Физика и техника полупроводников, 2007, том 41, вып. 4

# Photoluminescence study on defects in multicrystalline silicon

© T. Arguirov[†*¶], W. Seifert[†*], G. Jia[‡*¶¶], M. Kittler[†*]

[†] IHP, Im Technologiepark 25,
D-15236, Frankfurt (Oder), Germany
[‡] BTU Cottbus, Konrad Wachsmann Allee 1,
D-03046 Cottbus, Germany
[*] IHP/BTU Joint Lab, Konrad Wachsmann Allee 1,
D-03046 Cottbus, Germany

*(Получена 12 сентября 2006 г. Принята к печати 3 октября 2006 г.)*

We report on spatially resolved luminescence measurements on ribbon grown silicon samples. It is found, that the band-edge luminescence shows anomalous temperature behaviour, namely an increase of the radiation intensity with temperature. Phosphorous diffusion gettering is found to enhance this effect. The anomalous temperature behaviour is attributed to nonradiative recombination governed by shallow traps. A shift in the phonon replica of the band edge luminescence peak has been observed and associated with tensile stress.

PACS: 78.55.Ap, 78.55.Qr

## 1. Introduction

The photoluminescence technique allows characterization of the material without preparation of contacts and gives information about the radiative defects there. It has been successfully applied for characterisation of silicon of different cryslalline quality [1–4]. Commercially available techniques like SiPHER [5] allow resolving defects with the spatial resolution of several $\mu$m. Even though the scanning photoluminescence has been broadly applied for characterisation of silicon, its potential and limitations need to be further explored. The goal of the work is to demonstrate the applicability of photoluminescence technique for characterisation of silicon for photovoltaic applications. We analyse the radiation from samples at temperatures in the range 80–300 K. Dislocation radiation maps have been measured and the spatial correlation of band-edge radiation (BB) with the specific defect related lines were studied. Band-edge recombination maps deliver information about the lateral distribution of the recombination rate. In addition, the temperature dependence of BB gives information about nonradiative processes, which limit the radiative recombination. The two and three phonon assisted luminescence peaks are analysed in terms of mechanical stress.

## 2. Experimental

The samples studied were placed in a cryostat, which was used to adjust the sample temperature in the range from 80 to 300 K. The cryostat was placed on $xy$ positioning table, allowing to scan the sample at a fixed laser spot. A laser beam from an Ar ion laser (wavelength 514 nm) was focused at the sample surface to a spot of 100 $\mu$m size. The excitation light was directed to the sample surface normally and the back emitted luminescence was collected and analysed using a monochromator. Standard lock in technique was used for detecting the electrical signal generated by the radiation in a liquid nitrogen cooled Ge detector.

All samples were of *n*-type, phosphorous doped and they were prepared by the ribbon growth method. The samples were analysed in the as-grown state and after phosphorous diffusion gettering (PDG).

## 3. Results

### 3.1. Correlation between band edge and D1 luminescence at room temperature

The band-edge luminescence in silicon is an inefficient recombination route compared to the nonradiative recombination processes. Some of the defects like e. g. dislocations can be also radiatively active emitting the D band radiation. The photoluminescence (PL) scanning technique allows determining the spatial correlation between the dislocation related radiation and the band-edge emission. It has been shown that there is an anti-correlation between the BB and D1 radiation [1] when the dislocations are the limiting recombination routes for minority carriers. At the dislocation rich sites, the D1 radiation is strong and the band-edge luminescence is low. The band-edge luminescence increases with the concentration of injected carriers. When recombination active defects are presents the minority carrier concentration decreases due to the lowered lifetime and thus the BB luminescence decreases. In cases, when other centres but not dislocations are the factor limiting the lifetime the anti-correlation between D radiation and BB radiation lifts off. Strong nonradiative routes are the surface and grain boundary recombination. The wavelength used in our study (514 nm) allows photoexcitation in the depth of 1–2 $\mu$m, thus the surface recombination plays a significant role and modulates the entire luminescence. The situation where different recombination mechanisms are limiting for the recombination rate is illustrated in Fig. 1.

