Dissociation-Width–Dependent Radiative Recombination of Electrons and Holes at Widely Split Dislocations in Silicon

R. Sauer[a]

Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany

and

Ch. Kisielowski-Kemmerich and H. Alexander

Abteilung für Metallphysik, II. Physikalisches Institut, Universität Köln, D-5000 Köln 41, Federal Republic of Germany

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Resolved fine structure on the broad $D5$ photoluminescence band in silicon—recently associated with straight dislocations—gives evidence that the band is a superposition of at least eleven "line" spectra with systematic energetic positions and reaction-kinetic features. We suggest that the lines originate from the radiative recombination of electrons and holes at Shockley partial dislocations split apart by different widths.

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In most semiconductors, dislocations have an unfavorable effect on the optical properties of the material since they act as recombination-radiation killers. A few semiconductors only, as, e.g., germanium,[1,2] α-SiC,[3] or diamond,[4] exhibit optical emission due to dislocations, and such luminescence has tentatively been attributed to intrinsic or extrinsic states localized at different points on the dislocation line, or to defects created or affected by the dislocations.

In silicon, in particular, a set of four photoluminescence (PL) bands $D1$ through $D4$, with photon energies of ~ 0.812, ~ 0.875, ~ 0.934, and ~ 1.000 eV, respectively, is associated with the presence of dislocations.[5–7] Despite intense investigations, their nature is unknown; however, it was argued[7] that $D1$ and $D2$ might rather be due to pointlike defects induced by the dislocations whereas $D3$ and $D4$ seemed to be more intrinsically related to them. Irrespective of their nature, the four D bands are a characteristic optical signature of *kinked* and *curved* dislocations as introduced into silicon by conventional deformation procedures such as crystal bending or compression along $\langle 213 \rangle$.

In contrast to all these cases, this Letter is concerned with PL spectra associated with a particular dislocation morphology. Practically all glide dislocations in silicon are dissociated into partial dislocations of Shockley type, enclosing an intrinsic stacking-fault ribbon.[8] The distance d between two coupled partial dislocations is of the order of $d_0 = 50$ Å in the stress-free state. At temperatures above 400 °C, d can be increased by a high shear stress to 100–150 Å. This nonequilibrium width can be frozen in by cooling under stress.[8] Therefore, low-temperature, high-stress deformation following a predeformation at higher temperature under low stress produces widely dissociated dislocations; they are straight and parallel to $\langle 110 \rangle$ crystal directions.[8]

The PL feature which we address here is a recently reported broad band $D5$ (~ 0.96 eV) accompanied by a weaker satellite $D5'$ (~ 0.90 eV) which exclusively emerges in crystals containing such well-defined straight dislocations. The elusive $D5$, $D5'$ bands disappear and are replaced with $D3$ and $D4$ upon sample annealing at around 300 °C or higher when the dissociated dislocations narrow and the straight dislocation structure relaxes.[7]

We have studied in detail fine structure on the $D5$, $D5'$ bands in more than twenty floating-zone crystals which were undoped (some 10^{12}-cm^{-3} B atoms) or doped with boron or phosphorus up to 10^{16} cm^{-3}; one floating-zone crystal with 5×10^{18}-cm^{-3} oxygen atoms showed the same fine structure as the oxygen-lean samples. All crystals received a two-step deformation treatment as mentioned above. It is found that the $D5$ and $D5'$ features are not bands at all but are actually a superposition of at least eleven overlapping "line" spectra exhibiting no-phonon (NP) transitions as well as momentum-conserving TA- and TO-phonon satellites. Selected fine-structure spectra of four samples are shown in Fig. 1. At first sight, these spectra seem complex and very different. A clue to our interpretation is given by the line pair 2,3 (sample Ei a) at around 1.30 μm showing two replica pairs at lower energies displaced by ~ 18 and ~ 58 meV, as corresponds to TA or TO momentum-conserving phonons.[9] Higher excitation powers cause line 3 to increase over line 2 in all three replicas, confirming this explanation of the lines and demonstrating as well that the lines 2 and 3 are emitted by different initial states. Simultaneously, the high excitation spectrum of sample Ei a virtually equals the low excitation spectrum of sample AIIIb. In a similar way, by studying excitation dependences over a wide range of excitation levels, 100:0.01, we have analyzed the spectra of all samples:

