Combined DLTS/MCTS investigations of deep electrical levels of regular dislocation networks in silicon

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Abstract. Local electronic states of regular dislocation networks produced by n- and p-type silicon wafer bonding with different screw dislocation density were studied with deep-level transient spectroscopy (DLTS) and minority carrier transient spectroscopy (MCTS). A drastic sudden changes of the electric level spectrum with increasing of dislocation density from two shallow bands located near the edges of valence and conduction bands towards two deep bands with energy positions about E₁ - (0.22-0.26) eV and E₂ + (0.4-0.53) eV were found. The origin of the electric level spectrum changes is ascribed to the changes of dislocation core structure from dissociated to perfect ones that occur when interdislocation distances became comparable with the dislocation equilibrium dissociation width. The obtained results correlate well with the results of recent studies of recombination activity of grain boundaries in mc-Si.

1. Introduction

The electrical activity of the grain boundaries (GBs) in mc-Si was intensively investigated over the last decades since the carrier recombination at the GBs is one of the main factors limiting the solar cells efficiency [1,2]. It was found that the recombination activity greatly depends on degree of contamination by transition metals impurities as well as on GB atomic structure. Unfortunately, the energy spectrum of GBs intersecting the wafer surface of mc-Si wafers could not be unambiguously established by deep level transient spectroscopy (DLTS) method due to a background signal of other defects. An alternative approach to obtain necessary information is to investigate special model objects that possess well controlled and monitored GB properties. The samples produced by silicon wafer bonding method containing regular dislocation network (DN) are well suited for this goal as their dislocation structure can be precisely controlled by misorientation between the wafers [3]. Moreover, it was found that the variation of the dislocation density accompanies with the changes in dislocation core structure that enables to trace corresponding changes of GB electronic properties [4].

In this work we investigated n- and p-type samples produced by silicon wafer bonding containing regular dislocation network of various density by means of DLTS and MCTS methods. We showed that a qualitative transformation of DN-related gap states takes place when the dislocation core structure changes from dissociated towards the non-dissociated one. The achievements in the understanding of the relation between the core structure of dislocations in DNs and their recombination properties would be essential for production of the effective mc-Si solar cells as well as for optimization of possible future devices exploiting the unique properties of dislocations in Si [5].
2. Experimental details
Samples for the experiments were fabricated by hydrophilic bonding of (001)-oriented CZ Si wafers. Doping level of n-type wafers was $10^{14}$ cm$^{-3}$ with phosphorous and of p-type - $10^{15}$ cm$^{-3}$ with boron. Details of the bonding procedure can be found elsewhere [3,4]. Samples were produced in high-purity conditions providing that they are free from the metal impurities. [6]. Regular dislocation network forms at the bonding interface due to the mutual misorientation of the wafers: square network of screw dislocations compensates the twist component of misorientation $\alpha_{TW}$, while the tilt component $\alpha_{TI}$ is compensated by a periodic array of 60° dislocations [3].

Investigated samples differ mainly by twist misorientation angle, i.e. by the distances between the screw dislocations while tilt misalignment was nearly the same for all samples in the range of 0.5-0.7°. DN parameters are summarized in table 1. TEM revealed that all samples irrespective of misorientation angle possess the similar structure of DN – square-like mesh of screw dislocations intersected by the array of 60° dislocations, with the interdislocation distances between the neighboring screws or screw and 60° dislocations decreasing with $\alpha_{TW}$ increase. Dislocation network in all samples lies parallel to the front surface at the depth of approximately 160 nm being, thus, inside the space-charge region of the Schottky diode even at zero bias. Accordingly, forward bias pulses have to be applied in DLTS measurements in order to fill the DN states with charge carriers.

To produce Schottky contacts, 100 nm-thick Au/Ti dots of 1.5 mm diameter were evaporated on the oxide free front surface of n-/p-type samples, respectively. Control samples were prepared by Schottky contacts evaporation on the mirror-polished rear surface of the bonded wafers. Ohmic contacts were prepared by rubbing of AlGa or InGa eutectic on the rear side of the samples. DLTS and MCTS measurements were performed by means of SULA spectroscopy system equipped with the closed cycle cryostat. To produce minority carrier flux in MCTS experiments a GaAs light emitting diode (LED) emitted at 890 nm was used. Samples for MCTS were thinned up to the thickness below 200 μm from the back side that was illuminated by LED.

