Origin of the D-Band Photoluminescence in Silicon

K. Weronek[1], *J. Weber*[1], *and R. Buchner*[2]

[1]Max-Planck-Institut für Festkörperforschung, Postfach 80 06 65, W-7000 Stuttgart 80, Fed. Rep. of Germany
[2]Fraunhofer-Institut für Festkörpertechnologie, Paul-Gerhard-Allee 42, W-8000 München 60, Fed. Rep. of Germany

Abstract. The D-band recombination in Si is found to be independent of impurities trapped at dislocations. On the other hand, deliberate contamination of high purity Si samples which contain dislocations results in a drastic reduction of the D-band photoluminescence in the case of Fe and Cu, whereas other impurities, e.g. Ni, lead to no detectable changes in the spectrum.

1. Introduction

Silicon samples containing dislocations exhibit at low temperatures a characteristic photoluminescence (PL) spectrum. Drozdov *et al.* labeled the PL-bands D_1-D_4.[1] The bands are not dependent on the generation of the dislocations. In samples which were plastically deformed, bent or twisted at high temperatures or where precipitates are formed, the D-band PL shows up at the same energy position: D_1:0.812 eV, D_2:0.875 eV, D_3:0.934 eV, D_4:1.00 eV. [2,3] The relative and total intensities, however, of the D-band spectrum depend strongly on the conditions during the generation process of the dislocations. [4-7] Extensive studies were performed to determine the nature of the D-band PL. [4,5] According to the similar optical properties the bands can be grouped into the pairs D_1/D_2 and D_3/D_4. [8]

Luminescence associated with dislocations was observed much earlier in Ge than in Si.[9] Several low-energy bands around 0.5 eV were investigated with respect to dislocation density and transition metal (TM) contamination. [10-13] Two close bands at 0.50 eV and 0.55 eV were detected and several recombination models proposed. Recently, the model of a one-dimensional exciton bound within the dislocation core was suggested and supported by careful temperature dependent PL measurements. [14]

The close relationship of the dislocation induced PL in Si and Ge was established by the investigation of SiGe alloys grown by liquid phase epitaxy on Si substrates.[15] A smooth variation of the D-band energy positions was found with increasing Ge concentration.

Drastic changes in the dislocation related spectra in Si could be generated after a two-stage deformation process: the dislocations are introduced first at elevated temperatures and low stress, in a second step the samples are again

Springer Proceedings in Physics, Vol. 54 **Polycrystalline Semiconductors II**
Editors.: J.H. Werner · H.P. Strunk

deformed at low temperatures and high stress. [8,13,16] With this technique, straight dislocations are formed and the concentration of geometrical kinks is rather small.[17] Only minor changes occur in the electrical properties of dislocations after this treatment, but striking changes were observed in the dislocation related PL-spectra. In Si the D-band PL disappears and two new bands D_5 and D_6 show up in the samples. The fine structure of the D_5 band was correlated with electron-hole recombination at localized centers on separated partial dislocations. After annealing at moderate temperatures (Si T>360°C) the dislocations relax and the new lines merge into the D_4 band and the D_1-D_4 bands dominate the PL spectrum. The two-step deformation experiments suggest that the D_1 and D_2 bands are related to geometrical kinks on the dislocations, whereas the D_3 and D_4 bands result from transitions at deeply bound states in the dislocation core.

The role of impurities in the generation of the D_1-D_4 bands is not clear. Whereas the dislocation density is not modified by low-temperature annealing, the PL-bands broaden and decrease in intensity after long annealing times. [18, 19] No direct influence of specific impurities was found on the D-band spectrum. Doping with oxygen and TMs such as Au produced broadenings and shoulders on the D-bands. Higgs *et al.* [20] observed the D-band PL, however, only after additional TM doping (in particular Cu-doping) in their deformed crystals. Special care was undertaken in these experiments to produce the dislocations by plastic deformation of the samples in a clean quartz system. It was suggested that the D-band PL is associated only with those dislocations that are decorated with TMs.