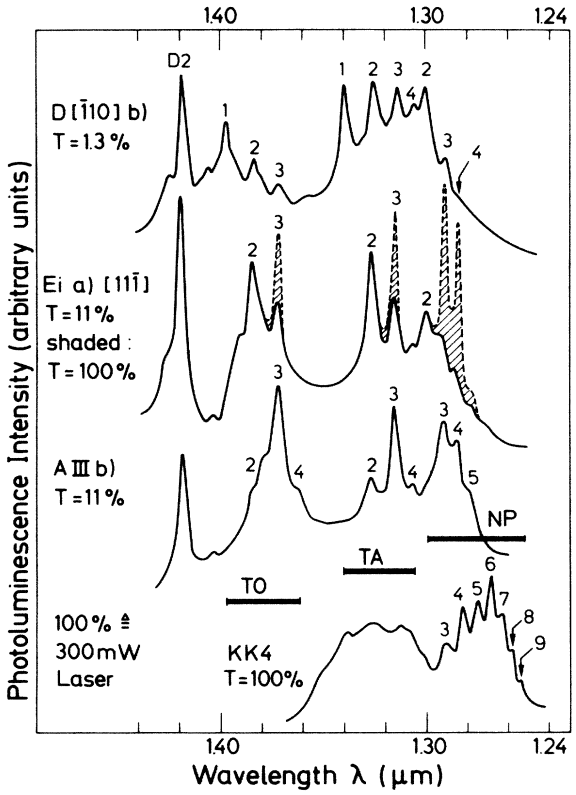

FIG. 1. Photoluminescence "line" spectra at 4.2 K of four selected as-deformed samples at different excitation levels T of a Kr ion laser (647 nm). The previously unresolved broad bands $D5$ and $D5'$ correspond to the NP or TO-phonon region, respectively. The width of the lines is of the order 3 meV.

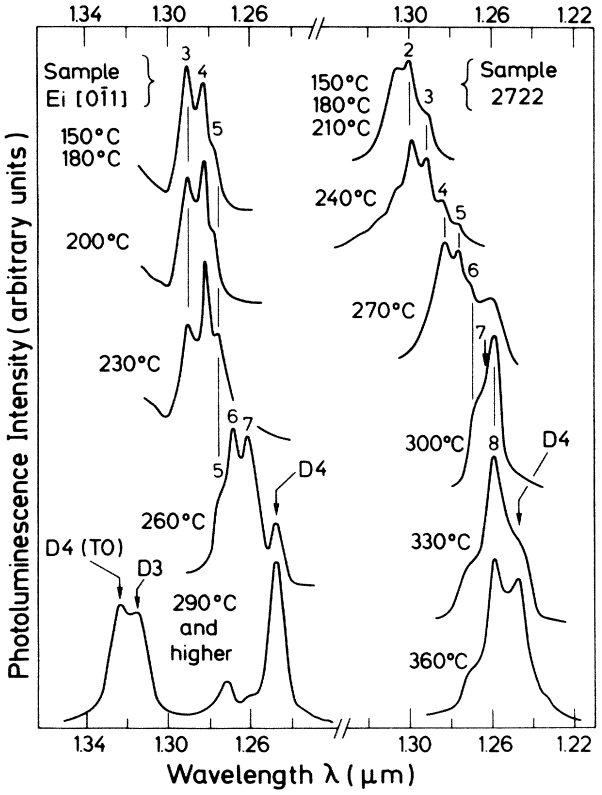

FIG. 2. PL spectra in various stages of isochronal annealing (1 h). The final spectrum $D4$ (bottom) is related to "relaxed" dislocations as in standard deformed samples (Ref. 7).

Eleven individual transitions are identified with line positions as listed in Table I, and with a systematic decrease of their phonon coupling strength from $n = 1$ to 11 indicating a related increasing local perturbation of the different radiative states in this ordering. To specify the latter statement we note that the $n = 1$ spectrum exhibits only phonon-assisted transitions but no NP line, the $n = 2$, 3, and 4 spectra show all of the replicas, and the $n \geq 5$ spectra consist only of NP transitions. At constant full excitation power of 300 mW, the predominance of one or the other spectrum in a given sample depends evidently on subtle details of the sample deformation procedure.

