Oxygen-related minority-carrier trapping centers in *p*-type Czochralski silicon

Jan Schmidt,[a] Karsten Bothe, and Rudolf Hezel
Institut für Solarenergieforschung Hameln/Emmerthal (ISFH), Am Ohrberg 1, D-31860 Emmerthal, Germany

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We investigate minority-carrier trapping centers in *p*-type Czochralski (Cz) silicon by means of the quasi-steady-state photoconductance method. Boron and gallium-doped Cz silicon wafers of varying resistivities and oxygen contamination levels are examined. A clear correlation of the trap density with the interstitial oxygen concentration as well as with the boron and the gallium concentration is detected. The experimental data suggest that oxygen is a direct component of the defect complex responsible for the trapping, while the role of boron and gallium is not fully resolved. Using a simple single-level trapping model, we determine the energy level and the trapping/detrapping time constant ratio of the oxygen-related trapping center. [DOI: 10.1063/1.1483908]

The results of photoconductance-based carrier lifetime measurements can be difficult to interpret if trapping centers are present in the semiconductor under investigation.[1] In the past, trapping centers have found to be present in significant concentrations in solar-grade multicrystalline silicon (mc-Si) wafers[2] as well as in polycrystalline Si films[3] and polycrystalline compound semiconductors, such as CdSSe (Ref. 1) and CdTe.[3] For transient photoconductance decay measurements,[4,5] the relatively slow detrapping of minority carriers causes a long tail in the photoconductance decay curve, pretending an extremely high lifetime, which is not the actual recombination lifetime but an *apparent* lifetime.[2] Moreover, traps may also have a significant impact on the steady-state photoconductance of a semiconductor. At excess carrier concentrations comparable to or below the trap density, charge neutrality implies that the presence of minority-carrier traps causes a relative increase in the concentration of *majority* carriers, leading to an increase in the steady-state photoconductance.[2,6] As has been shown recently by Macdonald and Cuevas[2] on mc-Si wafers using the quasi-steady-state photoconductance (QSSPC) technique,[7] this effect can hamper the measurement of recombination lifetimes at low injection levels, where excessively high apparent lifetimes are obtained. They found that it is possible to extract the most relevant trap parameters (trap density N_t, ratio of trapping/detrapping time constants τ_t/τ_d, and trap energy level E_t) from their injection-level dependent QSSPC measurements using a simple theoretical trapping model.[8,2] Hence, the approach of Macdonald and Cuevas[2] can be considered a new and convenient method for investigating minority-carrier traps in semiconductors. Most recently, it was shown that trapping effects can not only be observed in mc-Si material but also in monocrystalline boron-doped Czochralski (Cz) silicon.[9] However, an in-depth analysis of the trapping phenomenon observed in Cz silicon has not been performed so far. In this letter, we apply the QSSPC method in order to systematically examine trapping effects in boron and gallium-doped Cz silicon wafers of different oxygen contamination levels and various dopant concentrations.

All Cz silicon wafers investigated in this study are *p*-type, (100)-oriented and their thickness ranges between 250 and 450 μm. After degreasing the as-sawn wafers, they are damage etched, RCA cleaned and, finally, both wafer surfaces are coated with plasma silicon nitride films at a low temperature (400 °C), providing an outstanding degree of surface passivation.[10] The practical application of the QSSPC technique is described in detail elsewhere.[7] Data analysis is performed using a recently proposed generalized approach.[11] The interstitial oxygen concentration $[O_i]$ of the different Cz materials is determined on shiny-etched wafers using a Bruker Equinox 55 Fourier-transform infrared (FTIR) spectrometer. Peak absorption coefficients are determined according to DIN 50438-1 for the 1107 cm^{-1} band. The IOC88 calibration factor of 3.14×10^{17} cm^{-2} is used to calculate the interstitial oxygen concentrations.[12]

