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DLTS Study on Deep Level Defects in Cz-p-Si Due to Heat Treatment at 600 to 900 °C

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It is observed by means of DLTS that in the case of Czochralski-p-Si deep levels with $E_T - E_V = 0.4$ to 0.6 eV can be introduced due to longer heat treatment at temperatures in the region 600 to 900 °C. A detailed kinetics study is given of these deep level defects in dependence on the oxygen and carbon concentration. Attempts are made to correlate the DLTS data with TEM results to obtain information on the relationship between the deep levels and the structural defects, formed due to oxygen precipitation. The experimental results suggest that the deep levels are related to a large supersaturation of Si-interstitials achieved by the growth of oxygen precipitates, leading also to the begin of secondary defect formation.

Es wird mittels DLTS beobachtet, daß für Czochralski-p-Si infolge längerer Wärmebehandlung im Temperaturbereich von 600 bis 900 °C tiefe Störstellen eingeführt werden mit Energieniveaus im Bereich $E_T - E_V = 0,4$ bis $0,6$ eV. Die Bildung dieser tiefen Störstellen wird detailliert untersucht für Cz-Si in Abhängigkeit von der Sauerstoff- und Kohlenstoffkonzentration. Die DLTS-Ergebnisse werden Resultaten aus TEM-Untersuchungen gegenübergestellt, um Aussagen zum Zusammenhang zwischen den infolge Sauerstoffpräzipitation eingeführten Störstellen und Volumendefekten zu gewinnen. Die Ergebnisse deuten darauf hin, daß die Bildung der tiefen Störstellenniveaus vermutlich mit einer hohen Übersättigung an Si-Zwischengitteratomen infolge Wachstum von Sauerstoffpräzipitaten korreliert, die auch zum Beginn der Sekundärdefektbildung führt.

1. Introduction

The problems of oxygen behaviour in Cz-Si are of great practical importance for device technology regarding the fact that device parameters can be influenced significantly by effects related to oxygen precipitation [1]. Thereby, the investigation of heat treatment (ht) induced changes in the electrical properties of Cz-Si is of particular interest.

A ht at temperatures in the range 400 to 900 °C can lead to the formation of different kinds of oxygen-related donors [2 to 4]. Besides this, it has been reported that recombination/generation centres can be introduced by oxygen precipitation [5 to 9], and that heavy metal induced recombination/generation centres can be redistributed by gettering sites formed due to oxygen precipitation [10, 11]. The intensive research using different spectroscopic methods in the field of oxygen-related donors, especially for the 450 °C thermal donor, has given an essentially better knowledge concerning the structure of these donors, see e.g. [12]. In contrast to this, oxygen precipitation related recombination/generation centres are mainly investigated by means of lifetime measurement techniques and EBIC giving only an integral characterization of these electrically active defects. From the obtained results it has been deduced that

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deep levels are induced either by oxygen precipitates or by a heavy metal decoration of precipitates and secondary defects.

In an previously published note it has been found that a deep level (dl) with $E_T - E_V$ of about 0.5 eV [13] can be introduced in oxygen-rich silicon by a respective ht at 600 to 900 °C.

The purpose of the present work is to give a more detailed kinetics study of these dl defects by investigation of Cz-Si materials with oxygen and carbon concentrations in a wide range. An attempt has been made to correlate DLTS data with TEM results to obtain clearer information on the relationship between dl defects and structural defects.

The experimental results concerning the formation of dl defects due to oxygen precipitation in the temperature range 600 to 900 °C could be explained assuming that the dl defects are related to a large supersaturation of Si interstitials (Si_i) achieved by the growth of oxygen precipitates, leading to secondary defect formation.

2. DLTS Spectra of Cz-p-Si Heat Treated at 600 to 900 °C

It has been found in the present work that the electrical activity of oxygen precipitation induced volume defects depends on the parameters of the Cz-Si used, especially on the oxygen and carbon concentrations. Hence, some characteristic features of the DLTS spectrum should reflect certain stages of volume defect formation achieved in dependence on the as-grown Cz-Si due to the different heat treatments.

Further information concerning this relationship has been obtained by a kinetics study on the formation of dl defects. The experimental details are the same as described in [13]. The heat treatments were terminated by a fast pull of the samples to the cool ($\approx 300K$) region of the furnace tube. In Table 1 the as-grown parameters of Cz-Si samples investigated are given (oxygen concentration $[O_i]_0$, carbon concentration $[C_s]_0$, effective acceptor concentration N_A).

For illustration, in Fig. 1 DLTS spectra are presented for E-samples ($[O_i]_0 = 9 \times 10^{17} \text{ cm}^{-3}$, $[C_s]_0 = 3 \times 10^{16} \text{ cm}^{-3}$) which were measured after ht at 700 to 850 °C in N_2 for a duration of up to 240 h ($2N \cdot \Delta C/C$ effective dl concentration, N effective acceptor concentration after ht).

After short ht at 750 °C a DLTS peak appears the shape of which is characteristic of a point-like defect. With longer ht the peak amplitude increases and the peak is broadened towards lower temperatures. Furthermore, for very long ht the broadened peak transforms into a "broad" band-like spectrum with superimposed peak.

A similar result is found for ht at 800 °C (cf. Fig. 1c), but the signal amplitude $2N \cdot \Delta C/C$ is somewhat reduced as compared to ht at lower temperatures. It should be noted that qualitatively different DLTS spectra were measured after ht at 850 °C

Table 1
Parameters of the investigated Cz-Si slices

slice	$[O_i]_0$ (10^{17} cm^{-3})	$[C_s]_0$ (10^{16} cm^{-3})	N'_A (10^{15} cm^{-3})
E	8.7	3.2	1.6
d	9.6	<1	1.8
c	14.7	10.5	2.1
f	9.1	8.1	1.8
g	6.3	<1	1.3
i	6.2	35	2.4
A	9.0	<1	0.6

(cf. Fig. 1d). The peak (C) has a considerably smaller amplitude, and the "broad" spectrum is not formed.

