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Experimental evidence of electron capture and emission from trap levels in Cz silicon

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Up to now the existence of trap levels – defect levels in the forbidden band gap which temporary trap minority charge carriers – in Cz silicon was controversially discussed. We directly monitor the transient dynamics of the free electron density in the conduction band by the means of a time correlated single photon counting of photoluminescence. A variation of the experimental conditions reveals both a decrease of the electron density on a timescale of microseconds, which is not governed by recombination and an apparent generation of electrons on a scale of up to multiple seconds. We discuss that the transient dynamics may be excellently described by trap levels, providing strong evidence for their existence.

1 Introduction In 1955, Hornbeck and Haynes isolated energy levels of defects in Czochralski grown (Cz) silicon which have large, unexpected impact on the measurable conductivity of a sample. From their investigations on the light pulse stimulated transient photoconductance (PC) decay they concluded the existence of electron trap levels in p-type Si [1] and hole trap levels in n-type Si [2]. By our definition, trap levels (or traps) are defects that feature a strong asymmetry in electron and hole capture, and the property that a minority carrier captured by the trap is preferentially re-emitted into the respective band rather than annihilated by capture of a majority carrier by the same defect. Their PC decay curves were confirmed by other authors [3–5] and the postulated trap levels were discussed later in the context of the apparently high lifetimes at low charge carrier densities in PC-based lifetime techniques [6–8] – a typical measurement is shown here in Fig. 1 – and free-carrier emission experiments [9, 10]. Furthermore, traps may be investigated using lifetime spectroscopy [7], DLTS [11, 12] and noise spectroscopy [13], where a trap manifests in random telegraph noise [14].

Up to now, however, the existence of trap levels is still controversially discussed, as there are other possible explanations for the behaviour, in particular of the PC measurements, which are not covered by standard Shockley-Read-Hall statistics [15, 16]: Bail, Cousins and Neuhaus have pointed out that the presence of a (minority carrier) depletion region, given by a p/n-junction or a dielectric surface coating, also may cause the peculiarities in PC measurements [17–19]. Their experimental and theoretical analyses of a depletion region modulation (DRM) during a PC measurement showed that DRM may explain the apparently high lifetimes at small injection levels.

Recently, time correlated single photon counting of the photoluminescence (PL) emission of silicon was shown to allow assessment of the dynamic behaviour of the free charge carrier density in silicon on a large dynamic range from nanoseconds to seconds [20] and down to very low injection densities of $\sim 10^6\,\mathrm{cm}^{-3}$ [21]. With this approach a behaviour of the electron lifetime resembling the 'trapping effect' occurring with lifetime curves from PC measurements was observed, too. In [21, 22] the authors argued that in contrast to PC measurements, the DRM effect does not play a role for PL measurements.

In this contribution, we present a set of purely PL-based measurements at varying experimental conditions to strengthen the assumption that trap levels exist by direct observation of electron capture and emission on

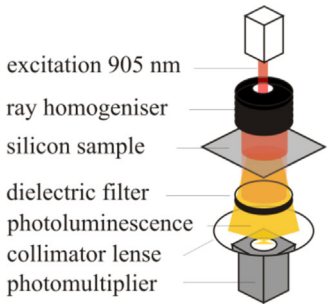

Figure 1 Experimental setup.

time scales which are well separated from the recombination lifetime.

Aside from the importance of the existence of trap levels for the measurement metrology, a detailed knowledge of the properties of trap levels may give access to other material parameters or defects in a unique way. *A priori* it is possible that the material defect, which induces the trap level, also causes recombination. While recent studies reveal an influence of dislocations [7, 9, 10], oxygen [3, 11, 23], and thermal donors [3], no defect has been unambiguously correlated to the trap levels at present.