Figure 1 shows the QSSPC apparent lifetime data (symbols) obtained from three boron-doped silicon wafers with different oxygen contamination levels, but similar boron doping levels. In order to investigate the impact of the oxygen concentration, three silicon materials fabricated with different growth techniques are examined. The material grown with the conventional Cz technique (circles) has the highest interstitial oxygen concentration of 7.5×10^{17} cm^{-3}, which is a typical value for Cz-grown silicon. The high oxygen concentration in silicon ingots grown with a conventional Cz single crystal puller is due to the partial dissolution of the silica crucible during the growth process. The oxygen concentration can be strongly reduced by damping the melt flows with magnetic fields.[13] In Fig. 1, the silicon wafer grown with the magnetically confined Czochralski (MCz) technique (squares) has an interstitial oxygen concentration of only 6.5×10^{16} cm^{-3}, which is about one order of magnitude below the oxygen content of the Cz sample. The increase in apparent lifetime τ_a with decreasing apparent ex-

[a]Electronic mail: j.schmidt@isfh.de

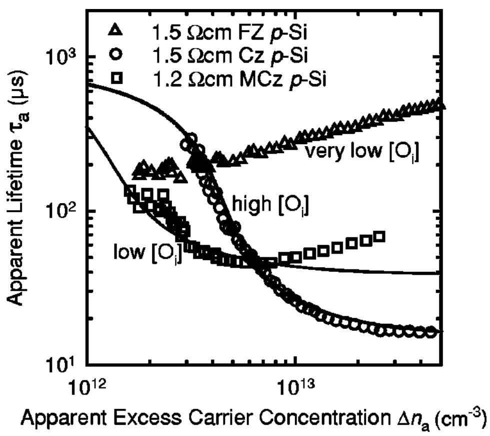

FIG. 1. Measured apparent lifetime τ_a as a function of the apparent excess carrier concentration Δn_a (symbols) for three silicon materials with different interstitial oxygen concentrations. The lines show the fitted trapping model (parameters see Table I). $[O_i]=7.5\times10^{17}$ cm^{-3} for the high-O_i material, $[O_i]=6.5\times10^{16}$ cm^{-3} for the low-O_i sample, and $[O_i]<5\times10^{15}$ cm^{-3} for the very low O_i sample.

cess carrier concentration Δn_a, which is indicative of the presence of minority-carrier traps, can be observed in the Cz and the MCz samples. However, in the case of the MCz material, the increase in τ_a with decreasing Δn_a is shifted toward lower Δn_a values. As will be shown next, the latter result shows that in the low-O_i MCz material, a lower concentration of traps is present than in the high-O_i Cz material. Also included in Fig. 1 is a QSSPC measurement of a float-zone (FZ) silicon wafer (triangles) of very low oxygen concentration ($<5\times10^{15}$ cm^{-3}), which is below the detection limit of our FTIR spectrometer. The very low O_i content is due to the fact that the FZ growth process is a contactless method where the silicon ingot does not come in contact with any crucible. The FZ sample does not show any trapping within the measured injection range.

The lines in Fig. 1 show the fits to the apparent lifetime measurements using the simple single-level trap model applied by Macdonald and Cuevas.[8,2] According to this model, for a given trap concentration N_t and a given ratio of trapping/detrapping time constants τ_t/τ_d, the apparent lifetime is

$$\tau_a=\tau_r\left[1+\frac{N_t}{(\Delta n+N_t\tau_t/\tau_d)}\,\frac{\mu_p}{(\mu_n+\mu_p)}\right], \tag{1}$$

where τ_r is the recombination lifetime, Δn is the excess minority-carrier concentration, and μ_n and μ_p are the electron and hole mobilities. In this study, all measurements are performed under low-level injection conditions and, hence, τ_r is assumed to be constant. Moreover, the measured apparent excess carrier concentration is given via the expression

$$\Delta n_a=\frac{\tau_a}{\tau_r}\Delta n. \tag{2}$$

The trap parameters N_t and τ_t/τ_d can be determined by fitting Eqs. (1) and (2) to the measured QSSPC data. The energy level E_c-E_t of the minority-carrier trap below the conduction band can also be estimated via[8]

$$E_c-E_t=kT\ln\left(\frac{N_c\tau_d}{N_t\tau_t}\right), \tag{3}$$

TABLE I. Values of the trapping model parameters and calculated trap energy levels for different Cz silicon samples.