Annealing data and a study of excitation-dependent effects yield a straightforward suggestion as to the nature of the "line" series. Isochronal annealing of the samples causes the spectra to transform into one another from $n = 1$ to 11 (Fig. 2). If we start with the spectrum of an as-deformed sample (predominantly $n = 2$ or 3 in Fig. 2), higher-label spectra emerge consecutively for $T \gtrsim 180\,^{\circ}\mathrm{C}$ while the lower-label spectra disappear to the extent that essentially one spectrum is dominant at a time. The relevant transformation temperatures scatter for different samples. The final emission thus obtained for $T \gtrsim 360\,^{\circ}\mathrm{C}$ is the $D4$ spectrum known to be related to relaxed dislocations. We note that the energetic positions of the lines as a function of the label n form a smooth curve converging to the $D4$

TABLE I. Line positions of the various replicas at low excitation and spacings corresponding to momentum-conserving TA or TO phonons.

Line n	Line positions (eV) TO	TA	NP	Differences (meV) NP-TA	NP-TO
1	0.8866	0.9247	Not obs.	· · ·	· · ·
2	0.8951	0.9345	0.9527	18.2	57.6
3	0.9031	0.9430	0.9611	18.1	58.0
4	~0.909	0.9483	0.9668	18.5	57.8
5	Not observed		0.9721	· · ·	· · ·
6	Not observed		0.9770	· · ·	· · ·
7	Not observed		0.9811	· · ·	· · ·
8	Not observed		~0.985	· · ·	· · ·
9	Not observed		~0.988	· · ·	· · ·
10	Not observed		~0.991	· · ·	· · ·
11	Not observed		~0.994	· · ·	· · ·

position. These observations suggest strongly that the line series under discussion is determined by a structural parameter which takes a variety of discrete values during relaxation of the dislocations. We tentatively associate this parameter with the dissociation width d of the Shockley partial dislocations.

Support to this hypothesis comes from the excitation-dependent effects (Fig. 3): (1) The integrated PL intensity of all lines is strongly sublinear as a function of the excitation level (this enabled us to vary the excitation by a factor of 10^4 as mentioned) and indicates easy saturation of the radiative states due to very long decay times. (2) The "lines" broaden and shift to higher energies at increasing excitation powers; hence the spectra are generally less well resolvable under high excitation. The linewidths vary typically (e.g., for $n=2,3$) from ~ 3 to ~ 5 meV; measured shifts amount to ~ 2 meV. (3) The intensity ratios, NP/TA or NP/TO, depend for $n=2,3,4$ dramatically on the excitation level; thus high excitation causes the NP lines to be absolutely dominant over the phonon replicas. All these reaction-kinetic features are highly reminiscent of donor-acceptor (DA) pair recombination as familiar for many years and as recently also intensely studied in silicon.[10]

In conjunction with the annealing data we are led to suggest a microscopic model (Fig. 4) assuming that the optically excited electrons and holes are localized on the well-defined straight, widely dissociated dislocations. Previous transmission electron microscopy[8] has shown that in samples prepared identically to ours the dissociation widths d can be as large as 150 Å and the length of the straight dislocation segments amounts to the order of 1 μm. In the model, a particular PL spectrum with label n is attributed to electron-hole recombination at partial dislocations of a specific dissociation width d. The possible variations of d are 3.3 Å as determined by the lattice structure; hence d only could take ~ 30 values at maximum, 11 of which would have been observed in our experiments. At low excitation, only few of the localized states on a given pair of partial dislocations are occupied with large average distance R between the electron-hole pairs and small wave-function overlap (Fig. 4). Increasing optical powers excite closer pairs, and these are assumed to have lower capture probabilities and higher recombination rates (as characteristic of DA pairs). This explains all the reaction kinetic features outlined above: (1) R-dependent saturation of those pairs which, by virtue of sufficient overlap, can contribute to a PL line, this favoring lines with larger n (or smaller d) at higher powers as these saturate later, (2) the line broadening and shift to higher energies in a particular spectrum, and (3) the excitation-dependent NP/TA and NP/TO intensity ratios. The latter effect is consistent with the experimental finding in the basic work on DA pair luminescence in silicon by Enck and Honig (their Fig. 4)[11] and must be thought of as being due to a prerecombination interaction between the localized states depending on both their distance and *occupancy*. This would also explain that spectra with larger n (or smaller d) show consecutively stronger NP transitions as compared to their phonon replicas at the same excitation level. Our temperature-dependent measurements yield a typical line broadening by a factor of 2 from 2 to 25 K. This weak—below kT—broadening discards every model involving energy bands (irrespective of their dimensionality); however, it is again very similar to DA pair spectra in silicon.[11] The absence of any experimental splitting of the lines 3,4,5 in external

