

The recombination statistics of the visible photoluminescence of silicon nanocrystals

J. Diener[†], D. I. Kovalev^{°*}, S. D. Ganichev^{*}, G. Polisski[°] and F. Koch[°]

[†] *Department of Physics, University of California, Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720-7300, USA*

[°] *Technische Universität München, Physik-Department E16, D-85747 Garching, Germany*

^{*} *A. F. Ioffe Physicotechnical Institute, Russian Academy of the Sciences, St. Petersburg, 194021, Russia*

ABSTRACT

A pulsed, high-power TEA CO₂ laser with lines in the region from 9.2 to 10.6 μm has been used to irradiate luminescent porous Si samples. The IR laser pulses heat the sample on a time scale much shorter than the PL decay time which is at 300 K for the PL at 1.65 eV in the order of tenth of μs . One IR pulse serves to increase the temperature of the luminescing particles in ~ 2 μs up to 100°C. This increase of temperature leads to an efficient reduction of the photoluminescence (PL) intensity. However, the PL decay times are almost not affected by the heating pulse. Based on these measurements a picture of the recombination statistics that takes account of the granular nature of the material is developed.

INTRODUCTION

Since the discovery of visible photoluminescence (PL) of porous silicon at room temperature in 1990 by Canham [1] several models were proposed to explain this phenomenon. While the quantum-size nature of the radiative recombination processes is now generally accepted and is becoming predominant in the literature, a wide variety of models is applied to describe the time evolution of the PL under pulsed optical excitation [2,3,4,5,6]. At low temperatures, the temperature dependence of the PL intensity and the corresponding change in lifetimes has been explained by Calcott et al. [7] as a result of singlet-triplet splitting of the excitonic state. The variation of lifetimes and quantum yield versus temperature in the high temperature region has been reported by Vial et al.. A model taking into account both, radiative and nonradiative recombination has been proposed. We will discuss an appropriate description of the recombination statistics of the slow-red PL band at room temperature, taking into account the granular structure of the material. The general behavior of the PL lifetimes as a function of different measurement parameters is well documented. At room temperature the PL lifetimes depend strongly on the detection energy, ranging from several μs at 2.2 eV to tenth of μs at 1.6 eV. An increase of the sample temperature leads to faster luminescence lifetimes and to a decrease of the PL intensity. Several experiments were performed to clarify the physical processes responsible for the time evolution of the PL. The importance of Auger-recombination, leading to efficient damping of the PL was pointed out [8]. While this process with nonradiative lifetimes on the order of ns is important for the initial stage of the decay of the photoexcited carriers, the longtime component could only be addressed by conventional methods such as heating, oxidizing or changing the porosity of the samples.

In this work we show that an IR laser source is able to heat the Si nanocrystals on a time scale much shorter than the PL decay time. Due to the strong absorption of the IR radiation by

the Si-O₂ bonds in the overlayer on the Si nanocrystals, one IR pulse serves to heat the luminescing particles on a time scale of ~2 μs up to 100°C. This gives an opportunity to investigate the temperature dependence of the slow component of the PL decay directly. Here, we focus our attention on the relation of lifetimes and intensity of the PL. The measurements show that a relation of the type:

$$\eta = \frac{\tau_{nr}}{\tau_r + \tau_{nr}}$$

(where τ_r and τ_{nr} are the radiative and nonradiative lifetimes and η is the quantum efficiency) cannot be applied at room temperatures for the red PL band. The observed decay time is argued to be to a large extent the radiative time.

SAMPLES AND EXPERIMENTAL SETUP

The samples used in this work are prepared from (100) p-type B-doped, 1 Ωcm Si wafers. Before anodisation an ohmic back contact is provided by B implantation. Anodisation is carried out in a 1:1 vol. mixture of ethanol:HF (49% in water). The etching current density is 30 mA/cm². The typical sample thickness is in the range of 2 μm. Following anodisation the samples are removed from the cell, washed with propanol and left to dry under ambient conditions. The freshly prepared samples have very weak luminescence. Thereafter they are aged for several weeks before the measurements in order to form a native oxide [9]. Free-standing samples are produced in a similar manner. After the etching procedure, the PS layers are detached from the substrate by an electropolishing step [10] with a current density of 500 mA/cm². The free-standing samples are removed from the etching cell, rinsed with ethanol and dried in CO₂ gas ambient.