In the following, samples will be denoted according to their conductivity type and $\alpha_{TW}$ angle. Moreover, as it will be discussed later, all investigated samples could be divided into two categories: low twist angle (LTA) samples with $\alpha_{TW} \leq 3.5°$ and high twist angle (HTA) samples with $\alpha_{TW} \geq 4°$.

| $\alpha_{TW}$, ° | n-type | $D_{screw, nm}$ | $\alpha_{TW}$, ° | p-type | $D_{screw, nm}$ |
|-----------------|--------|----------------|-----------------|--------|----------------|
| Low Twist Angle Samples (LTA) | 1.4 | 23 | <1 | 60 |
| | 2.6 | 16 | 2.5 | 9 |
| | 3.5 | 8.5 | 2.8 | 8 |
| | 6.3 | 3 | 7.3 |
| High Twist Angle Samples (HTA) | 4.2 | 5.2 | 3.9 | 5.6 |
| | 4.7 | 4.6 | 4.2 | 5.2 |
| | 5.7 | 4 | 4.5 | 4.9 |

3. Experimental results
3.1 LTA-samples.
DLTS spectra measured on LTA samples are presented in figure 1. Implying the two-dimensional distribution of the traps related with DN, DLTS signal magnitude $AC$ was recalculated to represent the surface density of captured carriers (electrons or holes) $N_t$ according to
Figure 1. DLTS spectra of LTA-samples of (a) p-type and (b) n-type conductivity. DLTS-scan parameters: filling pulse duration $t_p=1$ ms, reverse bias $U_r=1$V, forward filling pulse voltage $U_p=-1$V, rate window period $T_C=20$ ms.

$$N_e = \frac{S^2 \varepsilon^2}{x_d} N_D \frac{\Delta C}{C^3}$$

where $\varepsilon$ is the dielectric constant, $x_d$ is the dislocation network depth (160 nm), $S$ is the diode capacitance, $C$ is the diode area and $N_D$ is the doping density. Similar features of DLTS spectra were revealed for all LTA samples of both conductivity types, namely the broadened low-temperature peaks STp and STn dominating the spectra and a set of overlapped peaks appearing at 100-250K of considerably smaller magnitudes. Since no DLTS peaks were detected on control samples without DN, all detected DLTS peaks could be directly related with the defect states introduced by DN. Note also, that due to the peak broadening the real values of trapped carriers could be considerably higher than the values estimated from the DLTS peak magnitudes following equation (1).

The magnitude of low-temperature STp and STn peaks increases with twist misorientation angle $\alpha_{TW}$ and reaches the maximum at the angle of about 3-3,5° in n-3,5 and p-3 samples, respectively. Minority carriers transient spectroscopy (MCTS) studies have confirmed that two shallow bands exist simultaneously in the opposite parts of the band gap in LTA n- and p-type bonded samples, implying that they are not related with the main dopant kind [7]. Previously, we have reported the observation of the effect of field enhanced emission from the shallow traps responsible for STp/STn peaks in LTA samples [8,9].

Figure 2. Comparison of the Arrhenius plots for the deep traps revealed in LTA bonded samples (filled symbols) with those ones for deep traps in plastically deformed Si samples reported previously in [10] (lines) and [11] (open symbols).
The effect was attributed to the dislocation related Poole-Frenkel effect – barrier lowering for carrier thermoemission as a result of the interaction of dislocation deformation potential and the potential of external electric field, whereas STp and STn traps – to the shallow core states of 60° dislocations. The existence of shallow dislocation-related states was predicted for dissociated dislocations in Si by theory [12,13] and subsequently confirmed by experiments (see [14] for review). The activation energy of STp/STn traps at zero electric field was estimated to be about 0.12-0.13 eV. Activation enthalpies for carrier emission from deeper traps are shown as a part of the corresponding DLTS peaks notations (in eV) in figure 1.

In p-type LTA samples at least four deep traps could be identified with similar characteristic parameters in each sample. DTp-0.33 peak correlates well with H0.33 trap [10] in plastically deformed Si samples known also as F-line as it is seen from Arrhenius plots in figure 2. This line was attributed to the oxygen-related defects located at (or close to) the dislocations. Close coincidence was established between the Arrhenius graphs for DTp-0.19 and DTp-0.49 peaks with those for H.21 and H.49 peaks, respectively, observed in [10] in moderately deformed p-type Si that do not survive upon annealing.