Besides this, it is interesting to remark that in difference to ht at $T \leq 800^\circ\text{C}$ there were found the Cu-induced dl (A) [14] in a concentration of a few 10^{11} cm^{-3} , whereby for longer ht the concentration decreases, and the Mo-induced dl (B) [15]

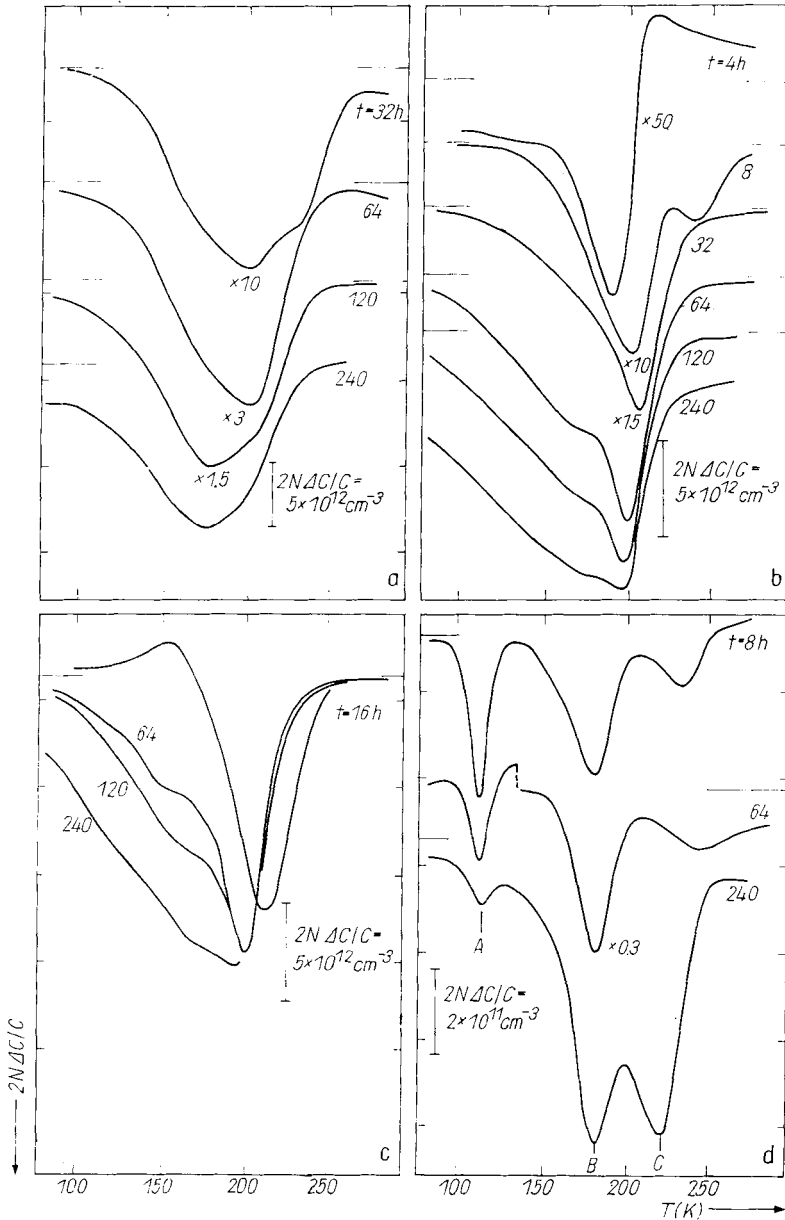


Fig. 1. DLTS spectra of Cz-Si (slice E) after heat treatment at temperatures a) 700, b) 750, c) 800, and d) 850 $^\circ\text{C}$ ($e_0 = 2.2\text{ s}^{-1}$, $t_p = 50\text{ ms}$, $U_R = 10\text{ V}$, $U_1 = 8\text{ V}$)

Table 2

DLTS-spectrum parameters obtained for A-samples ($e_0 = 220 \text{ s}^{-1}$, $t_p = 50 \text{ } \mu\text{s}$, $U_R = 10\text{V}$, $U_1 = 8\text{V}$)

T ($^{\circ}\text{C}$)	t (h)				
N_2	16	32	64	120	
750	9	5	14	28	$2N \Delta C/C$ (10^{11} cm^{-3})
	0.24	0.18	0.18	0.58	$\Delta T/T_M$
800	9	7	6	15	$2N \Delta C/C$ (10^{11} cm^{-3})
	0.17	0.15	0.18	0.28	$\Delta T/T_M$
850	11	5	2	22	$2N \Delta C/C$ (10^{11} cm^{-3})
	0.20	0.18	0.19	0.32	$\Delta T/T_M$

in a concentration of about 10^{11} cm^{-3} , indicating either that for higher temperatures the heavy metal contamination is higher or, assuming the same contamination level, that for lower temperatures of ht a higher internal gettering efficiency is obtained.

In difference to ht at 750 and 800 $^{\circ}\text{C}$, respectively, in the case of ht at 700 $^{\circ}\text{C}$ it is not possible to separate the spectrum in a peak-like part and a "broad" band (cf. Fig. 1a). There appears only a strongly broadened peak.

The shape of the peak and the formation of the band-like spectrum are found to be strongly dependent on $[\text{C}_s]_0$ for samples with nearly the same $[\text{O}_i]_0$.

For carbon-lean samples A ($[\text{O}_i]_0 = 9 \times 10^{17} \text{ cm}^{-3}$, $[\text{C}_s]_0 < 10^{16} \text{ cm}^{-3}$) the peak broadening occurs significantly slower than for samples E with the higher carbon content ($[\text{C}_s]_0 = 3.2 \times 10^{16} \text{ cm}^{-3}$).