A TEA CO₂ laser, tunable in the range from 9.2 μm to 10.8 μm (1087-926 cm⁻¹) is used as IR radiation source. Maximum radiation intensities used are 6 MW/cm², with a pulse duration of 150 ns. The laser light is passed through a thick Ge window, in order to reject visible and near IR light. Calibrated CaF₂ attenuators are used to vary the intensity of the IR light. The intensity of the incident radiation is measured using a fast photon drag detector. The PL is excited with a pulsed N₂-laser (3.67 eV). Both lasers (UV and the IR) are synchronized using a delay generator. The luminescence is detected with a fast photomultiplier and the PL kinetics are recorded with a storage oscilloscope. Spectral resolution is achieved using a 22cm Spex monochromator. To calibrate the temperature of the sample the beam of a HeNe-laser is traversed through freestanding PS layers. The change in the transmission following one IR pulse is monitored and the temperature calibrated according to the values obtained for conventional DC heating of the same specimen. The experimental arrangement is described in details elsewhere [11].

EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 1 shows the temperature of a PS sample following an IR pulse (1076 cm⁻¹, 2 MW/cm²) over a wide time scale. Starting from room temperature the sample temperature is increased to ~70°C within a time scale of ~2 μs. Afterwards the temperature stays constant for a long time. It takes about 1 sec. until the specimen completely cools down to room temperature. The temperature increase versus the applied IR intensity has an apparent linear slope (see inset Fig. 1).

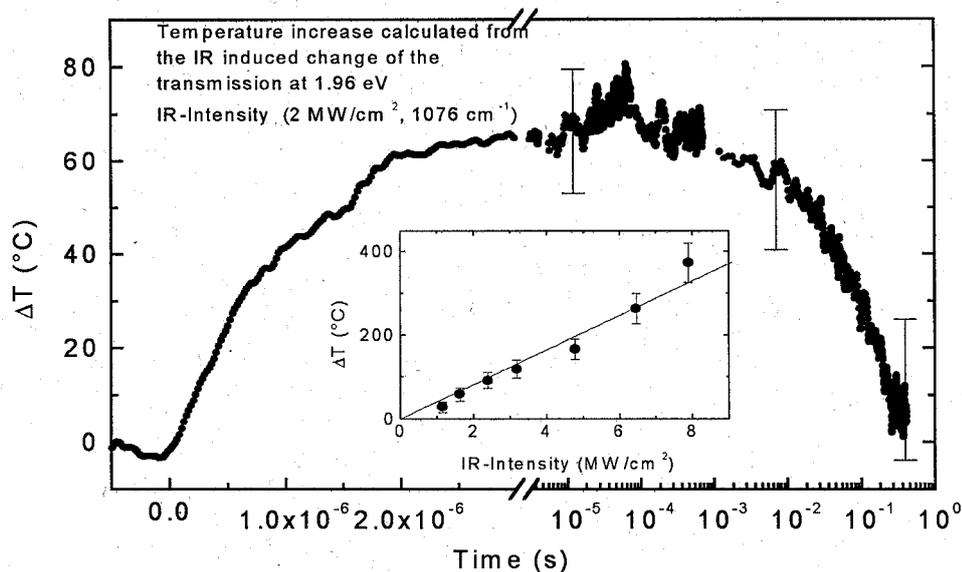


Fig. 1: The increase of the sample temperature caused by one IR pulse (2 MW/cm^2 , 1076 cm^{-1}), calculated from the induced change in transmission at 1.96 eV . The inset shows the temperature increase as a function of the incident IR laser intensity.

