	d4	$6.3 \times 10^{-6} \pm 3 \times 10^{-8}$	$1.1 \times 10^{-4} \pm 1.5 \times 10^{-6}$	$1.5 \times 10^{-8}$
b2-1	d1, 807 meV	$5.4 \times 10^{-6} \pm 4 \times 10^{-8}$	$6 \times 10^{-5} \pm 3.4 \times 10^{-6}$	$2.14 \times 10^{-10}$
	d2	$8.3 \times 10^{-6} \pm 2.4 \times 10^{-7}$	$6 \times 10^{-5} \pm 3 \times 10^{-6}$	$3 \times 10^{-10}$

**Figure 3.** The fit of the decay of D1 band using a double exponential decay  $y = y_0 + A_1 \exp(-x/t_1) + A_2 \exp(-x/t_2)$  with  $y_0 = 0.006$ ,  $A_1 = 1.226$ ,  $t_1 = 5.928 \times 10^{-6} \pm 1.13 \times 10^{-7}$ ,  $A_2 = 0.2$ ,  $t_2 = 7 \times 10^{-5} \pm 7 \times 10^{-6}$ .

exclude the effect of point defects in our measurements. Another distinction from [9] is our measurement of different decay times for the D1 and D2 bands. The time decay for the D2 band is generally 30 to 50% longer than that of the D1 band. This difference is well above the uncertainty in measurements of the corresponding time constants (see table 2). The presence of more complicated decays than simple exponentials can be attributed to the heterogeneity of deformed samples due to fluctuations of dislocation density.

In the region of the D1 band, the PL decay has been measured at three different energies: at the D1 line itself (807 meV), at the low-energy shoulder (780 meV) and at the high-energy band (813 meV). The latter can have a maximum position up to 845 meV, which varies due to the particular thermal conditions of deformation and annealing [14]. Different mechanisms of recombination in these three regions allow us to expect different decay times. However, no noticeable difference has been observed. The only sample that demonstrates both the D1 line and the low-energy shoulder (780 meV) simultaneously is a2d13 (table 2). In this case the 780 meV decay is slightly shorter than that of the D1 line, but the difference is negligible. We can therefore say that the decays of the D1 line and the low-energy shoulder are approximately the same.

**Figure 4.** The difference in thermal quenching of D1 and D2 bands. The inset shows the intuitive level scheme, following from the experiment. Here  $E_{S1}$  and  $E_{S2}$  are shallow levels and  $E_D$  is a common deep level.

The high-energy shoulder is present only in Czochralski sample b1-1, which was subject to a prolonged anneal at 450 °C (table 1), which is known to produce TDs [15]. Before this annealing, the shape of the D1 band was the same as in sample b2-1 (figure 1). According to [7, 10] the dependence of the high-energy shoulder on the excitation power implies its DA origin, as has been previously assumed for the low-energy shoulder [6]. It should be noted that these two shoulders in general cannot be observed simultaneously. Typically, the low-energy shoulder appears only in samples with low concentration of interstitial oxygen ( $[O_i]$ ), while the high-energy shoulder is the characteristic of samples with high  $[O_i]$ , as is the case for Czochralski Si [10]. Therefore, the similarity of time decays in the region of D1 band implies a similarity between the mechanisms responsible for the transitions.

The small but reproducible difference between time decays of D1 and D2 bands can be a result of difference between shallow states, discussed in [4]. Close inspection of the thermal quenching of the D1 and D2 bands shows a slight thermalization effect at very low temperatures (figure 4). It must be emphasized that this effect is observable only for specially prepared samples, in which the contribution of nonradiative recombination centres is diminished by

annealing and/or gettering procedures. The evaluation of activation energy for the thermal quenching of D1 bands in the low-temperature range gives a value very close to the ionization energy of the free exciton ( $\sim 14$  meV), which would be consistent with thermal dissociation of excitons limiting the luminescence output of this band. On the other hand, the onset of thermal quenching of the D2 line is characterized by a much smaller activation energy with a value of a few meV. The simultaneous growth of D1 intensity clearly shows that at least some fraction of carriers released from the D2 centre is captured by the D1 centre.

Due to the fact that competition between shallow levels happens independently of the history of sample preparation, we must attribute these levels to fundamental properties of dislocations. The first candidates for the origin of such levels are potential barriers caused by band bending due to the stress field around dislocations. According to calculations performed for the  $60^\circ$  dislocations in Ge [16, 17], the deepest bound state in the valley caused by a deformation-induced potential can be as low as 100 meV. If we take into account the fundamental property of the  $60^\circ$  dislocation to lower its elastic energy by splitting into two partial dislocations:  $90^\circ$  and  $30^\circ$ , we get the two overlapping one-dimensional bands split from the conduction band. Now, the deepest bound state can be expected on the  $90^\circ$  partial [17], while the states at the  $30^\circ$  partials must be much shallower. Of course, some splitting of the one-dimensional band can be expected in the valence band, but we are mainly interested in understanding the conduction band sublevels.

If we assume such a perturbation of the conduction band in the vicinity of a dislocation, and deep state in the core of  $90^\circ$  partial, then we can explain the peculiarities of the D1 and D2 PL bands discussed above. We must place the deep state on the  $90^\circ$  partial to explain the difference in decay times of the D1 and D2 bands. According to this assumption, the recombination producing D1/D2 bands happens between shallow 1D bands split from conduction band and a deep state. The low-energy transition (D1) happens between the deepest of the shallow states at the  $90^\circ$  partial and the deep state at the core of same dislocation (see figure 4). The maximum overlapping of wavefunctions in this case leads to a maximum recombination probability and short decay time. On the other hand, recombination between a 1D band caused by  $30^\circ$  partial and same deep state in the core of  $90^\circ$  partial can be attributed to a high-energy D2 band. However, due to a larger spatial distance between these two states, the probability of this recombination would be less than in the first case, and the corresponding decay time must be longer.

This assumption is in good agreement with experimental observations.

#### 4. Conclusions

In conclusion, we have measured the decay times of dislocation-related PL bands D1 to D4. The difference in decay times leads us to a model of recombination between shallow states split from conduction band minima and deep core state on the  $90^\circ$  partial. This model is in agreement with observed decay times as well as with model of donor–acceptor recombination causing the PL subbands in the region of D1 PL band.

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