In Table 2 for the samples A the effective dl concentration $2N \Delta C/C$ and the normalized half-width $\Delta T/T_M$ are given. Only for the longest ht of 120 h $\Delta T/T_M$ increases significantly. It is obvious that a larger broadening is also correlated with a higher dl concentration. Compared to oxygen-rich samples with low $[\text{C}_s]_0$ for oxygen- and carbon-rich samples the formation of the dl defect is yet possible at essentially higher temperatures of ht (at 900 $^{\circ}\text{C}$, cf. Table 3). It is, however, essential to note that for the sample i with very high carbon, but low oxygen concentration even after long ht at 800 $^{\circ}\text{C}$ for up to 240 h dl were not introduced ($2N \Delta C/C < 10^{11} \text{ cm}^{-3}$).

For the oxygen- and carbon-rich samples f and c, respectively, after ht at 900 $^{\circ}\text{C}$ DLTS spectra with strongly broadened peak are measured. These spectra are similar

Table 3

DLTS-spectrum parameters obtained for f- and c-samples after ht at 900 $^{\circ}\text{C}$ N_2 ($e_0 = 220 \text{ s}^{-1}$, $t_p = 50 \text{ } \mu\text{s}$, $U_R = 10\text{V}$, $U_1 = 8\text{V}$)

sample	t (h)				
	8	16	32	64	
f	3.2	2.6	2.3	2.2	$2N \Delta C/C$ (10^{12} cm^{-3})
	0.36	0.40	0.36	0.27	$\Delta T/T_M$
c	2.3	0.7			$2N \Delta C/C$ (10^{12} cm^{-3})
	0.74	0.56			$\Delta T/T_M$

to the ones observed for the oxygen-rich sample with lower $[C_s]_0$ after long ht at 700 °C suggesting that similarity in dl defects can be achieved for different as-grown parameters of Cz-Si by a respective ht procedure.

It is of interest that the half-width of the strongly broadened peak depends significantly on the duration of ht indicating defect transformation due to ht.

For the samples f and c heat-treated at 900 °C the peak parameters $\Delta T/T_M$ and $2N \Delta C/C$ can be found in Table 3. It is seen that for sample f $\Delta T/T_M$ decreases for long ht without remarkable change in $2N \Delta C/C$. This is a further argument for assuming that the properties of dl defects can be gradually changed by ht.

The dl defect is also formed due to ht at temperatures 600 to 650 °C (see, e.g. Fig. 3a), but the detection is difficult because of the enhanced formation of oxygen related donors at these temperatures [2, 3]. The donor formation can be lead for p-Si to an inversion of the conductivity type. Furthermore, due to the inhomogeneous oxygen distribution the inversion begins in regions of highest oxygen concentration. In this case the usual interpretation of DLTS results may be incorrect. Therefore, in this work only the DLTS spectra of samples are discussed for which the compensation degree was lower than 0.5.

Only in the case of oxygen-lean samples i and g, respectively, the conductivity type did not change due to ht at 600 °C for 240 h. The $2N \Delta C/C$ of these samples was about 10^{12} cm^{-3} due to this long ht at 600 °C.

The investigation of Cz-Si samples with ht at 600 °C, N_2 for 240 h, and a post-ht at 900 °C, N_2 partly destroying the oxygen related donors [3], has given evidence that for such ht procedures DLTS spectra consist of a broad band-like background signal and the broadened characteristic peak. Thereby, the duration of the post-ht (4 h or 240 h) has no essential influence on the signal amplitude and the shape of the spectrum, as it was observed, e.g., for the sample d (cf. Fig. 2). The broad background signal extends in the DLTS spectrum from the peak temperature T_{M1} to another characteristic temperature T_{M2} at lower temperatures. In dependence on $[O_i]_0$ and $[C_s]_0$ after the two-step ht 240 h 600 °C + 240 h 900 °C the weights at T_{M1} and T_{M2} , respectively, are different, but the characteristic features of the DLTS spectra are qualitatively the same. If $2N \Delta C/C$ at T_{M1} is taken as a measure for the dl concentration, values ranging from 10^{13} to 10^{14} cm^{-3} are estimated with the higher ones for Cz-Si with higher $[O_i]_0$ and $[C_s]_0$.

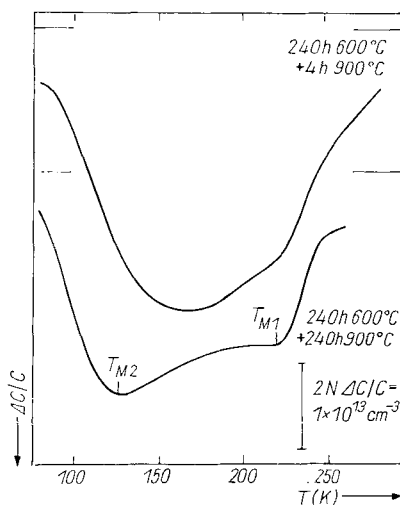


Fig. 2. DLTS spectra of Cz-Si (slice d) after heat treatment 240 h 600 °C + ht 900 °C ($e_0 = 220 \text{ s}^{-1}$, $t_p = 50 \mu\text{s}$, $U_R = 8 \text{ V}$, $U_1 = 6 \text{ V}$)

Analysing the DLTS results for Cz-Si samples heat-treated at 600 to 900 °C it is possible to distinguish four qualitatively different types of DLTS spectra as follows:

type I: a sharp DLTS peak the peak temperature T_M of which is somewhat shifted in dependence on the parameters of the Cz-Si used. This peak is clearly pronounced for carbon-lean Si with high oxygen concentration after shorter ht at temperatures 650 to 800 °C;

type II: a DLTS peak strongly broadened mainly toward lower temperatures. The peak half-width is significantly changed due to ht. This spectrum type was observed for instance for Cz-Si with high carbon and oxygen concentrations after ht at 900 °C;

type III: going out from the DLTS peak a broad band is formed toward lower temperatures;

type IV: a broad band in the DLTS spectrum; this spectrum is characteristic of two-step ht e.g. 240 h 600 °C + ht at 900 °C.