As the IR wavelength is tuned to resonance with the Si-O absorption band, known from FTIR measurements [12], the main part of the IR energy is absorbed on the surface of the Si nanocrystallites. This gives an opportunity to heat these crystallites in a very short time scale in spite of the big heat capacity of the whole structure, obvious from the long cooling time. Comparing the temperature of the layer measured using the change in the transmission of a HeNe laser beam (mainly governed by the fraction of big crystallites) and the characteristic lifetimes of the photoexcited PL (contribution of the fraction of small crystallites) lead to similar temperatures. This indicates the homogeneity of the heating and thermal equilibrium of the sample after the IR heating step. Two points must be mentioned. First, the heating time is significantly faster than the lifetime of the PL in the red spectral region. Second, following the temperature increase, the sample remains hot in a much longer time scale than the PL decay. This is comparable to the condition achieved with conventional heating and allows to neglect cooling of the sample during the PL decay. This provides an opportunity to compare the measured lifetimes and intensities for both conditions, pulsed IR heating and conventional DC heating. The time evolution of the PL at room temperature detected at 1.65 eV and excited at 3.67 eV is shown in Fig. 2 as the dashed line. One IR pulse (1076 cm^{-1} , 3 MW/cm^2) delayed on $10 \mu\text{s}$ with respect to the UV excitation leads to a drastic change of the time behavior. Before the IR pulse the decay is identical to that of the unperturbed case (dashed line). Simultaneously with the IR pulse a fast drop of the PL is observed, with a decay time of $\sim 2.5 \mu\text{s}$. After this drop a slow time evolution is detected. The corresponding lifetime is only slightly faster than seen for the unperturbed case. Both, the lifetimes of the PL and the position of the PL maximum are temperature dependent. To clarify the point whether the observed behavior is caused by a shift of the PL spectrum to lower energies the PL kinetic was measured at different detection energies. The PL spectrum is afterwards constructed from the time evolution of the PL at different energies and normalized to the sensitivity of the detection system. The result of this measurement is shown in Fig. 3.

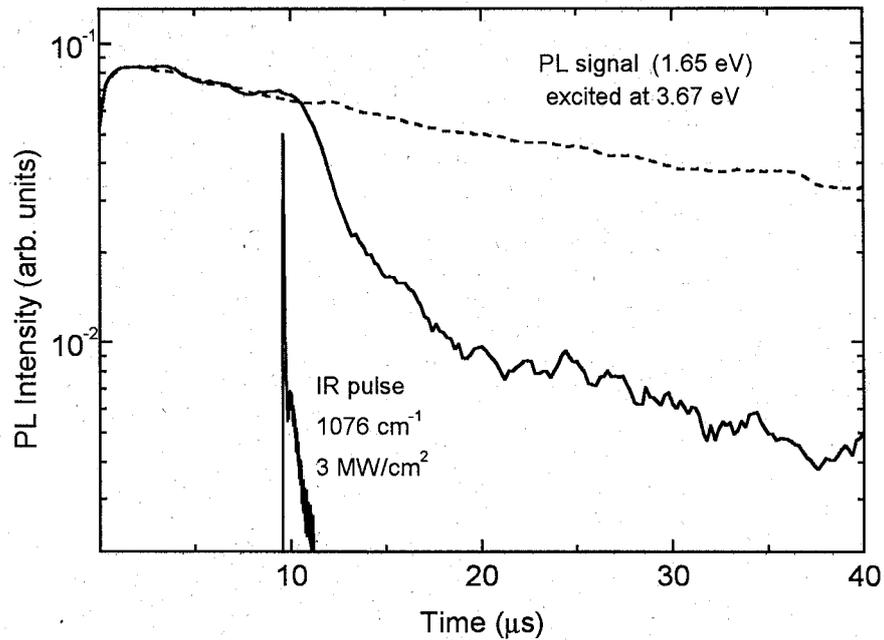


Fig. 2: The time evolution of the PL excited at 3.67 eV and detected at 1.65 eV (dashed line). The solid line shows the dynamic of the PL when an IR pulse (1076 cm^{-1} , 3 MW/cm^2) is applied. The IR pulse is shown for comparison.