For two deep traps in n-type LTA samples with the activation energies of 0.26 eV and 0.29 eV reasonable agreement was found with so-called A and B-lines previously observed in plastically deformed n-type samples [11]. We suppose that interstitial clusters and/or some kinds of oxygen-related defects (for example, embryos of oxide precipitates which are too small to be detected by TEM) created during the hydrophilic wafer bonding processing as a result of oxide layer dissolution and stabilized by the strain field of dislocations in DN are responsible for the deep traps in LTA samples.

3.2 HTA-samples.

DLTS spectra of HTA samples are presented in figure 3. For comparison, the spectra of LTA samples p-3 and n-3,5 are shown, too. As one can see, DLTS spectra of HTA n- and p-type samples differ significantly from the corresponding spectra of LTA samples.

In p-type samples, the magnitude of low-temperature STp peak decreases abruptly by 3-4 times when twist angle increases from 3° to 3.9° and at 4.5° it disappears completely. Instead, the asymmetrically broadened peak DHp appears at the temperature of about 200-210 K, see figure 3a. Near the low-temperature shoulder of DHp peak an additional signal due to DTp-0.29 traps could be recognized whose intensity also decreases with the twist angle increase. However, the overlapping with DTp-0.29 peak is not the only reason for DHp peak broadening.

![Figure 3](image_url)

**Figure 3.** DLTS spectra of HTA-samples of p-type (a) and n-type conductivity (b). For comparison, DLTS spectra of LTA samples p-3 and n-3,5 are shown, too. DLTS-scan parameters: filling pulse duration \( t_f = 1 \) ms, reverse bias \( U_r = 1 \) V, forward filling pulse voltage \( U_p = -1.5 \) V, rate window \( T_C = 5 \) ms.
With increase of the number of captured carriers, DHp peak grows and its maximum shifts towards the lower temperatures and the high-temperature tails remain coincide (not shown here for brevity). Such kind of the behavior was observed previously for dislocation ring bounding the NiSi2 precipitates in Si and is a characteristic of band-like states [15,16]. As was revealed from the Arrhenius graphs, the band of states responsible for DHp peak lies in the range from 0.4 eV till 0.53 eV above the valence band edge, being close to the middle of the band gap.

In HTA n-type samples low-temperature STn peak is absent, whereas a new DHn peak around 130K and also a negative peak NPn around 220K appear (see figure 3b). A small difference in shape and temperature position of DHn peak in different samples is caused probably by the interplay of the intensity of two unresolved components composing the DHn peak that might be due to a non-uniformity of the DN structure along the wafer. Similar to DHp peak in p-type HTA samples, DHn peak possesses band-like behaviour, too, with the energy band ranges from $E_c-0.22$ eV to $E_c-0.26$ eV, what indicates on the extended character of the states responsible for DHp and DHn peaks [15].

3.3 Results of MCTS investigations.
A distinctive feature of the DLTS spectra of HTA n-type samples is the negative peak NPn (figure 3b). Usually, negative peak in DLTS experiments corresponds to the emission of minority carriers (in our case – holes) from the trap levels located in the opposite (lower) half of band gap [17]. Accordingly, this requires the presence of the levels in the lower half of the band gap and the possibility of their recharging by minority carriers. The latter is quite unexpected for schottky barrier diodes which are considered as the majority-carrier unipolar devices [18]. Additional DLTS measurements performed with the external resistance connected in series with the sample in order to validate that the sign inversion was not due to a large series resistance of the samples have confirmed, that the negative peak is indeed a true minority carrier signal [19].

Validity of the minority carrier trap assignment for NPn signal was further demonstrated by MCTS measurements. Figure 4a compares the MCTS spectrum measured with pulsed optical excitation with the spectrum of conventional DLTS measured on the same n-5.7 sample. Temperature position of the main MCTS peak at 230K is in a good agreement with the negative NPn peak of the DLTS spectrum. Moreover, the temperature position of negative NPn peak in HTA n-type samples was close to that of the dominant DHp peak in HTA p-type samples. Close correspondence was also revealed for the Arrhenius plots of these peaks, see figure 5a. Thus, it can be concluded that the negative NPn peak corresponds to the emission of holes from the levels located in the lower half of band gap which are also responsible for DHp peak in HTA p-type samples.