In this paper, we examine the origin of the D-band PL: whether the bands are due to recombination at the dislocation core or due to recombination at impurites bound to dislocations. We use a clean method to generate the dislocations and by deliberate doping with different TMs we study their influence on the D-band PL.

2. Experimental

A method is adopted that is normally used for annealing of ion-implantation induced damage or recrystallisation of amorphous materials to generate dislocations in high purity float-zone (FZ) silicon wafers. [21,22] Illumination with a focused CW argon laser beam (20 W, TEM00 multi-line mode) melts the surface layer of the Si wafer. The molten zone was scanned over the wafer leading to parallel stripes (separation $\sim 30\mu m$) of recrystallized Si with a high dislocation density ($\sim 10^8 cm^{-2}$). The scanning speed was 10cm/s. Two different wafer temperatures (room temperature (RT) and 500°C) were used to study diffusion processes during the generation of the dislocations. Before the laser treatment, the wafers were cleaned by a standard RCA cleaning procedure.[23] The wafer holder was made out of quartz to avoid direct TM contamination.

The diffusion process used to introduce TMs into Si is very simple, but proved to be the cleanest way. After the laser recrystallization, the samples were cut and heated in a clean quartz tube above a Bunsen burner. A flow of high purity nitrogen gas was blown across the sample during the heat treatment. After the diffusion process, the samples were blown in ethylene glycol at RT to produce a fast quench. For each diffusion a new quartz tube was used. We did not detect any unintentional contamination with TMs when we applied this diffusion method.

Photoluminescence was excited using the 514 nm line of an Ar-ion laser. The samples were mounted in a He-bath cryostat. PL signals were analyzed by an 1-m grating monochromator and detected with a liquid nitrogen cooled Ge-detector. The signals were processed in standard lock-in technique. Data storage, lock-in and monochromator settings were controlled by a desktop computer.

3. Influence of Transition Metals on the D-Band Recombination

Contamination of Si wafers with TMs is one of the major problems in device fabrication. While the bulk concentration of TMs after crystal growth is low ($n<10^{12}cm^{-3}$), the surface contamination due to the polishing can be considerably higher. [24] Before the laser treatment our samples were cleaned (RCA) to ensure a low TM concentration on the surface. All samples exhibit intense D-band PL after laser melting and subsequent epitaxial regrowth. For direct comparison with the diffused samples, the reference samples underwent the same thermal treatment, but without the TM surface contamination. Figure 1 gives the result of the deliberately Cu-doped sample (Fig. 1b,1c) and the reference sample (Fig. 1a). The reference sample clearly shows the D-band PL

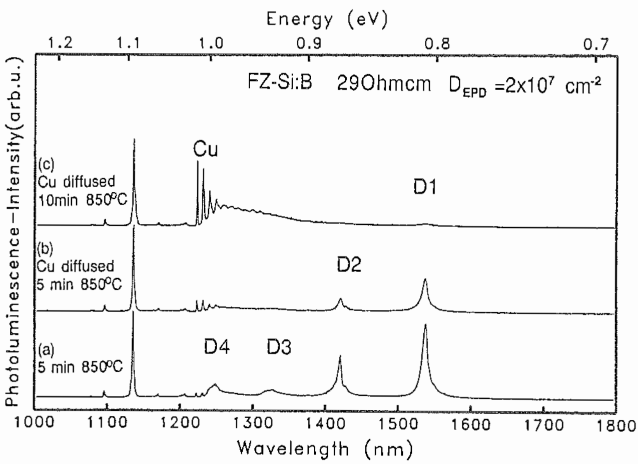

Fig. 1. a) Laser melted and recrystallized Si sample after heat treatment for 5min at 850°C. b) Laser melted and recrystallized Si sample after Cu diffusion for 5min at 850°C. c) Same as b) but Cu diffusion for 10min at 850°C.