2 Experimental The experimental setup is depicted in Fig. 1. Parallel excitation of the silicon sample (grey) is realised with a pulsed laser diode with an emission peak wavelength of 905 nm. The laser spot is homogenised to an area of 19 mm in diameter. Laser pulses of about 1 ns duration are used for excitation. Intense pulses are obtained by running several pulses with 80 MHz pulse repetition rate. In the following, up to 100 pulses (within 1.25 µs) are treated as a single, effective pulse, and the pulse distance denotes the distance between effective pulses. The laser intensity is determined with a low power-sensitive photo diode. The surface opposing the detector is illuminated, that is, the sample is measured in transmission. The emitted PL photons are detected with an ultra-low noise (<4 cps) InP photomultiplier tube (PMT) operating in Geiger mode. A 1000 nm OD4 dielectric long pass filter is used for laser attenuation. A collimator lens is placed in front of the PMT to ensure a homogeneous detection probability within an area of 17 mm in diameter, outside of which the detection probability rapidly drops within 1 mm. Time resolution is obtained using the time correlated single photon counting technique [24]. With the used components a temporal resolution of well below 1 ns is obtained. To resolve the fast decay constants involved in trapping we use a time discretisation bin width of 160 ns.

3 Sample preparation The sample was prepared from an industrial Cz boron doped six inch silicon wafer. After wet-chemical etching of the mechanically damaged region arising from wafer sawing, the wafer was subjected to a $POCl_3$ diffusion step at 850 °C to getter fast-diffusing contaminations. The resulting phosphor-silicate glass and diffused region were etched off. A laser was used to cut the square sample with 5 cm side length from the wafer. After wet-chemical cleaning, 10 nm of Al_2O_3 were deposited on both sides of the wafer via plasma-assisted atomic layer deposition at 230 °C in an Oxford Instruments OpAL reactor. To enhance the surface passivation quality and for additional mechanical protection, a 70 nm thick layer of a-SiN_x was deposited on top. The surface passivation was thermally activated by annealing at 425 °C for 20 min. The passivation is identical to the passivation used for the FZ sample in [25], where no PL decay could be observed subsequent to an excitation pulse (i.e., surface recombination is negligible).

The wafer doping concentration was determined to $N_A = (7.0 \pm 0.1) \times 10^{15}\,cm^{-3}$ via resistivity measurements. The sample thickness is $W = (166 \pm 5)$ µm. FTIR measurements according to DIN 50438–1 were performed on sister samples to determine the concentration of interstitial oxygen and resulted in a concentration of interstitial oxygen of $(5.8 \pm 0.2) \times 10^{17}\,cm^{-3}$. Due to the presence of both boron and oxygen, the sample is prone to light-induced degradation as a result of BO complex formation [26]. Comparison of the recombination lifetime τ_r directly after dark annealing the sample at 200 °C for 10 min and after extended light soaking confirmed a strong limitation of τ_r through BO defects in the wafer bulk. A measured $\tau_r > 1.4$ ms throughout the range of Δn of 10^{14}–$10^{15}\,cm^{-3}$ in the annealed state (i.e., without limitation due to BO defects) demonstrate the excellent passivation quality of the used passivation layer and the effectiveness of the gettering step. After activating the BO defects, the injection-dependent recombination lifetime shown in Fig. 2 was measured using steady state PL calibrated by modulated PL [27] and transient PC. In the PC lifetime curve, the apparently high lifetime at low charge carrier densities is the very artefact typically discussed with respect to trapping or DRM. The low-injection lifetime is about 39 µs. The comparably low lifetime in relation to the lifetime of the annealed sample ensures that the recombination lifetime with activated BO defects is limited by the silicon bulk only. In the following, the sample was always measured in this state.

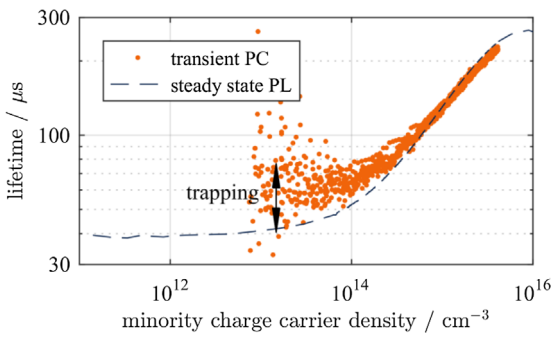

Figure 2 Minority charge carrier lifetime measured with transient PC and steady state PL.