---

[¶] E-mail: arguirov@tu-cottbus.de
[¶¶] E-mail: jiaguobi@tu-cottbus.de

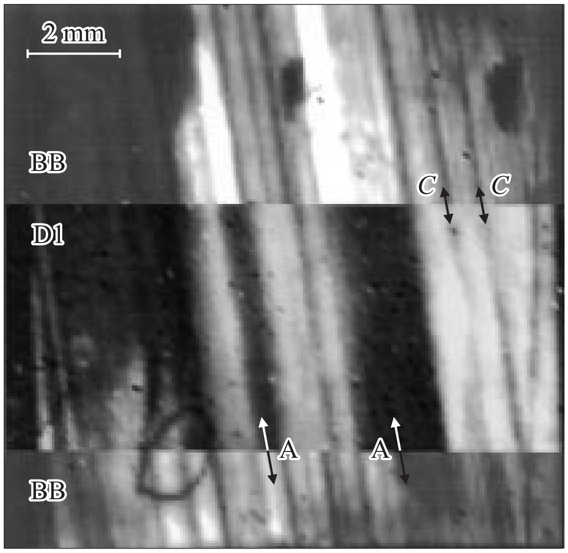

**Figure 1.** The positions marked C show a correlation and those marked A an anti-correlation of the band-edge luminescence and the defect related D1 luminescence. The nonradiative recombination dominates at places like grain boundaries or areas of enhanced surface recombination, so there is a correlation between the band-edge and D1 luminescence.

The figure compares two intensity maps of the band-edge and D1-line radiation at room temperature. Is is seen that there are areas of clear anti-correlation between the D1 emission and the BB emission (marked A), but also areas of correlation between both emissions can be observed (marked C). Correlation between D1 and BB intensity occurs at grain boundaries and areas of increased surface recombination (dark on the map).

### 3.2. Anomalous temperature behaviour

Our setup allows spot wise temperature dependent measuments. The BB radiation for silicon is known to decrease upon increasing of temperature [6]. Measurements on pure float zone silicon (FZ, Fig. 2 inset) show the expected temperature behaviour. In the case of multicrystalline ribbon silicon the temperature dependence was observed to be opposite. Fig. 2 shows the dependence of the peak area on temperature. The overall intensity of band-edge luminescence increases when increasing the sample temperature. The anomalous temperature behaviour observed on the as-grown material is even amplified after phosphorous diffusion gettering.

The intensity of the band-edge luminescence is strongly influenced by the minority carrier lifetime. To explain the anomalous temperature behaviour we have to look for a process causing an increase of the effective carrier lifetime upon increasing the temperature. The rise of the temperature leads to a shift of the Fermi level towards the mid of the band gap. Shallow levels, which are partially occupied at low temperature, allow effective recombination. They become unoccupied upon increasing the temperature, and the probability of recombination through them decreases. Fig. 3 illustrates the change of the lifetime $\tau$ upon increasing the temperature. The curves are normalized to the lifetime at 100 K and were calculated according the Shockley–Read–Hall (SRH) theory for two different excitation levels, $\beta$, defined as the ratio between the minority carrier concentration generated by the light excitation and the majority carrier concentration. The position of the shallow level was chosen $\Delta E = 45$ meV beneath the conduction band edge in the phosphorous doped material [7]. Both curves show a general trend of lifetime increase with temperature. So, an increase of the lifetime on increasing the temperature occurs independently on the excitation level. The origin of the shallow levels can not be identified from the measurements, but one

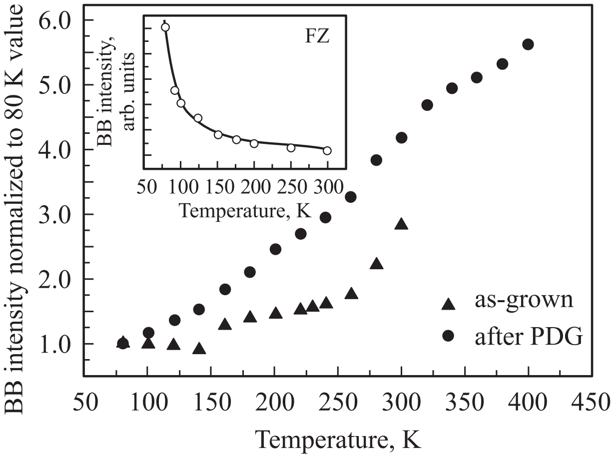

**Figure 2.** The band-edge luminescence shows anomalous temperature behaviour, which enhances after PDG. In the inset is given the temperature dependence of the band-edge luminescence of float zone (FZ) material measured at similar conditions.