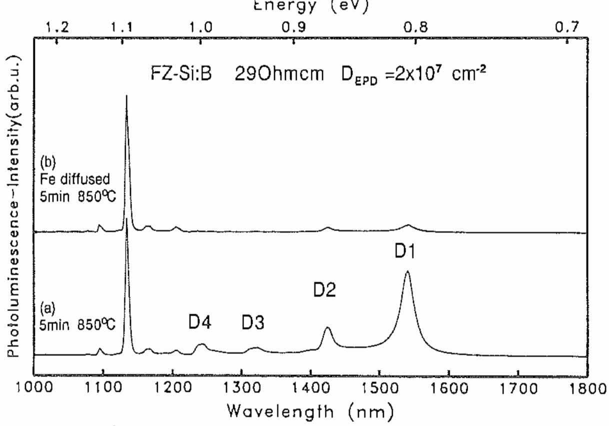

Fig. 2. a) Laser melted and recrystallized Si sample after heat treatment for 5min at 850°C. b) Laser melted and recrystallized Si sample after Fe diffusion for 5min at 850°C.

with D_2/D_1 more intense than D_4/D_3. After Cu diffusion for 5min at 850°C (Fig. 1b) the D-band PL-intensity is reduced and disappears for longer diffusion times (Fig. 1c). The presence of Cu in the samples is confirmed by the known Cu-related PL at 1.22 μm (1.014 eV). [25] Even the reference sample exhibits a small Cu contaminaton, which was typical for one set of wafers and could be related to a bulk contamination of the wafers. Other wafers did not show a Cu-related PL without deliberate Cu doping. Iron doping results in the same quenching of the D-band PL, as is presented in Figure 2. Diffusion for 5min at 850°C nearly extinguishes the D-band PL (Fig. 2b), whereas the reference sample shows an almost identical spectrum compared to the one directly after the recrystallization. Diffusion with other fast diffusing TM elements (e.g. Ni) has no effect on the D-band PL.

From our doping experiments we have to conclude that there is no enhancement due to TM incorporation into the dislocation. On the other hand, Fe and Cu suppress the D-band PL by forming precipitates near the dislocations. Presumably the surrounding strain fields of the precipitates lead to a rearrangement of the electronic levels at the dislocations. We cannot, from these experiments, however, totally rule out that a small TM concentration (e.g., at the kinks of the dislocations) is the origin of the D-band PL. The inherent residual TM contamination in the wafers would be enough for such a decoration. To exclude this possibility we use the effective gettering behavior of dislocations for TMs. By laser melting and regrowth at a sample temperature of 500°C we try to getter TMs out of the bulk of the wafer into the recrystallized zone near the surface. Chemical etching in CP6 and an RCA cleaning process remove the contaminated surface layer. No D-bands are detected in these wafers. Subsequent laser melting and recrystallization at RT of the wafer produces dislocations which show the same intense D-band PL as was detected in the wafer after the first laser treatment. Other gettering mechanisms (back surface roughening, heat treatment of Czochralski grown Si) always gave D-band PL with high intensities.

We therefore exclude the possibility that small concentrations of TMs near dislocations are responsible for the D-band PL. All our experiments suggest that the D-band PL arises from intrinsic states at the dislocations.

4. Summary

We used a clean procedure to generate dislocations in high purity Si wafers and were able to confirm that the D-band PL is due to an e-h recombination at the electronic levels of the dislocations.

Further studies have to clarify what electronic levels in the dislocations are independent of the type of dislocation and give rise to the D-band PL.

We thank H.-J. Queisser for his steady interest in this work. We acknowledge the technical assistance of A. Heidenreich, W. Heinz and W. Krause. This work was supported by the Bundesministerium für Forschung und Technologie under contract NT 2786.

References

[1] N.A. Drozdov, A.A. Patrin, V.D. Tkachev, Pis'ma Zh. Eksp. Teor. Fiz. **23**, 651 (1976) [Sov. Phys. JETP Lett. **23**, 597 (1976)].