4 Electron capture and emission We record PL transients $I_{pl}(t)$ for varied excitation fluxes J_{ph} between 8.75×10^7 and 2.77×10^{11} photons per pulse and for varied pulse distances from $t_P = 0.2$ to 2000 ms. Except of these two variations, all other experimental parameters like integration time and time bin width were identical for all measurements. From the photon flux, the reflectivity R and thickness W of the sample, the laser spot radius d and absorption coefficient $\alpha = 290\,\mathrm{cm}^{-1}$ we deduce the depth averaged, initial free electron density according to

$$n_{e,ini} = \frac{J_{ph}(1-R)}{W\pi d^2}. \quad (1)$$

Even the highest injection density of $5.9 \times 10^{13}\,\mathrm{cm}^{-3}$ is more than two orders of magnitude lower than the doping density N_A of the investigated sample, hence, we may directly infer the free electron density n_e (please note that in the presence of traps the free electron and hole density must not be equal) from the measured PL intensity $I_{pl} \propto n_e N_A$ by normalisation of the initial PL intensity $I_{pl}(t=0)$ to the calculated, injected free electron density $n_{e,inj}$:

$$n_e(t) = n_{e,ini}\frac{I_{pl}(t)}{I_{pl}(t=0)} \quad (2)$$

In Fig. 3 the decays of the free electron density for different excitation fluxes are shown. The pulse distance is 2 ms. For all transients, the free electron density drops two orders of magnitude from its initial value. Thus, the residual free electron density from the preceding decay period is negligible. The dashed line indicates the transient decay $n_{e,ini} \times \exp(-t/\tau)$ which would be expected when assuming the (injection dependent) lifetime $\tau_r(n_e)$ measured with steady state PL (cf. Fig. 2) and the injection level $n_{e,ini} = 5.9 \times 10^{13}\,\mathrm{cm}^{-3}$. The deviation of the measured transients with an excitation flux above 8.75×10^9 photons from this exponential decay being within the experimental error of the steady state lifetime determination, the initial decay of free electron density can be attributed to recombination for these transients. For low excitation fluxes, the initial decay is much faster than the recombination lifetime. For long decay times (with varying onset) there is a tail which exhibits a decay constant exceeding the recombination lifetime by far. In the following we show that these effects are in accordance with an electron trapping mechanism: traps with an energy level above the Fermi level are normally empty in thermal equilibrium and exhibit the property that the captured electron has a higher probability to be re-emitted to the conduction band than being annihilated by hole capture from the valence band. Within this model the observed fast initial decay for low excitation fluxes may be attributed to electron capture by such traps (at higher injection densities the traps are saturated) and the long tail can be assumed to arise from electron re-emission into the conduction band.

In order to verify this interpretation we measure the PL decay with varying pulse distance keeping the photon flux per pulse constant. If the pulse distance t_P is comparable to or shorter than the slow decay constant of the PL transient (governed by trap depletion), the trap centres gradually fill with each additional pulse. On the contrary, for long pulse distances, the traps may deplete completely before the next excitation pulse takes place. The transients are shown in Fig. 4 (symbols). The photon flux is 8.75×10^9 photons for all transients (corresponding to the blue curve in Fig. 3). With these precautions, the experimental conditions and the electronic state of the sample – besides trapping related effects – are similar when excitation takes place, irrespective of pulse distance. In particular, any luminescence from the laser, the optical components or the sample surface-related effects (non-ideal passivation), as well as