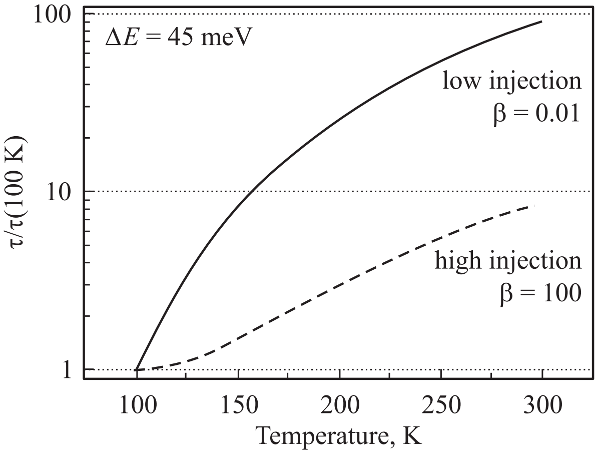

**Figure 3.** Temperature dependence of lifetime $\tau$ calculated from SRH theory for shallow level 45 meV from the conduction band. The lifetime increases 1 to 2 orders of magnitude upon increasing the temperature from 100 K to room temperature. The increase of the lifetime can thus overcompensate the temperature quenching of band-to-band radiative recombination.

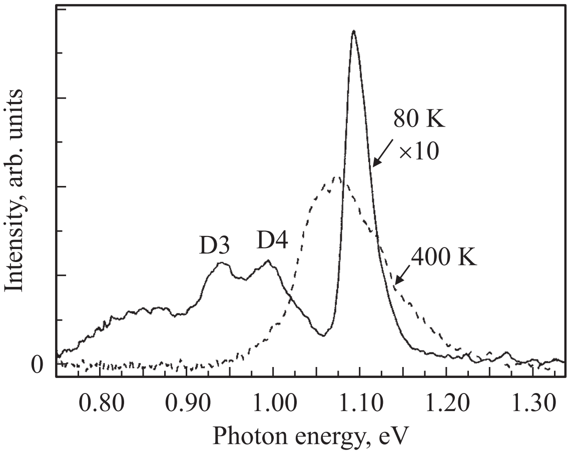

**Figure 4.** Typical spectra from the *n*-type ribbon samples, subjected to phosphorous diffusion guttering show distinct D3 and D4 features at 80 K. A spectrum at 400 K is given for comparison with the 10 times magnified 80 K spectrum.

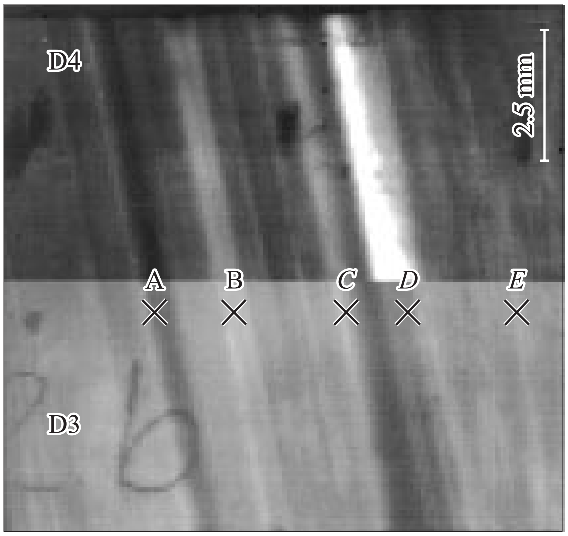

**Figure 5.** Intensity maps of D3 and D4 features in the photoluminescence spectrum. The letters A to E indicate the positions, where the spectra shown in Fig. 6 are taken.

of the candidates is a one-dimensional dislocation band below the conduction band. The characteristic dislocation features D3 and D4 were detected in the low temperature spectra of the samples, which show anomalous temperature behaviour of BB (Fig. 4). The lines are well seen in the low temperature spectra of the sample and not detectable at higher temperatures. It has been shown that clean dislocations are active at low temperatures [8].