For these types of DLTS spectra qualitatively different dependences on the filling pulse time t_p have been observed (cf. Fig. 3a, b, c, d). For the spectrum type I a t_p is needed in the range from about 50 μ s to 5 ms in dependence on the duration of ht

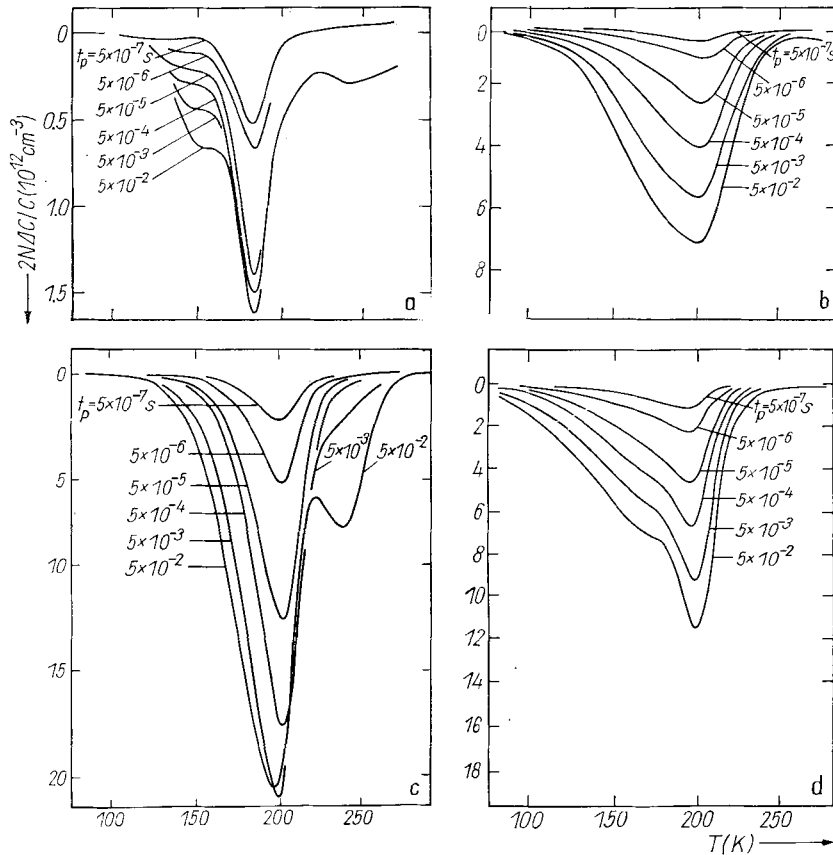


Fig. 3. DLTS spectra of Cz-Si (slice E) in dependence on the filling pulse time for the heat treatments a) 16 h 650 °C, b) 64 h 700 °C, c) 16 h 750 °C, and d) 64 h 750 °C ($e_0 = 2.2 \text{ s}^{-1}$, $U_R = 10 \text{ V}$, $U_1 = 8 \text{ V}$)

to reach saturation in the DLTS signal, whereby in most cases larger t_p corresponds to longer ht.

For the spectrum types II and III, respectively, saturation in the DLTS signal could not be obtained even for a t_p of up to 50 ms. In this case the t_p -dependence was a nearly logarithmic one being characteristic of a barrier-limited capture process [16].

But, in case of spectrum type IV (cf. Fig. 2) saturation has been already obtained for t_p of about 50 μ s.

Therefore, by means of the t_p -dependence the parts of spectrum types described above can be separated for a given DLTS spectrum (cf. Fig. 3 a, d).

Furthermore, the t_p -dependence gives clear evidence that from the characteristic peak the band-like spectrum is going out toward lower temperatures.

A classification of DLTS spectra as type II or III is in some cases not unambiguous, e.g. for E-samples with ht at 700 °C. It cannot be excluded that the type II is only a transition from type I to type III.

3. On the Electrical Parameters of Deep Level Defects

The foregoing discussion gives arguments to the assumption that the defects leading to the DLTS spectrum of type I should be the initial stage for further formation of deep level defects. Therefore, in the following the main attempt is to provide an analysis of the peak-like DLTS spectrum concerning electrical parameters of the corresponding initial dl defect.

It should be noted that the peak is more clearly resolved in the spectrum for shorter ht, which made it possible to perform a detailed investigation of the initial dl defect.

In Fig. 4 the Arrhenius plot for the normalized emission rate e_p/T^2 is given for the DLTS peak measured for E-samples after ht at 750 °C ($t_p = 50 \mu$ s).

From the Arrhenius plot of experimental points it is only possible to obtain an activation energy E_a and an effective capture cross section σ_p^* by $e_p/T^2 = 1.76 \times 10^{21} \sigma_p^* \exp(-E_a/kT)$, (e_p emission rate of holes).

It is assumed that E_a is nearly equal to the deep level energy in the gap $E_T - E_V$.

From the Arrhenius plot E_a was found to range from 0.4 to 0.6 eV. Even though the E_a given for heat-treated Cz-Si are different, it is clear that ht at 600 to 900 °C

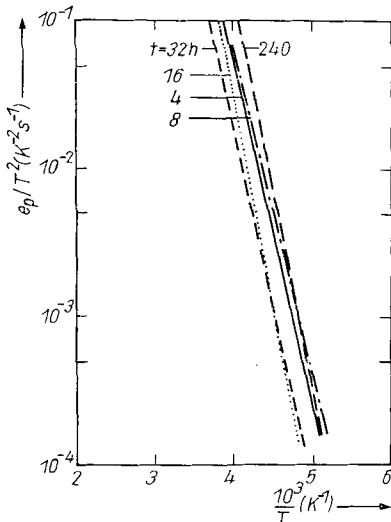


Fig. 4. Arrhenius plot of the DLTS peak for different durations of heat treatment at 750 °C (slice E)