Following one IR pulse the intensity of the whole PL spectrum is decreased. Only a small redshift of the PL maximum of $\sim 100 \text{ meV}$ is observed. We now turn to discuss the observed results. The mean lifetime τ_{eff} of the PL decay in bulk semiconductors described by:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}} \quad (1)$$

where τ_r and τ_{nr} are the radiative and nonradiative lifetimes respectively. Both are temperature dependent. Within the same model the quantum efficiency η is:

$$\eta = \frac{\tau_{nr}}{\tau_r + \tau_{nr}} \quad (2)$$

This analysis cannot explain the observed drop of the PL intensity after the heat pulse by more than one order of magnitude, while the lifetime of the PL after the IR pulse is only slightly affected (Fig. 2). We would like to mention that a similar behavior is also observed in measurements of the PL decay time for different excitation intensities [8]. At 300 K the long time component of the lifetimes is constant, in spite of the observed saturation behavior of the PL. We explain the observed response by a simple approach, which regards PS as a granular material consisting of luminescing and dark crystallites. The first are crystallites which do not contain a nonradiative center while the second part has at least one. In addition we assume that $\tau_{nr} \ll \tau_r$ and that the transfer of excitation between crystallites is not efficient at room temperatures.

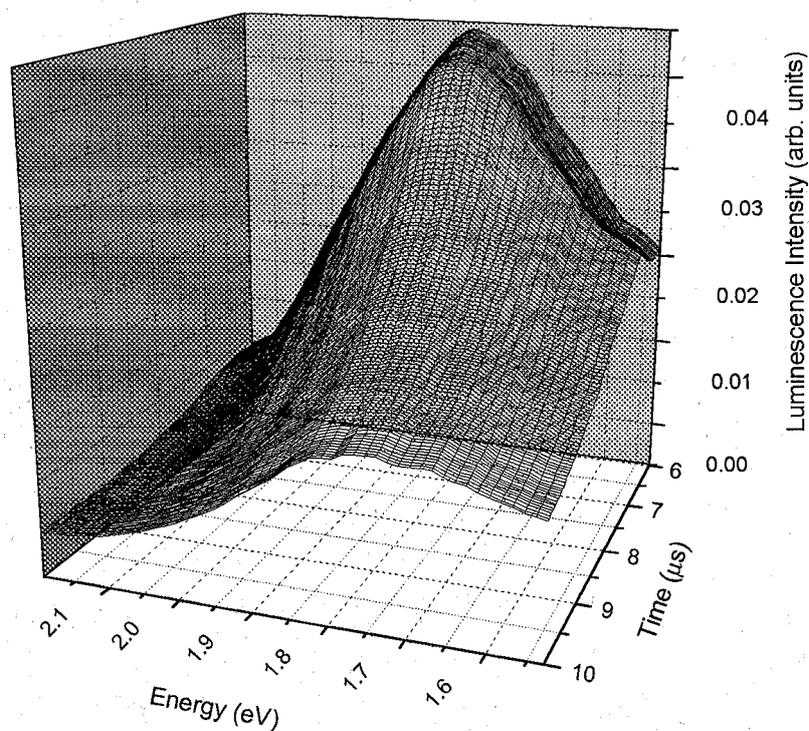


Fig. 3: The time evolution of the PL spectrum excited at 3.67 eV. An IR pulse (1076 cm^{-1} , 3 MW/cm^2) is applied within the PL decay $\sim 7\text{ }\mu\text{s}$ after the UV excitation.

The probability for photoexcited electron-hole pairs to recombine radiatively in dark crystallites is nearly zero. In a similar manner electron-hole pairs recombine radiatively in luminescing crystallites. Therefore the PL intensity (or η , respectively) is determined by the ratio of these two types of crystallites. Thus the PL intensity is a function of the concentration of nonradiative defects and the observed lifetime is τ_r . In order to explain the observed drop in intensity it is straight forward to assume the creation of additional nonradiative centers by the IR pulse. This is supported by the observed, spectral independent, quenching of the whole PL spectrum (Fig. 3). On the other hand the creation of metastable defects by pulsed IR radiation has already been proposed in [13]. As a result, the IR excitation leads to an increase of the number of dark crystallites by creation of additional dangling bonds or other nonradiative centers. This leads to a decrease in the intensity of the emitted light, but only to a slight change in the radiative lifetime which corresponds now to the increased sample temperature. To be able to resolve such a fast drop, the nonradiative recombination time for the dark crystallites has to be at least as fast as the observed $\sim 2.5\text{ }\mu\text{s}$ of the intensity drop. However, one of the basic assumption is that the transfer of excitation between crystallites is not efficient. This seems reasonable at room temperatures, taking into account the poor conductivity of the sample (a correlation between conductivity and PL intensity has been reported [14]). For temperatures above 370 K it was shown [2] that the temperature dependence of lifetimes and quantum efficiency behave in similar manner, following (1) and (2). This is the case when the electron-hole pairs are no longer localized in specific crystallites and have a finite probability to reach nonradiative centers. Obviously this is the limit of our assumption.