Sample	Trap density N_t (cm^{-3})	Trap/escape ratio τ_t/τ_d	Trap energy E_c-E_t (eV)
Cz-B, 0.2 Ω cm	5.0×10^{13}	3.0×10^{-4}	0.56
Cz-B, 1.5 Ω cm	1.6×10^{13}	5.0×10^{-3}	0.51
Cz-B, 8.0 Ω cm	2.5×10^{12}	1.0×10^{-2}	0.54
MCz-B, 1.2 Ω cm	4.5×10^{12}	1.0×10^{-2}	0.53
Cz-Ga, 0.4 Ω cm	1.0×10^{13}	2.5×10^{-2}	0.48
Cz-Ga, 1.4 Ω cm	4.0×10^{12}	5.0×10^{-3}	0.55
Cz-Ga, 4.0 Ω cm	2.5×10^{12}	5.0×10^{-3}	0.56

where $N_c=2.86\times10^{19}$ cm^{-3} is the effective density of states in the conduction band.[14]

From the fits to the experimental data shown in Fig. 1, trap concentrations of 1.6×10^{13} and 4.5×10^{12} cm^{-3} are determined for the high-O_i Cz and the low-O_i MCz material, respectively (see Table I). Obviously, there exists a direct correlation between the trap density and the oxygen concentration, suggesting that oxygen is involved in the defect complex acting as minority-carrier trapping center. The fact that FZ silicon with very low O_i content does not show any trapping effect in the investigated injection-level range further supports this conclusion. Due to their dependence on the oxygen concentration, the trapping centers might be related to thermal donors, which is the most famous oxygen-related defect species known in Cz silicon.[15]

Figure 2 shows three apparent lifetime curves (symbols) measured on boron-doped Cz wafers of similar oxygen concentrations $[(7.5\pm0.5)\times10^{17}$ cm$^{-3}]$ but varying doping levels. As can be seen from Fig. 2, the increase in τ_a with decreasing Δn_a shifts toward lower apparent excess carrier concentrations with decreasing doping level, indicating a decreasing trap concentration with decreasing boron concentration. The solid lines in Fig. 2 show the fits to the measured data. The trap concentrations N_t determined from these fits are given in Table I.

Figure 3 shows measured data of N_t versus doping level N_{dop} for various boron (closed circles) and gallium-doped (open circles) Cz wafers with similar oxygen contamination levels $[(7.3\pm0.7)\times10^{17}$ cm$^{-3}]$. Interestingly, we observe

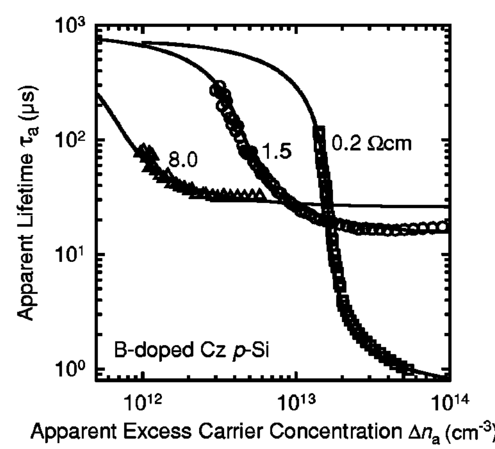

FIG. 2. Measured apparent lifetime τ_a as a function of the apparent excess carrier concentration Δn_a (symbols) for three boron-doped Cz silicon wafers of different doping concentrations. The lines show the fitted trapping model (parameters see Table I). $[O_i]=(7.5\pm0.5)\times10^{17}$ cm^{-3}.