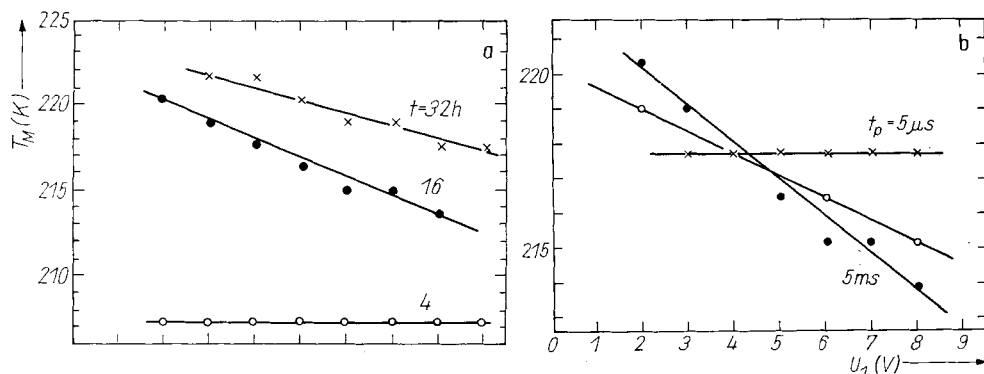


Fig. 5. Dependence of the DLTS peak temperature T_M on the amplitude of the filling pulse U_1 (for slice E): a) for different durations of heat treatment at 750 °C $U_R = 10$ V, $e_0 = 22$ s $^{-1}$, $t_p = 5$ ms, b) after 16 h 750 °C for different filling pulse times $\times t_p = 5$ μ s, \bullet 5 ms and the calculated dependence assuming only Poole-Frenkel effect (\circ), ($U_R = 10$ V, $e_0 = 22$ s $^{-1}$)

gives rise to the same group of dl. More precise values for E_a could not be estimated because the peak temperature T_M for a given rate window e_0 depends on the filling pulse time t_p as well as on the amplitude of the filling pulse U_1 for a given reverse bias U_R .

For shorter ht, i.e. when the sharp DLTS peak dominates the spectrum, T_M is shifted for longer t_p to lower temperatures, but in the case of longer ht for longer t_p to higher temperatures.

The dependence of T_M on U_1 (cf. Fig. 5a, b) obtained after ht at 750 °C for 16 and 32 h, respectively, shows that in contrast to short t_p in the case of a long filling pulse of $t_p = 5$ ms there is a dependence like that which would be expected due to the Poole-Frenkel effect [17]. (The theoretical dependence calculated in one-dimensional model is plotted in Fig. 5b.) However, such an unusual behaviour was not found after a short ht at 750 °C for 4 h (cf. Fig. 5a).

These experimental results could be explained based on the suggestion of ht-induced dl clusters. By the hole capture potential barriers would be formed at such clusters the height of which should depend also on the electric field in the space charge region of the Schottky diode used for DLTS measurement.

Therefore, short filling pulses have to be used for measuring the properties of dl defects. Nevertheless, the values of E_a and σ_p^* obtained in this way are somewhat

Table 4

Parameters obtained for E-samples ($t_p = 5$ μ s)

t at 750 °C (h)	E_a (meV)	σ_p^* (cm 2)
4	440 ± 20	2×10^{-14}
8	430 ± 10	1×10^{-14}
16	520 ± 10	4×10^{-13}
32	510 ± 20	2.5×10^{-13}
64	490 ± 10	1.5×10^{-13}
120	510 ± 5	1×10^{-12}
240	540 ± 15	9×10^{-12}

different, depending on the ht duration (cf. Table 4), what is presumably caused by the different stages of clusters after ht.

A further hint to the suggested cluster formation is the broadening of the DLTS peak at longer ht. In the simplest case peak broadening can be explained assuming a Gaussian distribution of dl energy centered around a mean value E_{a0} in the band gap [18]. In this case from the Arrhenius plot only a mean energy E_{a0} can be deduced. The width of the energetic dl distribution could be estimated from computer simulations for the peak shape. However, the peak shape can be fitted satisfactorily only for shorter ht (cf. Fig. 6). After longer ht an asymmetric shape is characteristic of the DLTS peak.

For the estimation of capture cross section σ_p the DLTS signal was measured as a function of filling time t_p . The experimental points obtained for sample E are plotted in Fig. 7. It is seen that the dependence is a logarithmic one in a wide range of t_p . The experimental results described above suggest that the capture kinetics is more complicated due to the formation of potential barriers. Therefore, the theoretical analysis was performed taking into consideration a barrier-limited capture process [16, 19].

