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Oxygen-related defects: minority carrier lifetime killers in n-type Czochralski silicon wafers for solar cell application

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Many authors (Haunschild et al., Phys. Status Solidi RRL **5**, 199-201 (2012) [1]) reported about areas in Cz-Si with an extremely low lifetime of minority carriers after high temperature stages of solar cell manufacture. In such regions the minority carrier lifetime may be fallen 100 times after annealing, what leads to a considerable drop in the solar cell efficiency. In present work the electrical and structural properties of phosphorus doped Bosch Cz-Si wafers with degrading areas were studied by means of photoluminescence, deep level transient spectroscopy, transmission electron microscopy, electron energy loss spectroscopy and Fourier transform infrared spectroscopy. Based on these data it is concluded that the dominant recombination channel in the degrading areas is related to strained oxygen precipitates. We found electronic states of traps which may cause their formation.

1 Introduction The recent research of oxygen-rich Cz-Si and oxygen precipitation in Si showed an extremely important role of the last in photovoltaic application. One of the factors that can limit the lifetime of charge carriers is a recombination on energy states related to precipitated oxygen. It is well known that a long annealing time above ≈20 hours is usually necessary for the formation of oxygen precipitates (OPs) of high density.

Haunschild et al. [1] reported about the existence of degrading areas (DA) with an extremely low lifetime of minority carriers in Cz-Si wafers even after short-time high temperature steps of solar cell fabrication. They take typically only a few hours. The minority carrier lifetime in those regions after heat treatment can be reduced by a factor of 100 in comparison to that in undegraded material. The authors observed a drop in lifetime by photoluminescence-mapping of wafers. An application of preferential etching allowed concluding that OPs are responsible for the recombination of charge carriers in these DA in the central parts of the wafers.

In the work here presented the analysis of the strong recombination centers in DA in solar grade Cz-Si is reported. The main purpose of this investigation was to identify origins of high recombination activity after short-time annealing. The solution to problem of DA is an important issue for solar cells production based on single-crystal silicon. The present research has been based on the study of electrical and optical properties as well as the crystallographic structure of defects by means of a wide variety of techniques.

2 Experimental methods Several Bosch Solar Energy phosphorus doped [100] Cz-Si crystals grown in vacancy mode with potentially degrading regions and one reference silicon crystal without DA were the subject under present study. The phosphorus concentration in the investigated samples is typically about 10^{15} cm^{-3}. In all measured samples with potential DA, oxygen concentration is similar and equals to 1.2×10^{18} cm^{-3} while reference samples represent slightly lower amount of 1.0×10^{18} cm^{-3}. The concentration of carbon was found less than 5×10^{15} cm^{-3}.

2 mm thick slices were cut from the interesting areas of the ingots and were double-sided polished to obtain a mirror-like surface. Additionally thin neighboring wafers with thickness of 150 µm were cut from the same crystals for estimation of DA sizes by band-band photoluminescence-mapping after heating. Several annealings were made for simulation of high temperature cell manufacturing steps. The treatments were carried out at 800-1000 °C for several hours at nitrogen ambient.

For DLTS measurement Schottky diodes on silicon material were produced. Before evaporation of gold Schottky contacts samples were placed in a solution of HF: $10H_2O$ for 1 minute to remove the surface oxide layer. The mechanical grubbing and further ion etching were used for preparation of foils for TEM investigations.

The IR-absorption measurements were carried out by means of FTIR-spectrometer Bruker CryoSAS at room and low temperatures. It allows determining concentrations of interstitial oxygen, substitutional carbon and doping elements. The wavenumber range was from 1250 cm^{-1} to 250 cm^{-1} and the spectral resolution was 0.5 cm^{-1} for each measurement. The IR-spectra were accumulated 200 times.

