Determining the defect parameters of the deep aluminum-related defect center in silicon

Philipp Rosenits,[a] Thomas Roth,[b] and Stefan W. Glunz
Fraunhofer Institute for Solar Energy Systems (ISE) Heidenhofstr. 2, D-79110 Freiburg, Germany

Svetlana Beljakowa
Lehrstuhl für Angewandte Physik (LAP), University of Erlangen-Nürnberg Staudtstr. 7, D-91058 Erlangen, Germany

Through a combined application of two characterization methods, deep-level transient spectroscopy and lifetime spectroscopy, the lifetime-limiting defect level in intentionally aluminum-contaminated Czochralski silicon has been analyzed and a complete set of defect parameters could be obtained. This aluminum-related defect center is found to be located at an energy level of $E_t - E_V = 0.44 \pm 0.02$ eV and exhibits an asymmetric capture cross section, with $\sigma_p = 3.6 \times 10^{-13}$ cm^2 and $\sigma_n = 3.1 \times 10^{-10}$ cm^2 being the hole and electron capture cross sections, respectively. The investigated defect center is attributed to the aluminum-oxygen complex (Al–O). © *2007 American Institute of Physics.* [DOI: 10.1063/1.2789378]

Identifying and investigating the properties of metal impurities in silicon are fundamental tasks in semiconductor physics and device engineering. A precise determination of the defect parameters, i.e., energy levels and capture cross sections, is of both enormous theoretical and technological interest—in particular, with regard to impurity atoms that are relevant in device processing.

Aluminum is one of the elements that is ubiquitous in the processing of many semiconductor devices. In solar cells, for instance, it is usually present in the metal back contact as well as in the back surface field region. The diffusivity D of interstitial aluminum in silicon, $D_{Al} = 2.5 \times 10^{-13}$ cm^2/s at $T = 1000$ °C,[1] is relatively low compared to the diffusivity of transition metals such as iron, $D_{Fe} = 2.2 \times 10^{-6}$ cm^2/s at $T = 1000$ °C.[2] Therefore, Al is not very likely introduced into the wafer bulk by unintentional diffusion during device processing. However, if aluminum is already present as a grown-in impurity in the starting material, it can act as an electrically active defect with detrimental consequences for the charge carrier lifetime.

Aluminum is one of the group III elements in the Periodic Table and thus is in the same group such as boron, gallium, or indium. On the one hand, it features a well-known shallow acceptor level at $E_t - E_V = 0.057$ eV,[3] with E_t and E_V being the energy level of the trap and the valence band edge, respectively, which makes it a potential doping substance for p-type silicon. On the other hand, aluminum and aluminum-related centers are also presumed to exhibit deep energy levels in the silicon band gap as well. However, despite a couple of investigations in the past on aluminum-related defect centers in silicon,[4–11] the results of these investigations disagreed with each other or failed to give an unambiguous set of defect parameters.

The samples investigated in this work were made from boron-doped Czochralski silicon with aluminum given as grown-in impurity into the melt. The p-type doping concentration $N_A = 1.7 \times 10^{15}$ cm^{-3} has been determined via four-point probe measurements. To characterize the aluminum-contaminated samples, deep-level transient spectroscopy (DLTS) measurements[12] have been carried out at two different institutes independently.

In order to prepare the samples for the DLTS investigations, Schottky and Ohmic contacts have been applied on both sides of the wafers. After removing saw damage and standard HF etching the contacts were sputtered onto the silicon wafers in a sputtering chamber at 2×10^{-6} mbar and temperatures not exceeding 55 °C. To achieve a Schottky contact on p-type material, 30 nm titanium and 60 nm aluminum have been deposited on one side of the samples through a mask allowing distinct circular contact areas. The requirement of an Ohmic contact on the other side was met with covering the back side of the wafer entirely with a 60 nm aluminum layer.