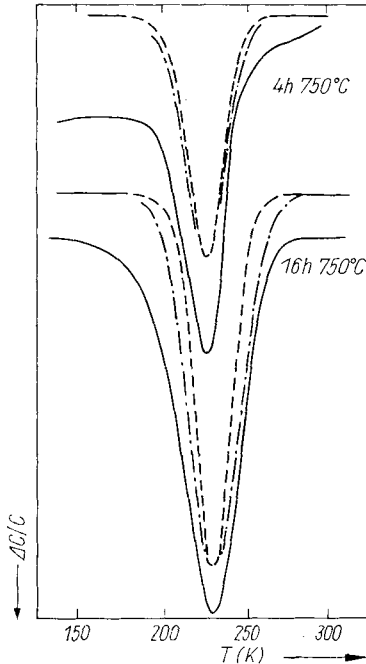


Fig. 6

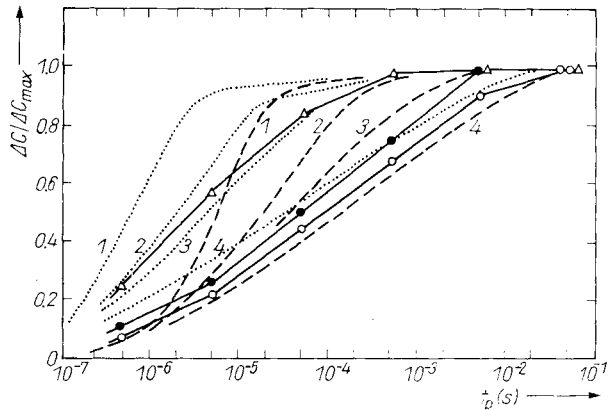


Fig. 7

Fig. 6. DLTS peak shape after heat treatment at 750 °C for 4 and 16 h, respectively, and the calculated shape assuming a Gaussian distribution of deep levels: for 4 h 750 °C: $E_{a0} = 460$ meV, $\sigma_p^* = 5 \times 10^{-14}$ cm², — — — $S = 0$, — · — · — $S = 15$ meV; for 16 h 750 °C: $E_{a0} = 520$ meV, $\sigma_p^* = 4 \times 10^{-13}$ cm², — — — $S = 0$, — · — · — $S = 35$ meV ($e_0 = 220$ s⁻¹, $t_p = 50$ μs, $U_R = 10$ V, $U_1 = 8$ V), S bending parameter

Fig. 7. Dependence of the DLTS-peak amplitude on the filling time t_p (for slice E) for heat treatment at 750 °C (Δ 4, \bullet 16, \circ 32 h) and the calculated plots with the parameters σ_p and α (— — — $\sigma_p = 10^{-17}$, 10^{-16} cm²)(1) $\alpha = 0$, (2) 3, (3) 5, (4) 10

With regard to this, the differential equation for the temporal change of dl occupancy $f(x, t)$ in the charge region is given by

$$\frac{df}{dt} = pc_p e^{-\alpha f} (1 - f) - e_p f,$$

c_p is the capture coefficient, p the concentration of holes, $c_p = \langle v_{th} \rangle \sigma_p$, $\langle v_{th} \rangle$ the average thermal velocity.

In Fig. 7 the simulated t_p -dependence is drawn for a dl with $E_a = 540$ meV and $\sigma_p^* = 10^{-12}$ cm² (corresponding to typical results from Arrhenius plots), for capture cross section $\sigma_p = 10^{-17}$ cm² and $\sigma_p = 10^{-16}$ cm², respectively, and for different parameters α .

It is seen that the experimental t_p -dependences can be well described by theoretical plots with parameters σ_p and α as follows: for 4 h 750 °C — $\sigma_p = 10^{-16}$ cm², $\alpha = 5$, for 16 h 750 °C — $\sigma_p = 10^{-16}$ cm², $\alpha = 10$, for 32 h 750 °C — $\sigma_p = 10^{-17}$ to 10^{-16} cm², $\alpha = 10$.

It is interesting that even in the case of short ht at 750 °C the capture of holes is limited by the formation of potential barriers. For longer ht the fit gives higher values for the parameter α corresponding to the formation of larger defect clusters due to ht.

The provided computer simulations (parameters $E_a = 540$ meV, $\sigma_p^* = 10^{-12}$ cm², $T = 202$ K, and $t_p = 50$ ms) have given the result that for $\alpha \leq 10$ the occupancy of dl after the filling pulse is larger than 0.8. Therefore, in this case it is not necessary to correct the measured effective dl concentrations.

4. Structural Characteristics in the Temperature Range Investigated

Using E-type samples, ht in the temperature range 700 to 850 °C leads primarily to the formation of SiO₂ precipitates being at low temperatures still spherically shaped (e.g., [21, 22]), at least for short durations of ht. With increasing temperature of ht plate-like precipitates [21, 23, 24] with a thickness of a few nm develop nearly independent of temperature and duration of ht [23]. The plate-like precipitates were shown to be amorphous. Precipitate growth is governed by oxygen diffusion; the precipitation rate depends on the sixth to the eight power of the initial oxygen concentration $[O_i]_0$ [22].

An increase in ht temperature in the temperature range 600 to 900 °C leads to (i) an increase of precipitate size, (ii) a decrease of precipitate density, (iii) reaching earlier the equilibrium for precipitation. As an example, respective values for 64 h heat treatment in N₂ (A-type samples) are given in Table 5. The fraction of precipitated volume is estimated assuming 4 nm thick, plate-like precipitates only [23]. The relatively high values in case of A-samples could be attributed mainly to an essentially changed nucleus spectrum, compared to the other material types. Nevertheless, the above-mentioned trends hold also for d-type samples [13] under comparable conditions of ht (64 h ht at 900 °C in N₂, cf. Table 5).

From electron-microscopic investigations a somewhat reduced strain within the silicon matrix (near a precipitate interface) can be deduced after ht at 850 °C (cf. Fig. 8). The reason could be a reduced back stress due to piled-up silicon interstitials Si_i caused by enhanced diffusivity [21]. Those Si_i must be emitted to accomodate the volume increase associated with oxygen precipitation [27] which in turn is facilitated by an enhanced Si_i redistribution.

After long duration of ht the resulting misfit strain at precipitate interfaces increasingly causes dislocation formation (120 h ht, cf. Fig. 8).

Table 5

Typical values characterizing defect formation due to different ht (HVTEM investigations)

ht conditions	sample type [O] _i (10 ¹⁷ cm ⁻³), [C] _s (10 ¹⁶ cm ⁻³)	N_p (cm ⁻³)	L_p (μm)	N_d (cm ⁻³)	fraction of precipitated volume
64 h, 750 °C, N ₂	A (9.0/<1)	7×10^{11}	0.11	increasing	1.7×10^{-5}
64 h, 800 °C, N ₂		2×10^{11}	0.20	*)	2.7×10^{-5}
64 h, 850 °C, N ₂		1×10^{11}	0.60		2.8×10^{-5}
16 h, 900 °C, N ₂	c (14.7/10.5)	3×10^{12}	0.03	2×10^{11}	1.1×10^{-5}
	f (9.1/8.1)	7×10^{11}	0.06	5×10^{11}	1.0×10^{-5}
	i (6.2/35.0)	1×10^{11}	0.04	—	0.6×10^{-6}
64 h, 900 °C, N ₂	d (9.6/<1)	7×10^9	0.75	7×10^9	1.6×10^{-5}
	c	4×10^{12}	0.03	3×10^{11}	1.4×10^{-5}
	i	2×10^9	0.38	—	1.2×10^{-6}
240 h, 600 °C, N ₂	d	4×10^{12}	0.03	2×10^{12}	1.4×10^{-5}
+ 64 h, 900 °C, N ₂	c	9×10^{11}	0.07	2×10^{11}	1.8×10^{-5}
240 h, 800 °C, O ₂	d	4×10^{11}	0.17	1×10^8	4.6×10^{-5}
	i	2×10^{11}	0.05	—	2.0×10^{-6}

N_p : average precipitate density, N_d : average density of dislocation loops (stacking faults included), L_p : mean precipitate size.