Deep level transient spectroscopy (DLTS) measurements were carried out by means of SULA DLTS spectrometer. The temperature scans from 300 K to 20 K were performed with Janis closed cycle helium cryostat. The reverse voltage of -6 V was kept and the filling-pulse voltage of 5V was applied with the period of 50 ms and duration (t_w) from 3 µs to 1 ms. The rate windows (t_e) were varied from 50 µs to 12.5 ms.

Table 1 Survey of energies below E_c, electron capture cross sections for the found levels (see labelling in Fig. 1)

Level	TD	DLe1	DLe2	DLe3
Energy (eV)	0.075	0.33	0.365	unknown
σ ($10^{-15}cm^2$)	4	6	2	unknown

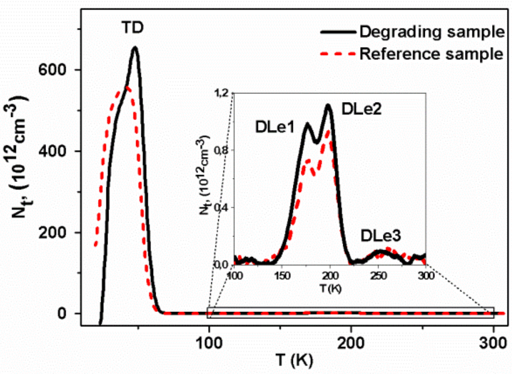


Figure 1 DLTS spectra of as-grown reference and degrading samples, central positions of wafers, t_e=2.5 ms, t_w=1 ms. The inset shows a temperature range between 100 K and 300 K in detail.

Transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) analysis were performed by means of TEM Zeiss Libra 200FE operating at 200 keV. EELS was extracted near oxygen-K edge (543 eV)/L23 edge (131 eV) and silicon-K edge (1852 eV).

We applied electrical quality inspection unit BT-imaging LIS-R2 for band-band photoluminescence (PL)-mapping and Sinton BCT-400 for measuring life-time of charge carriers by using method of quasi steady state photoconductivity (QSSPC).

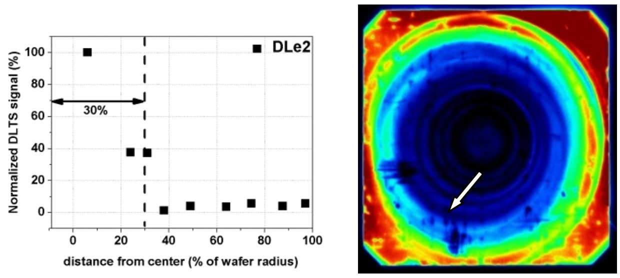
3 Experimental results Figure 1 represents the DLTS spectra of Schottky diodes on degrading and reference samples before annealing. The parameters of all states are listed in the Table 1. Four traps are observed on DLTS spectrum of as-grown samples. The extremely intense peak "TD" corresponding to shallow state is observed in both spectra. Resistivity data and analysis of the capacitance Schottky diodes also demonstrate the additional to the intentional doping donor concentration of about 5×10^{15} cm^{-3}. This level is associated with thermal donors, which dissolve almost completely during heat treatment. "DLe1", "DLe2" and"DLe3" are presented on spectra of both as-grown samples. The parameters of the last cannot be determined because of the weak signal. The intensity of "DLe1" is dependend on the HF treatment in comparison with more reliable state "DLe2".

In Fig. 2(b) it can be seen that PL-intensity in the center of wafer is dramatically dropped that indicates sharp fall in the lifetime of minority charge carriers. The QSSPC measurements showed that the lifetime reduces from 400-500 µs down to 50-60 µs after heat treatments while in the reference wafer it changes insignificantly.

The distributions of the deep level "DLe2" along the radius of the as-grown degrading wafer were matched with sizes of the DA on PL-mapping after heat treatment (see Fig. 2). The maximum concentration of the as-grown centers "DLe2" is localized in the inner region of the wafer with a radius of 30% to full wafer radius. At the same time, after annealing the area with the largest fall in the lifetime has a similar radius of 30%.