### 3.3. Role of phosphorous diffusion gettering

We suggest that PDG leads to elimination of deep level assisted recombination routes and, additionally, to cleaning of the dislocations, without influence on the shallow levels. So, the shallow dislocation levels become the limiting factor for the minority carrier lifetime. Accordingly the anomalous temperature behaviour is more pronounced after PDG.

### 3.4. Correlation between D3 and D4 lines at 80 K

The D3 line is considered as a replica of the D4 line [8,9] and thus spatial correlation between both lines is well established across the samples. However, in some cases demonstrated in Fig. 5 the correlation between both lines seems to be violated. Namely, the intensity of the D4 line exceeds the intensity of the D3 line. The closer look at the low temperature spectra (Fig. 6, *a*) shows that the effect is caused by an additional peak close to the D4 line, which influences the overall intensity of the radiation at that energy (1.0 eV).

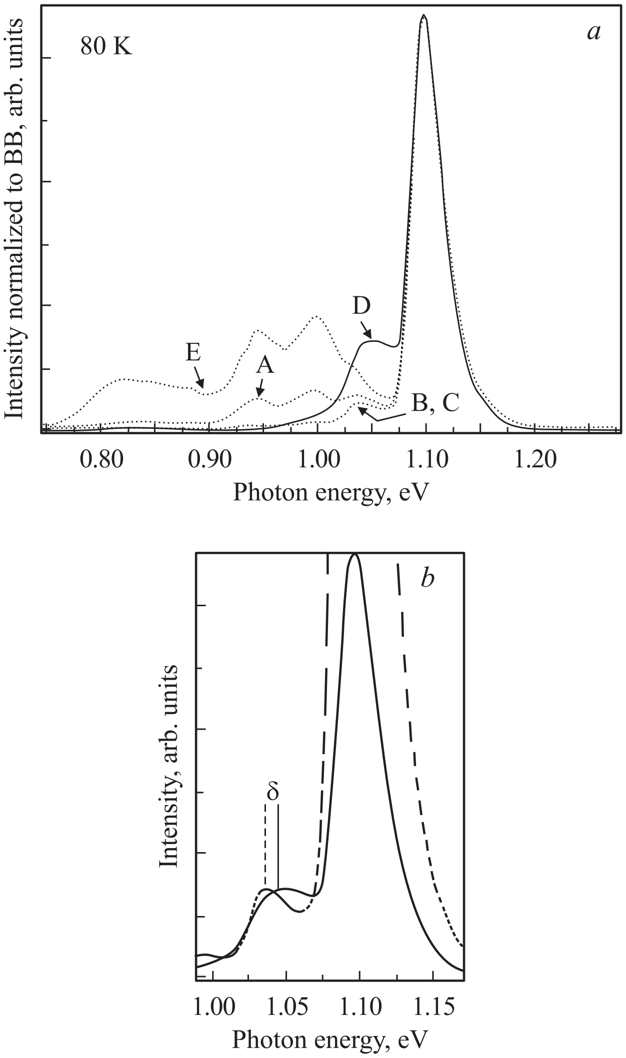

**Figure 6.** *a* — normalized spectra on the sample before PDG. The position D shows a strong feature at ~ 1.05 eV, which we related to enhancement of the 2-phonon-assisted radiative recombination. *b* — the magnified band edge luminescence shows the shift of the 2-phonon process, which can be related to lower phonon energies.