Figure 4. MCTS and DLTS spectra measured on (a) n-5.7 sample showing the NPn peak coinciding for both measurement methods, (b) on p-4.5 and n-5.7 samples, respectively, showing the peaks due to DHn traps. Reverse bias $U_r=1$V, rate window $T_c=5$ ms, filling pulse voltage $U_f=1,5$V and duration $t_p=1$ ms for DLTS and light pulse width $t_p=10$ ms for MCTS measurements.
MCTS measurements were performed on HTA p-type samples as well. MCTS spectrum measured on p-4,5 sample is shown in figure 4b together with the DLTS spectrum of n-5,7 sample. A peak corresponding to the minority carrier emission is clearly visible on MCTS spectrum of p-4,5 sample at the temperature of about 120K. Its temperature position as well as Arrhenius plot (figure 5a) is in a good agreement with those for majority carrier DHn peak in n-5,7 sample confirming the identity of the traps responsible for these peaks.

3.4 Minority carrier injection in n-type HTA samples.

The question about the source of holes in space charge region of n-type Schottky diode for capturing on DHp traps still has to be clarified. In the work [20], authors have observed the minority carrier DLTS peak on bonded p-type Si samples with hybrid (110)/(100) orientation of the wafers and suggested that the mid-gap interface states produce a significant generation current under reverse bias, so that the minority carriers accumulated during reverse bias phase could conceivably be trapped during the filling pulse application. In our samples, the traps producing the generation current could be the near mid-gap DHp traps.

Another possible source of the minority carriers could be their thermionic emission from the metal Schottky contact. It was reported previously [21], that it is possible in DLTS experiments to detect a minority carrier signal from the traps located close to the semiconductor / metal interface in the forward biased Schottky diodes with high potential barrier. For n-type Schottky diodes, the minority carrier injection ratio $\gamma$ defined as the minority carrier current $J_p$ to the total current through the diode $J_p + J_n$ [18] is equal to

$$
\gamma = \frac{J_p}{J_p + J_n} = \frac{q n^2 D}{N_D A^{**} T^2 e^{-\phi_b/kT}} \approx \frac{e^{-(E_G - \phi_b)/kT}}{N_D} \tag{2}
$$

where $q$ is the elemental charge, $D$ and $L$ are the minority carrier diffusion constant and diffusion length, $A^{**}$ - effective Richardson constant. Considering the temperature dependence of the intrinsic carrier density $n_i$, injection ratio $\gamma$ would increase with Schottky barrier height $\phi_b$ (what leads to the decrease of the potential barrier height for minority carrier injection $\phi_m = E_G - \phi_b$, where $E_G$ is the band gap width), with temperature of the sample $T$ and with decrease of the dopant concentration $N_D$. Since in our DLTS measurements the forward bias pulses have to be applied to fill with charge carriers the DN states located at the depth of only 160 nm from the sample surface, emission of the minority carrier across the Schottky barrier may take place in our samples, too.

Figure 5. (a) Comparison of the Arrhenius plots for DLTS and MCTS peaks in HTA samples. Symbols are the experimental data, lines represent the best linear fits. (b) DLTS of n-5,7 sample measured on Al (solid lines) and Au (dashed lines) Schottky diodes with different values of filling pulses $U_f$ (shown in the legend). Pulse duration $t_p=1$ms, reverse bias $U_r=1$V, rate window $T_C=5$ ms.
In order to define which of two mechanisms provides minority holes for capturing at DHp traps, DLTS measurements were repeated on n-type HTA samples with Al Schottky contacts which produces lower barrier height of 0.7 eV as compared with 0.8 eV for Au-barriers [18]. Reduction of the barrier height would decrease the minority carrier emission across the Schottky contact (equation (2)), but will not influence on the generation current as the defect structure of DN remains the same for both contact types. Results of DLTS measurements on Au and Al contacts are presented in figure 5b. It’s appeared, that for the forward filling pulse of \( U_p = -1 \) V negative NPn peak is visible only on Au Schottky diode, but not on Al one. At higher forward filling pulse of \( U_p = -1.5 \) V negative peak becomes visible on Al contact as well, however on Au contact for the same filling pulse its magnitude is 4 times higher. Thus, smaller amplitude of the negative peak on a sample with lower Schottky barrier height evidences in favour of minority carrier emission across the Schottky barrier as a source of holes for capturing at DHp traps.