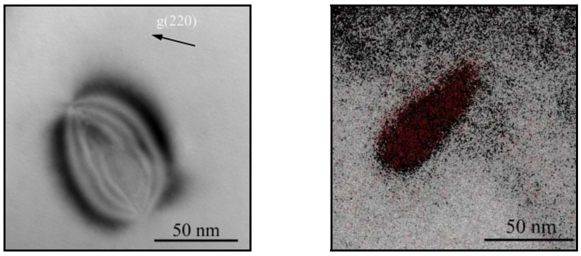
The TEM measurements revealed the presence of extended defects only in the annealed sample from the DA. We distinguished {100}-plane platelets with sizes of about 50 nm which is surrounded by coffee bean contrast of strain field (see Fig. 3(a)). The concentration of these defects reaches 10^{11} cm^{-3}. We did not find any extended defects in as-grown DA matter and annealed reference samples. For this reason, these defects might be responsible for the recombination activity in the DA. EELS found that platelets consist of silicon and oxygen (see Fig. 3(b)). We can conclude that observed extended defects in the DA after annealing are most likely plate-like oxygen precipitates surrounded by stress field.

FTIR found that the concentration of interstitial oxygen in as-grown DA ingot is higher by 20% in comparison with



a b

Figure 2 (a) The distribution of state DLe2 along the radius of wafer before annealing. (b) PL-image of the same wafer after annealing. Red color on mapping corresponds to the highest photoluminescence intensity and dark blue color to the lowest one. White arrow represents a radius of 30%.



a b

Figure 3 TEM-image of typical extended defects in DA after annealing (a). Results of EELS-mapping near the same type of extended defects in DA (b). Grey color corresponds to the distribution of silicon, red color to that of oxygen.

the reference as-grown crystal. We could not estimate a consumption of oxygen by growing OPs because the dissolving of oxygen thermal donors led to appearance of significant concentration of additional interstitial oxygen.

4 Discussion The application of DLTS found two deep states “DLe1” and “DLe2” in inner part of as-grown wafers regardless of the presence of DA after annealing (see Fig. 1). We tentatively ascribe these deep levels to the embryos of oxygen precipitate in silicon matrix. The higher concentration of oxygen in central region of crystal and inner vacancy-rich area [2] can both stimulate nucleation of oxygen precipitates during silicon crystal growth.

The maximum concentration of as-grown levels “DLe2” along wafers strictly correlates with sizes of the DA and the distribution of “DBe” after heat treatment (see Fig. 2). This fact might indicate that the traps “DLe2” take part in the formation of recombination-active centers in the DA. Nevertheless, the same deep levels “DLe1” and “DLe2” are presented in the control sample which means that their presence is not the only reason of formation of recombination channels in the DA.

The presence of stressed plate-like OPs with the density of 10^{11} cm^{-3} only in DA was found by TEM and EELS techniques (see Fig. 3). In according to recent works [4] the strained OPs are much stronger recombination centers in comparison to unstrained OPs. Haunschild et al [1] also found the presence of OPs in DA by preferential etching. Probably, observed OPs were stressed, since unstrained OPs are undetectable by etching [3].

The application of all methods did not reveal any difference in defects between degrading and reference material before annealing. Because of the only difference is the amount of oxygen, it is likely that the higher interstitial oxygen concentration plays an important role in formation of strained OPs in DA.

5 Conclusion Based on experimental data we conclude that the strained plate-like oxygen precipitates are the origin of recombination activity in degrading areas. This assumption is corresponds to the conclusions of previous authors [1]. The sizes of region of strained precipitates depend on distribution of “DLe2” before annealing which cause the growth of OPs at high temperature steps of solar cell fabrication. We tentatively attribute these states to nuclei of precipitates. In the reference crystal such embryos are also observed before annealing but they do not lead to the formation of the OPs during heat treatment. The influence of the concentration of interstitial oxygen in the formation of problematic regions should be a subject of further investigations.

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