The last point to be addressed is the small redshift of the PL after the heat pulse (Fig. 3). Two effects could be accounted for this shift. On the one hand, the "bandgap" of PS is temperature dependent. It decreases ~ 24 meV from 300 K to 400 K [11]. Conventional heating results in a red shift of the PL band as well. In addition under pulsed UV excitation the same behavior could be seen with increasing delay time between excitation and detection. This is caused by the energy dependence of the lifetimes. The time resolved PL spectrum in the first few μ s is usually governed by the faster decaying high energy part of the PL spectrum ~ 2 eV [4]. As a result of the relatively long delay between the UV and the heat pulse, the measurements only address the spectral region with long lifetimes. This was performed in order to ensure that the heating time is short compared to the decay of the PL. On the investigated time scale the PL maximum shifts in the unperturbed case only slightly. This proves that the observed redshift is temperature induced.

To summarize, we have shown that one IR laser pulse heats the PS sample on a time scale much shorter than the PL decay time at the low energy part of the PL. The time, temperature and spectral resolved measurements show that the PL decay time at roomtemperature is mainly the radiative one. Contrary to the recombination statistics at very high temperatures PS behaves at room temperature like a granular system of luminescing and dark crystallites. This indicates that the photoexcited carriers are still to a large extent localized in these crystallites.

Acknowledgments

J. Diener and D. I. Kovalev thank the Alexander von Humboldt Foundation for a research fellowship.

References

- [1] L.T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
- [2] J.C. Vial, A. Bsiesy, F. Gaspard, R. Herino, M. Ligeon, F. Muller, R. Romestain, and R. M. Macfarlane, Phys. Rev. B **45**, 1417 (1992).
- [3] I. Mihalcescu, J. C. Vial, and R. Romestain, J. Appl. Phys. **80**, 2404 (1996).
- [4] A.V. Andrianov, D.I. Kovalev, V.B. Shuman, I.B. Yaroshetskii, Semiconductors **27**, 71 (1993).
- [5] S. Finkbeiner, J. Weber, M. Rosenbauer, and M. Stutzmann, J. Luminescence **57**, 231 (1993).
- [6] S.N. Kuznetsov, V.B. Piculev, Yu. E. Gardin, I.V. Klimov, and V.A. Gurtov, Phys. Rev. B **51**, 1601 (1995).
- [7] P.D.J. Calcott, K.J. Nash, L.T. Canham, M.J. Kane, and D. Brumhead, J. Luminescence **57**, 257 (1993).
- [8] C. Delerue, M. Lanoo, G. Allan, E. Martin, I. Mihalcescu, J.C. Vial, R. Romestain, F. Muller, and A. Bsiesy, Phys. Rev. Lett. **75**, 2228 (1995).
- [9] T. Maruyama and S. Ohtani, Appl. Phys. Lett. **65**, 1346 (1994).
- [10] R.L. Smith, S.D. Collins, J. Appl. Phys. **71**, R1 (1992).
- [11] D. Kovalev, G. Polisski, M. Ben-Chorin, J. Diener and F. Koch, J. Appl. Phys. **80**, 5978 (1996).
- [12] H.D. Fuchs, M. Stutzmann, M.S. Brandt, M. Rosenbauer and J. Weber, Phys. Rev. B **48**, 8172 (1993).
- [13] J. Diener, S. Ganichev, M. Ben-Chorin, D. Kovalev, V. Petrova-Koch, and F. Koch in Microcrystalline and nanocrystalline semiconductors, edited by Ed. L. Brus, R. W. Collins, M. Hirose und F. Koch (Mater. Res. Soc. Proc. **358**, Boston 1994) pp. 501-506.
- [14] M. Ben-Chorin und A. Kux, Appl. Phys. Lett. **64**, 481 (1994).