*) in the range 10^9 to 10^{10} cm⁻³.

At $T \leq 700$ °C the formation of rod-like (RL) defects dominates [8] which have been identified as a ribbon-like high-pressure polymorph of SiO₂ [25], and being easily transformed into dislocation loops and dipoles, respectively, during subsequent ht at 900 °C [21]. For example after 240 h ht at 600 °C in N₂ in c-type samples a RL density of about 2×10^{12} cm⁻³ is found electron-microscopically.

After a subsequent 20 min ht at 900 °C a RL density of 2×10^{11} cm⁻³ is observed, associated with an increase of dislocation loops (≈ 0.5 μm diameter) from 5×10^{10} cm⁻³ to 1×10^{11} cm⁻³. After 64 h post-ht RL defects are completely dissolved, whereas plate-like precipitates and dislocation loops have been developed (cf. Table 5). Contrarily, in case of d-type material two-step ht leads to a higher density of precipi-

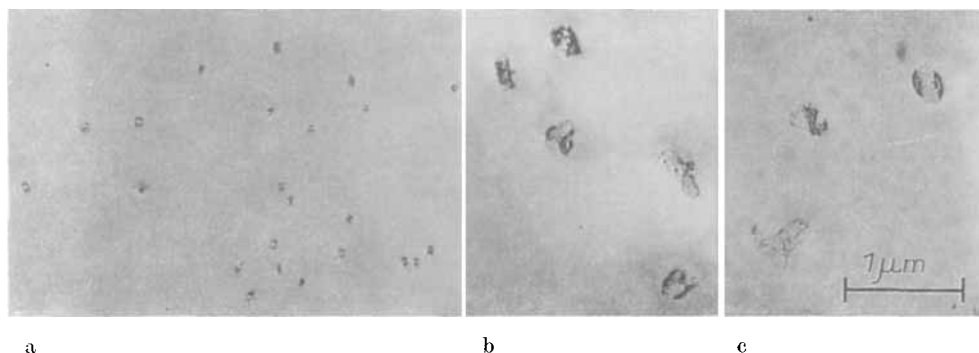


Fig. 8. HVEM image of volume defects in heat-treated Cz-Si (slice A); bright field, diffraction vector $\langle 440 \rangle$ a) heat treatment 64 h 750 °C, N₂; b) heat treatment 64 h 850 °C, N₂; c) heat treatment 120 h 850 °C, N₂

tates as well as to dislocation loops (Table 5). Additionally, stacking faults ($\approx 7 \times 10^{11} \text{ cm}^{-3}$; diameter $\approx 1 \mu\text{m}$) have been generated.

The situation is reversed if only 900°C ht is used. For example, a 64 h ht causes by far more defects in c-type material including stacking faults with a density of $5 \times 10^{10} \text{ cm}^{-3}$ (Table 5). The large precipitates generated in d-type samples under the same ht conditions are partly associated with dislocation loops [13] similar as indicated after 850°C ht (cf. long-time ht, Fig. 8). This phenomenon is discussed below.

The nucleation of oxygen-related precipitates can be homogeneous or heterogeneous (e.g., [21, 29]). Homogeneous nucleation becomes more probable with decreasing temperature of ht, and vice versa.

The maximum nucleation rate is found to be near 750°C [29]. Significant differences in defect formation in dependence on the initial content of substitutional carbon atoms C_s can be explained as being caused by C_s influencing the oxygen nucleation [21, 27, 29]. After 24 h ht at 600°C we find a reduced RL defect density (about one order of magnitude) in d-type samples as compared to c-type material (see above).

This results essentially from an advanced transformation of RL defects into dislocation loops and isolated spherical precipitates mainly collinear with dissolved RL defects [21]. The advanced transformation stage in case of carbon-lean material should be caused by enhanced Si_i supersaturation compared to carbon-rich material. In the latter case, C_s is assumed to interact with Si_i [30] thereby reducing their overall concentration. Therefore, the critical Si_i concentration necessary to collapse into interstitial-type dislocation loops (including stacking faults) is reached relatively early at 600°C with carbon-lean material [21, 27]. These secondary defects, once created act as additional heterogeneous nucleation sites during subsequent ht and, at the same time, as efficient Si_i sinks. Both effects support further oxygen precipitation [31]. Consequently, the observed differences in defect formation in c- and d-type samples after two-step ht ($600^\circ\text{C} + 900^\circ\text{C}$, cf. above) can be explained. At the same time, the differences in defect formation due to 900°C ht only (cf. above) can also be interpreted as being caused by C_s - Si_i interaction.

In carbon-rich material this could lead to a lowering of the critical size of nuclei for precipitation or compensation of the so-called exigent volume at precipitations [27, 31].

Another possibility is a decrease of the nucleus interfacial energy due to carbon [32]. As a consequence in oxygen-rich material an extra-ordinarily high precipitate density in conjunction with strong secondary defect formation is observed (cf. Fig. 9, Table 5).