The DLTS signal for a given correlation function (sine correlation) measured with a digital DLTS system FT1030 at the University of Erlangen-Nürnberg is depicted in Fig. 1. As can be seen, the signal-to-noise ratio is satisfying, which is mainly due to a relatively high defect concentration of $N_t = 3 \times 10^{-3} N_A$. The peak around 200 K was evaluated for each rate window. In Fig. 2, the resulting Arrhenius plot, a loga-
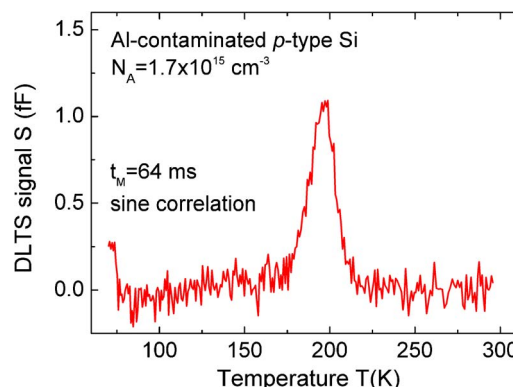

FIG. 1. (Color online) DLTS spectrum of the boron-doped Czochralski silicon sample contaminated with aluminum that was given into the melt during crystal pulling.

[a] Electronic mail: philipp.rosenits@ise.fraunhofer.de
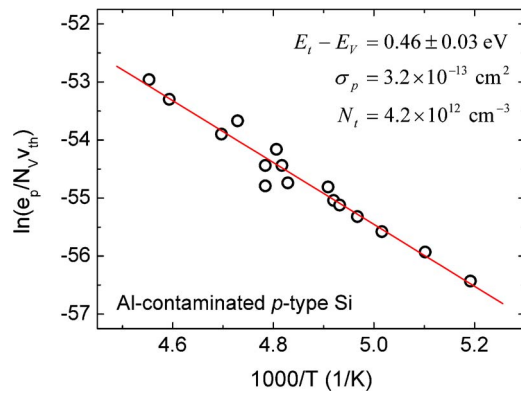[b] Electronic mail: thomas.roth@ise.fraunhofer.de

FIG. 2. (Color online) Arrhenius plot of the aluminum-contaminated sample. In the inset, the extracted defect parameters, i.e., energy level, hole capture cross section, and defect concentration, are shown.
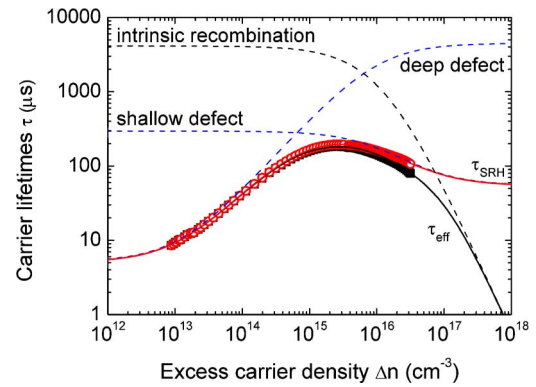

FIG. 3. (Color online) Injection-dependent lifetime measurements by means of QSSPC on the Al-contaminated samples. After correcting the measured effective lifetime τ_{eff} (black, closed squares) with the relevant intrinsic recombination channels (Auger and radiative recombination), a two-defect SRH fit is performed on the corrected τ_{SRH} (red, open circles). Given the energy level $E_t-E_V=0.44$ eV and hole capture cross section $\sigma_p=3.6 \times 10^{-13}$ cm^2 from DLTS measurements, a symmetry factor $k=870$ for the deep defect center has been determined. For the shallow defect center, various parameter sets lead to an equal fit quality, with $E_t-E_V=0.15$ eV and $k=1.3$ depicted exemplarily here.

rithmic plot of the hole emission rate e_p at the temperature where the DLTS signal has its maximum, divided by the effective density of states in the conduction band N_V and the thermal velocity v_{th}, of the different DLTS spectra (for different rate windows) is shown. From these data, an energy depth of $E_t-E_V=0.46\pm0.03$ eV, a majority carrier capture cross section of $\sigma_p=3.2\times10^{-13}$ cm^2 (at $T=200$ K), and a defect density of $N_t=4.2\times10^{12}$ cm^{-3} could be extracted.[13]

DLTS measurements on a sample of the same wafer, performed at the Australian National University (ANU) in Canberra with a lock-in type setup,[14] yielded the defect parameters of $E_t-E_V=0.42\pm0.03$ eV, $\sigma_p=4.0\times10^{-13}$ cm^2, and $N_t=1.9\times10^{11}$ cm^{-3}, which are in good agreement with those presented in Fig. 2. Only the defect concentration N_t differs between the two measurements, but preference is given to the trap concentration obtained from the initial experiments as the DLTS spectrum measured at ANU was significantly noisier and more difficult to analyze.