4. Discussion

As a result of the performed DLTS / MCTS investigations, considerable changes of the structure of DN-related defect levels were revealed for n-type and p-type bonded silicon samples when the twist misorientation angle exceeds the value of about 3-4°. In LTA samples with \( \alpha_{TW} \leq 3.5° \) the spectrum of DN-related defects is dominated by two shallow levels located symmetrically near the edges of the valence and conduction bands which were ascribed to the deformation-induced states of 60° dislocations [8,9]. However, further increase of the twist angle above 4° leads to the radical transformation of the energy levels structure. In HTA samples two deep levels (bands) located at \( E_{c} - (0.22 - 0.26) \) eV and \( E_{v} + (0.4 - 0.53) \) eV dominate, whereas the signal from the shallow levels disappears (n-type) or decreases markedly (p-type).

Owing to high potential barrier of Au/n-Si Schottky contact and a low doping (\( 10^{14} \) cm\(^{-3} \)) of n-type samples, an effective minority carrier emission across the Schottky barrier becomes possible providing sufficient hole concentration at a depth of DN (160 nm) to be captured by DHp traps during the forward filling pulses leading then to the observation of the minority carrier peak due to the holes emission from DHp traps during DLTS measurements. In turn, no minority carrier peak due to electrons emission from DHn traps could be expected on DLTS spectra of HTA p-type samples in spite of the application of similar forward filling pulses. Higher doping level of p-type samples (\( 10^{15} \) cm\(^{-3} \)), considerably lower temperature of DHn peak appearance (130K vs. 230K for DHp peak) and moderate Ti/p-Si barrier height of only 0.6 eV [18] makes altogether the concentration of minority electrons emitted across the Schottky barrier negligibly small (equation (2)).
As for the origin of deep DHn and DHp traps, it is obvious, that the observed changes in the structure of the energy levels could not be related with the geometry of the dislocation network, since the DN structure remains the same in LTA and HTA samples. Consequently, the changes in the structure of the energy levels are most likely caused by the changes in the structure of the dislocations cores. Indeed, the transformation of the core structure of screw dislocations composing the DN when the twist misorientation angle exceeds the critical value of just around 3-4° (what corresponds to the interdislocation distances of about 5,5-7 nm) was reported previously [4]. For αyw below the critical value the screw dislocations at the bonding interface were found to be dissociated into partials – similar to the dislocations in silicon bulk introduced by plastic deformation at elevated temperatures $T_d>600 \text{ °C}$ [22]. Whereas for αyw > 4° the screw dislocations appeared to be non-dissociated, indicating the transformation of the “screw dislocations” to the “interfacial dislocations” with completely different core structure [4]. Obviously, such transformation is related with decrease of the distances between the neighboring dislocations: as two adjacent dislocations become closer, they push each other and the dissociation length decreases below the equilibrium value and finally the stacking fault width becomes smaller than the dislocation core radius resulting in the formation of non-dissociated dislocations. By analogy with screw dislocations, we may assume that if the distances between the segments of 60° dislocations and the neighboring screws become less than the critical distance of about 5,5-7 nm, the 60° dislocations in DNs become non-dissociated as well.

Consequently, we suppose that shallow STp/STn traps observed in LTA samples are the states of dissociated dislocations, whereas deep DHp/DHn traps in HTA samples – of non-dissociated ones. Early theoretical calculations have predicted for perfect non-reconstructed dislocations in Si the existence of two deep energy bands: one in the lower half of band gap due to the dangling bonds and the second one in the upper half of band gap caused by the stretched bonds between the neighboring atoms [23]. Thus, deep DHp and DHn traps could be identified just with these states of non-dissociated dislocations. Moreover, recent investigations of the recombination activity of small-angle grain boundaries in mc-Si have revealed the highest recombination activity for the GBs containing perfect dislocations, whereas only minor one – for the GBs containing dissociated dislocations [24]. This observation perfectly fits with the results of our work: undoubtedly, both revealed deep DHp and DHn traps in HTA samples would lead to a significant recombination activity unlike to shallow STp/STn traps in LTA samples [18].

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