[2] D. Gwinner, R. Labusch, Phys. Status Solidi A **65**, K99 (1981).

[3] M. Tajima and Y. Matsushita, Jpn. J. Appl. Phys. **22**, L 589 (1983).

[4] M. Suezawa, Y. Sasaki, Y. Nishina, K. Sumino, Jpn. J. Appl. Phys. **20**, L 537 (1981).

[5] M. Suezawa, K. Sumino, Y. Nishina, Jpn. J. Appl. Phys. **21**, L 518 (1982).

[6] M. Suezawa and K. Sumino, Phys. Status Solidi A **78**, 639 (1983).

[7] M. Suezawa, Y. Sasaki, K. Sumino, Phys. Status Solidi A **79**, 173 (1983).

[8] R. Sauer, J. Weber, J. Stolz, E.R. Weber, K.-H. Küsters, and H. Alexander, Appl. Phys. A **36**, 1 (1985).

[9] R. Newman, Phys. Rev. **105**, 1715 (1957)

[10] A.A. Gippius and V.S. Vavilov, Fiz. Tverd. Tela **4**, 2426 (1962) [Sov. Phys.-Solid State **4**, 1777 (1963)].

[11] Yu.L. Ivanov, Fiz. Tverd. Tela **7**, 629 (1965) [Sov. Phys.-Solid State **7**, 629 (1965)].

[12] E.D. Drigo, L.N. Safronov, and L.S. Smirnov, Fiz. Telk. Poluprovodn. **6**, 1787 (1972) [Sov. Phys.-Semicond. **6**, 1541 (1973)].

[13] A.I. Kolyubakin, Yu.A. Osip'yan, S.A.Shevchenko, and E.A Shteǐnman, Fiz. Tverd. Tela **26**, 677 (1984) [Sov. Phys.-Solid State **26**, 407 (1984)].

[14] Yu.S. Lelikov, Yu.T. Rebane, and Yu.G. Shreter, *Intl. Symp. on Struct. Prop. Disl. Semicond.*, Inst. Phys. Conf. Ser. No. 104, p. 119 (Oxford, 1989)

[15] J. Weber and M.I. Alonso, *Proc. ICSTDS*, Yokoma, September 1989.

[16] R. Sauer, Ch. Kisielowski-Kemmerich, and H. Alexander, Phys. Rev. Lett. **57**, 1472 (1986).

[17] K. Wessel, H. Alexander, Phil. Mag. **35**, 1523 (1977).

[18] Yu. A. Osip'yan, A.M. Rtishchev, and E.A Shteǐnman, Fiz. Tverd. Tela **26**, 1772 (1986) [Sov. Phys.-Solid State **26**, 1072 (1986)].

[19] A.N. Izotov, Yu. A. Osip'yan, and E.A Shteǐnman, Fiz. Tverd. Tela **28**, 1172 (1986) [Sov. Phys.-Solid State **28**, 655 (1986)].

[20] V. Higgs, E.C. Lightowlers, G. Davies, F. Schäffler and E. Kaspar, Semicond. Sci. Techn. **4**, 593-598 (1989)

[21] R.H. Uebbing, P. Wagner, H. Baumgart, and H.-J. Queisser, Appl. Phys. Lett. **37**, 1078 (1980).

[22] R. Buchner, K. Haberger, and B. Hu: In *Polycrystalline Semiconductors*, ed. by J. H. Werner, H.J. Möller, and H.P. Strunk, Springer Proc. in Physics, Vol. 35 (Springer, Berlin, Heidelberg, 1989) p. 289.

[23] W. Kern and D. Puotinen, RCA Rev. **31**, 187 (1970).

[24] K. Graff, Mat. Sci. Eng. **B4**, 63 (1989).

[25] J. Weber, H. Bauch, and R. Sauer, Phys. Rev. B **25**, 7688 (1982).