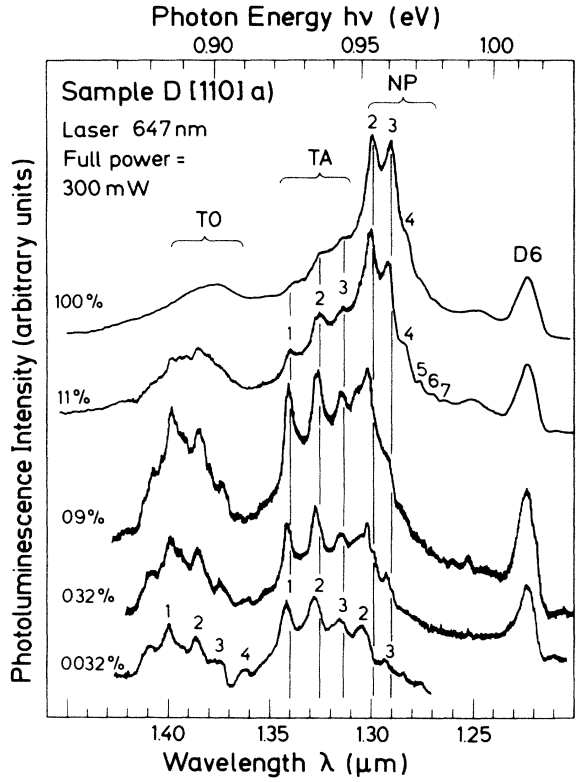

FIG. 3. Excitation dependence of a spectrum as typical of all of the two-stage deformed samples.

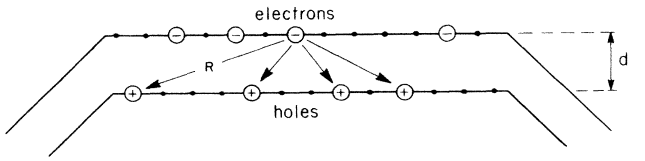

FIG. 4. Schematic sketch of partial dislocations along ⟨110⟩ directions dissociated by width d, and localized excess electrons and holes before recombination. Dots indicate possible localization sites.

uniaxial stress fields up to 350 MPa along ⟨001⟩, ⟨111⟩, and ⟨110⟩ is consistent with the model when the localized electrons and holes derive from their respective band edges, and the fourfold Γ_8 hole states are split into two Kramers degenerate states in the strain field of their associated partial dislocation with the lower-energy state occupied.

Our findings open up a direct means of studying partial dislocations and related energy terms. Basically, the model requires closer electron-hole pairs to be associated with higher photon energies. The line energies as a function of the width parameter d are entirely different from DA pair lines with respect to energetic progression and convergence indicating that Coulomb terms cannot play the dominant role, either in the initial or in the final transition states. This shows the absence of electrically active states effective in capturing the excess electrons and holes consistent with recent theoretical and experimental conclusions for the 30° and 90° partial dislocations.[12] Width-dependent energy contributions in the range of ~ 60 meV covered by the line series could come from stress and polarization terms as well as short-range potentials. Prior to an evaluation of the PL line energies future work will be directed towards a distinction between dissociated screw dislocations (consisting of two 30° partial dislocations) and dissociated 60° dislocations (consisting of one 90° and one 30° partial dislocation) which are all contained in the present samples.°

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[a]Present address: AT&T Bell Laboratories, Murray Hill, NJ 07974.

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