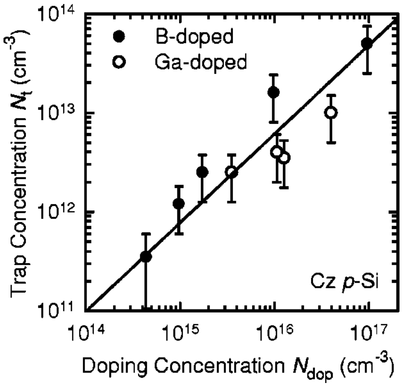

FIG. 3. Trap concentration N_t vs doping concentration N_{dop} for boron- and gallium-doped Cz silicon. The solid line serves as guide to the eyes. $[O_i] = (7.3 \pm 0.7) \times 10^{17}$ cm^{-3}.

the same general trend for the boron and the gallium-doped Cz silicon wafers: the trap concentration increases approximately linearly with the doping level. A similar dependence has been observed recently in intentionally metal-contaminated boron-doped FZ silicon samples.[6] However, this experimental finding does not necessarily imply a direct involvement of boron or gallium in the defect complex responsible for the trapping effect. In literature, it has been reported that a distribution of states within the band gap is capable of explaining a Fermi-level-dependent trap concentration without the direct involvement of the dopant species.[1] However, in our case, the situation seems to be somewhat different as, at similar doping levels, the trap concentrations of the gallium-doped Cz wafers are slightly below that of the boron-doped samples. Hence, the exact role of the acceptor atoms remains unresolved.

In order to exclude the involvement of metallic impurities in the trapping, we investigate the effect of an optimized phosphorus gettering treatment on the trap concentration. This particular treatment has been proven to be capable of effectively removing metallic impurities from the bulk of metal-contaminated silicon wafers.[16] As we do not observe any change in N_t after applying the gettering treatment, it is highly unlikely that the traps investigated in this study are metal-impurity related.

Boron-doped Cz silicon wafers show a degradation of the recombination lifetime when exposed to light. This effect has been attributed to boron–oxygen-related recombination centers, which are activated under illumination.[9,17] As the trapping centers investigated in this study are also correlated with the oxygen and the acceptor concentration, there could exist a certain linkage between the trapping centers and the light-induced recombination centers. In fact, we find a certain increase of the trap density (by about a factor of two) after illuminating the boron-doped Cz wafers for 10 h using a halogen lamp. However, for all samples investigated in this study, the increase in trap density is well below the increase of the concentration of the light-induced recombination centers, indicating that the physical origin of the trapping centers and the light-induced recombination centers in Cz silicon is probably not identical.

Table I summarizes the values of the trapping model parameters for various samples. The trap energies below the conduction band edge are very similar for each sample, indicating that the trapping centers in different samples are of the same physical origin. The average distance of the trap energy level from the conduction band edge is 0.53 ± 0.3 eV, which, at first glance, seems to be quite deep, and as such may be expected to act as a recombination center. The fact that this energy level does behave like a minority-carrier trap could be due to the defect being several times positively charged, causing a strong Coulombic repulsion of majority carriers. Alternatively, the single-level trap model may be an improper simplification. It could, for example, be possible that the observed trapping is in fact due to more than one trap level and that the energy level determined is an average of several trap levels.

In conclusion, characteristic deep-level minority-carrier trapping centers were found to be present in *p*-type Cz-grown silicon. It was shown that these traps are associated with the oxygen contamination level of the Cz material and that oxygen seems to be directly involved in the defect complex responsible for the trapping. Despite the experimental finding that the trap density depends linearly on the boron and the gallium concentration, respectively, a direct involvement of the acceptor atoms could not be established. From our phosphorus gettering experiments we could exclude the involvement of transition metal impurities.

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