In the following, another wafer of the same aluminum-contaminated Czochralski (Cz) silicon ingot has been prepared for lifetime measurements. To minimize the effect of surface recombination on the effective charge carrier lifetime, the lifetime samples have been passivated by a 70 nm silicon-nitride (SiN) layer deposited via plasma-enhanced chemical vapor deposition on both sides of the wafer.

The effective charge carrier lifetime at different injection levels was measured using the quasi-steady-state photoconductance (QSSPC) method, introduced by Sinton and Cuevas[15] in the 1990s. After correcting the measured lifetimes under consideration of contributions for intrinsic recombination (Auger and radiative recombination), the lifetimes which are only limited by Shockley-Read-Hall (SRH) recombination τ_{SRH} are obtained.[16,17] Both lifetime curves τ_{eff} and τ_{SRH} are shown in Fig. 3 (closed squares and open circles, respectively).

As can be seen from the presented SRH-lifetime curves, it is not possible to model one single defect to the measured lifetime data. In accordance with similar lifetime spectroscopy investigations,[11,18] we therefore chose to assume a second, shallow defect center that does not influence the SRH lifetime at low level injection but becomes dominant for high excess carrier concentrations. Under that condition, a two-defect SRH fit was performed for the aluminum-contaminated sample that fits the experimental data very satisfactorily. Taking the defect parameters of the aluminum-related defect from the DLTS measurements, we were able to

determine the symmetry factor $k=\sigma_n/\sigma_p$ of the deep defect center to $k=870$.

As already mentioned in the introduction, precedent works on intentionally aluminum-contaminated silicon wafers give a broad range of defect parameters. Our value for the energy level gives as a weighted average $E_t-E_V=0.44\pm0.02$ eV and is in good agreement with the energy levels determined by Marchand and Sah[5] ($E_t-E_V=0.40$ eV) and Davis *et al.*[8] (two levels detected at $E_t-E_V=0.43$ eV and $E_t-E_V=0.47$ eV). Furthermore, we obtained results for the carrier capture cross sections $\sigma_{n/p}$. The hole capture cross section σ_p has been measured independently with two different DLTS systems and coincides to be $\sigma_p=3.6\times10^{-13}$ cm^2. In order to obtain the electron capture cross section, it is assumed that the symmetry factor is temperature independent. With this, a value of $\sigma_n=3.1\times10^{-10}$ cm^2 could be determined quite accurately from the very sound fit of the SRH-lifetime curve with the measured QSSPC data. The combined application of the two physically fundamentally different characterization methods such as deep-level transient spectroscopy and injection-dependent lifetime spectroscopy led therefore to a complete characterization of the aluminum-related defect in silicon.

Finally, some aspects regarding the structure and configuration of the defect should be given. As already mentioned at the beginning, the aluminum atoms have been added into the silicon melt during pulling of the crystal. Due to the Czochralski technique, a considerable concentration of oxygen in the bulk material is expected. Revising the literature, on the one hand, the energy levels of defects such as interstitial aluminum, the aluminum-vacancy complex, or aluminum-iron pairs are reported elsewhere in the silicon band gap;[7,10] whereas, on the other hand, the defect level detected by Marchand and Sah at around $E_t-E_V=0.40$ eV is precisely attributed to the aluminum-oxygen pair (Al–O). We therefore conclude that the Al-related defect center investigated in the present work is probably due to the Al–O complex as well. Interestingly, the samples used in the study of Davis *et al.* also originated from a Cz silicon ingot with Al atoms given into the melt. Because of this, we tentatively

attribute the observed defect centers, which they do not specify further, to the same Al–O pairs. It should be stressed, however, that, in principle, any other species present in Cz silicon but not in, e.g., float-zone silicon in concentrations above 10^{13} cm^{-3} could be responsible for the detected defect configuration as well and that the attribution to the Al–O pairs still remains an assumption.

In conclusion, the combined application of DLTS and lifetime spectroscopy has been shown to be an efficient way to obtain the defect parameters of the lifetime-limiting defect in *p*-type boron-doped aluminum-contaminated Czochralski silicon. From the various energy levels reported in previous investigations, we identified one single energy level at $E_t - E_V = 0.44 \pm 0.02$ eV and an asymmetric capture cross section with $\sigma_p = 3.6 \times 10^{-13}$ cm^2 and $\sigma_n = 3.1 \times 10^{-10}$ cm^2. In comparison with the literature, this aluminum-related defect center is attributed to the aluminum-oxygen complex (Al–O).

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