The silicon band-edge radiation is always accompanied with an additional low energy peak, which we regard as a phonon replication of the band-edge peak. This peak is usually about ten times lower in intensity compared to the band-edge one and has similar non-symmetric shape [10]. The peark is either directly generated by the recombination of the carriers through the band gap with assistance of two phonons or is a result of a Raman Stokes shift of the band-edge emission. In both cases two phonons are involved in this process. Measurements on float zone silicon at 80 K show that a third peak with intensity one hundred times lower than that for band edge emission can be detected and ascribed to a three phonon assisted process. This third peak lies very close to the position of D4 line and at high temperatures, where the peaks are broadened, it can not be spectrally resolved from D4.

At position D marked on the map (Fig. 5), the intensity ratio of the two-phonons assisted radiation of the band-edge radiation is about 2–3 times higher compared to all other positions (Fig. 6, *a*). Fig. 6, *b* shows the position of this peak compared with that usually observed. It is seen that the peak is shifted to higher energies and lies closer to the position of the BB emission. If one assumes, that a phonon is responsible for the shift, its energy should be lowered by $\delta \approx 10\,\text{meV}$. Such lowering of the phonon energy corresponds to a tensile stress of several GPa [11].

## 4. Conclusion

We have demonstrated that the room temperature photoluminescence allows to locate dislocation rich areas by their specific D1 line radiation. The band-edge radiation in those areas is subdued because of decreased concentration of minority carriers. The presence of nonradiative routes like enhanced recombination at the surface or at grain boundaries modulates the intensity of both dislocation and band-edge related emissions and is the reason for their spatial correlation on the maps. The temperature dependence of the samples studied is anomalous and can be related to shallow levels in the band gap. The anomalous temperature behaviour gets even stronger after PDG. We consider that the PDG eliminates the nonradiative recombination routes related to deep levels. Thus recombination via shallow levels becomes main mechanism, which limits the band-edge radiative recombination. As a possible candidate responsible for recombination via shallow centres in our *n*-type samples we consider one-dimensional dislocation band below the conduction band. The low temperature maps of dislocation related D3 and D4 lines show correlation in their intensity. The exceptions which occur at some isolated grains can be explained by an additional peak arising from the three-phonon-assisted band-edge recombination. At those places the intensity of the two-phonon-assisted peak is increased and the peak is shifted to a higher energy. We attribute the shift of that peak to a lower energy of the involved phonons, caused by tensile stress.

## References

[1] I. Tarasov, S. Ostanko, C. Haessler, E.U. Reisner. Mater. Sci. Eng. B, **71**, 51 (2000).

[2] Y. Koshka, S. Ostapenko, I. Tarasov, S. McHugo, J.P. Kalejs. Appl. Phys. Lett., **74**, 1555 (1999).

[3] Tz. Arguirov, W. Seifert, M. Kittler, J. Reif. Mater. Sci. Eng. B, **102**, 251 (2003).

[4] V. Higgs, F. Chin, X. Wang. Sol. St. Phenomena, **63**–**64**, 235 (1998).

[5] V. Higgs, F. Chin, X. Wang, J. Mosalski, R. Beanland. J. Phys.: Condens. Matter, **12**, 10 105 (2000).

[6] H. Schlangenotto, H. Maeder, W. Gerlach. Phys. Status Solidi A, **21**, 357 (1974).

[7] H.J. Leamy, L.C. Kimerling, S.D. Ferris. In: *Scanning Electron Microscopy / 1976* (Pt IV) p. 529. [*Proc. Workshop on Microelectronic Device Fabrication and Quality Control with the SEM* (Chicago, IL, 1976) p. 60 616].

[8] V.V. Kveder, E.A. Steinman, H.G. Grimmeiss. Sol. St. Phenomena, **47**–**48**, 419 (1996).

[9] V.V. Kveder, E.A. Steinman, S.A. Shevchenko, H.G. Grimmeiss. Phys. Rev. B, **51**, 10 520 (1995).

[10] M.A. Vouk, E.C. Lightowlers. J. Phys. C: Sol. St. Phys., **10**, 3689 (1977).

[11] I. De Wolf. Semicond. Sci. Technol., **11**, 139 (1996).

*Редактор Л.В. Шаронова*