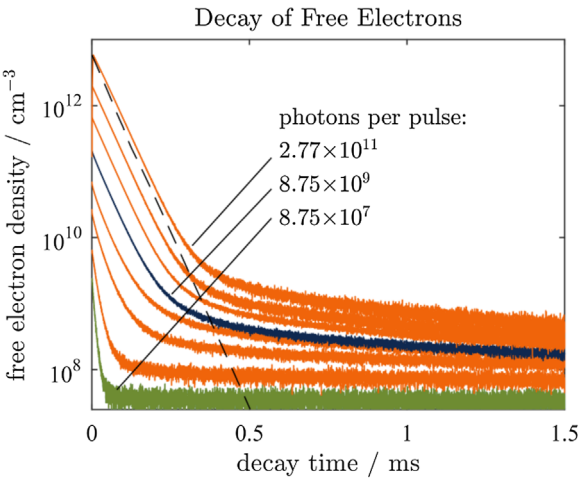

Figure 3 Free electron density decay for varying photon flux of the excitation pulse (pulse distance of 2 ms kept constant). The dashed line shows an exponential decay assuming the excitation of curve 1 and a recombination lifetime measured with steady state PL.

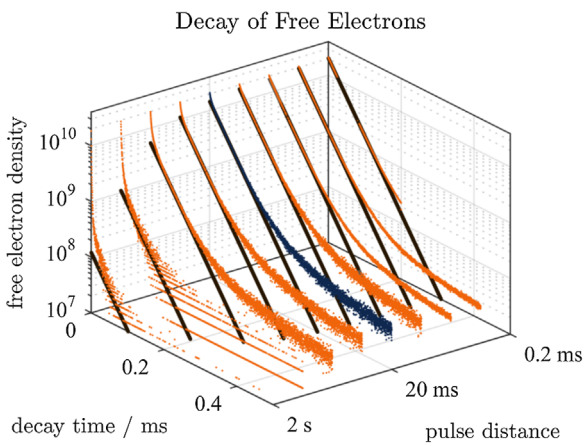

Figure 4 Initial fast decay of the free electron density subsequent to the laser pulse as a function of laser pulse distance. The solid lines depict an exponential fit to the intermediate regime with a lifetime of 39.9 μs (the recombination lifetime).

reabsorption of PL and electron dilution [28] do not change.

For short pulse distances (as used in Fig. 3) an exponential behaviour up to 150 µs is evident before the curve is dominated by electron emission from trap states. The solid lines indicate exponential fits to all decay curves using only one decay constant τ_r for all fits to the regime of the curves in which recombination governs the transient electron dynamics. We obtain a lifetime of $\tau_r = 39.9\,\mu s$, in good accordance with the steady state recombination lifetime at low injection.

For longer pulse distances, an additional fast decay mode occurs, resembling the fast initial decay in Fig. 3 when using low photon fluxes. The fast initial decay in both experiments can be explained by the presence of traps. In the first experiment (Fig. 3), the traps are still mostly filled when excitation takes place (short pulse distance). By lowering the excitation flux the small amount of electrons, which are captured by mostly filled traps, can be resolved. In the second experiment (Fig. 4), sufficiently long pulse distances lead to a complete depletion of initially filled traps before the next pulse takes place and thus, a larger total amount of the generated electrons can be captured. Please note that from the presented decay transients, the capture and emission time constants cannot be extracted directly as we measured the density of the excess electrons n_e. The time constants of capture and emission are, however, related to the density of occupied traps n_t. This manifests in an initial decay time of n_e in Figs. 3 and 4 which depends on the initial trap filling.

Finally, to exclude a measurement artefact, we compare the lowest curve (green) of Fig. 3 run to a measurement with rectangular illumination. The cycle length of 4 ms was chosen to be such that steady state conditions were reached within the illumination period, and the excitation intensity such that a steady state free electron density equal to the pulse injection density of the lowest curve in Fig. 3 is settled ($n_e = 2.4 \times 10^9\,cm^{-3}$), that is, the average occupation $n_e(t = 0)$ of the conduction band when turning off the steady state illumination is identical to $n_e(t = 0)$ when using pulsed excitation. If there were traps, they should be filled within the steady state illumination period. Figure 5 shows the lowest curve of Fig. 3 (solid line) and the decay curve obtained from the measurement with rectangular illumination (red symbols). The dashed line depicts an exponential decay assuming the steady state lifetime. It can be seen that (i) although the electron density is the same, the decay after pulsed excitation is much faster than after steady state illumination initially (which corresponds to the recombination lifetime); and (ii) a higher trap emission is observable after steady state illumination. Both strengthen our hypothesis of observing electron capture (fast decay if sample was in dark) and emission from traps (strong emission when sample was light-soaked).

4 Considerations on the trap density In the perception of electron trapping, the difference at $t = 0\,s$ of the decay transients and the fitted exponentials in Fig. 4 is equal to the electron density which is captured by vacant traps. If the de-trapping follows an exponential behaviour, the density of captured electrons should evolve according to $N_t(1 - \exp(-t/\tau))$, where N_t and τ_g are the trap density and the emission time constant of electrons from the traps. Figure 6 shows the measured amplitude of the initial decay and two fits assuming one or two trap levels. It can be seen that if the trap depletion follows an exponential behaviour two species of traps are necessary to describe the trap depletion in a satisfactory way. In this case we obtain $(\tau_{g,1}, N_{t,1}) = (0.15\,s,\ 1.3 \times 10^{10}\,cm^{-3})$ and $(\tau_{g,2}, N_{t,2}) = (3.6\,ms,\ 4.5 \times 10^9\,cm^{-3})$. The existence of two trap levels was proposed before [2, 21]. Yet, it cannot be excluded that a more complex emission mechanism is responsible for the observed behaviour rather than the existence of two sets of traps.

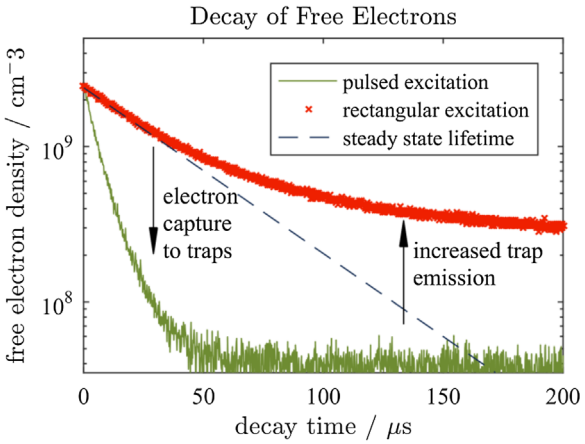

Figure 5 Comparison of free electron density decay after pulsed or rectangular excitation.

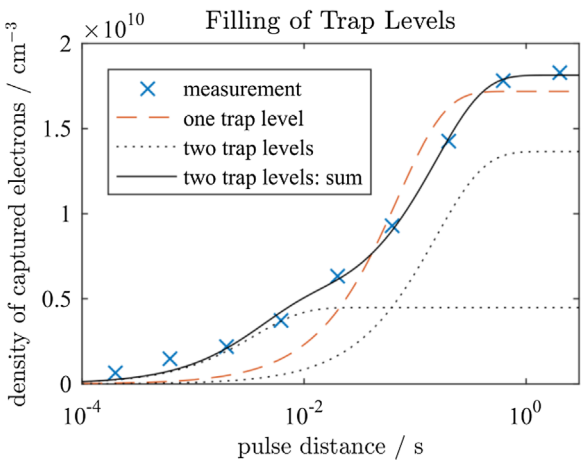

Figure 6 Total amount of electrons captured per volume subsequent to the excitation pulse for different pulse distances (i.e., for different initial trap occupation densities). Two trap levels need to be assumed to obtain a satisfactory description.

5 Conclusions We have shown dynamic photoluminescence investigations on Cz-Si giving evidence for both electron capture and electron emission by an intrinsic mechanism, which may resolve the – up to now – controversial discussion about the existence of traps in their favour. By variation of the experimental conditions a set of measurements is presented which may be interpreted consistently assuming traps in the Si band gap. The experimental approach has the potential to allow for future investigations on the trap density, the capture cross sections for electron and holes, and the trapping and recombination statistics of trap levels.

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