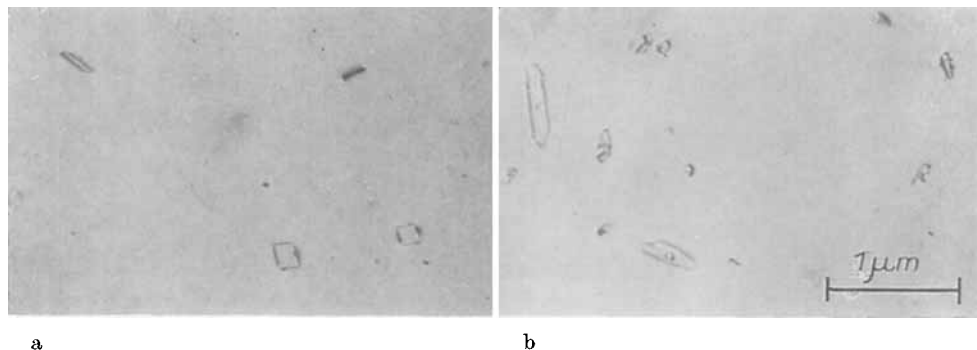


Fig. 9. HVEM image of volume defects in Cz-Si after treatment 16 h 900°C , N_2 ; bright field, diffraction vector $\langle 440 \rangle$ a) slice c, b) slice f

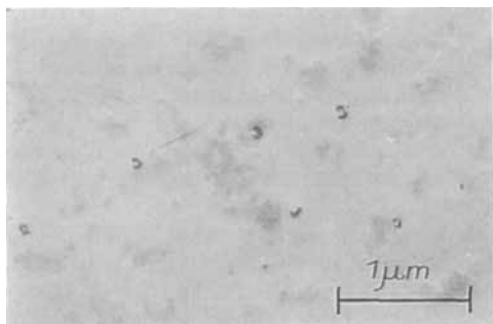


Fig. 10. HVEM image of volume defects in Cz-Si (slice i) after heat treatment 240 h 800 °C, O₂; bright field, diffraction vector $\langle 440 \rangle$

In carbon-lean material precipitation at 900 °C is clearly dominated by growth-induced microprecipitates as indicated by the low precipitate density in d-type samples (cf. Table 5).

Extremely carbon-rich material (i-type) with medium oxygen content shows also a retardation of nucleation (cf. Table 5). Thus, a reduced fraction of precipitated volume in conjunction with a suppression of dislocation loops is observed for ht at 800 and 900 °C (cf. Table 5, Fig. 10).

The growth kinetics (at 900 °C) seems to be totally different, as compared to c-type material (Table 5).

This behaviour can be explained assuming an enhanced growth of relatively large precipitates at the expense of relatively small ones (dissolution after reaching/approaching the equilibrium due to respective O_i-concentration decrease).

5. Discussion

Deep level defects with energies of about $E_T - E_V = 0.4$ to 0.6 eV have been shown to be generated in the temperature range of high oxygen precipitation rate (at 600 to 900 °C). In the existence region of dl defects a great variety of defect spectra (primarily formed precipitates and secondary defects) can occur. The actual defect formation depends not only on the ht conditions used, including also ambient effects, but also on $[O_i]_0$, $[C_s]_0$, and grown-in as well as pre-heat-treatment induced precipitate nuclei. As stated above, the occurrence of secondary defects, as dislocation loops, is not a prerequisite for the generation of dl defects.

On the other hand, the formation of oxygen precipitates should not necessarily result in dl defect generation in the temperature range investigated.

The occurrence of dl defects with sharp energetic distribution is associated with an early stage in the generation of dislocation loops and/or precipitate transformation (ribbon-like low-temperature polymorph, spherical or plate-like precipitate). Such a stage is established under definite conditions of ht and parameters of the Cz-Si used. A common characteristic seems to be a large supersaturation of silicon interstitials Si_i in the surrounding of a growing precipitate.

From that it is concluded tentatively that Si_i are involved in dl defects. They should be located either in the region of highest Si_i supersaturation near a growing precipitate or at the precipitate interface. The simplest case is that of Si_i clusters in the immediate surrounding of precipitate interfaces which grow in size with increasing duration of ht. The formation of dl defects could be supported by back stress due to piled-up Si_i (in addition to the stress arising from misfit strain) at precipitate interfaces.

Thus, stress relief due to the generation of inner Si_i sinks (secondary defects) would cause the Si_i clusters (or Si_i-related clusters) to shrink and, finally, to dissolve.

Maybe, they can also switch over, to some extent, to newly created defects thereby transforming into other electrically active configurations which are energetically stable in the vicinity of certain dislocation core structures. This could be the reason for the strong broadening of the dl energetic distribution at long duration of ht.

The formation and dissolution of clusters assumed would also depend on other Si_i sinks in the Si matrix as, e.g., substitutional carbon atoms. This would explain the observed ht temperature dependence of dl defect concentration in carbon-rich and carbon-lean Cz-Si.

It has to be remarked that results of a recent work of Hwang and Schroder [6] do not contradict the model discussed above. Though their Cz-p-Si samples have similar carbon and oxygen concentrations ($[\text{O}_i]_0 = 9 \times 10^{17} \text{ cm}^{-3}$, $[\text{C}_s]_0 = 7.5 \times 10^{16} \text{ cm}^{-3}$) as the samples investigated in our work, the volume defect spectrum was quite different after 800 °C ht for 96 h. The TEM results have shown in this case a high density of small-sized oxygen precipitates ($\leq 0.01 \mu\text{m}$) with high density in the order of about 10^{13} cm^{-3} , and secondary defects were rarely observed. For this volume defect spectrum DLTS spectra were measured not showing a peak-like structure at higher temperatures of the DLTS spectrum as observed for our samples with an early stage of secondary defect formation, but only a smooth gradual DLTS signal increase toward lower temperatures. From DLTS results and lifetime measurements the authors have concluded that the small-sized oxygen precipitates are mainly responsible for the observed lifetime degradation.

Compared to this proposed electrical activity of small-sized oxygen precipitates for the volume defect spectra investigated in our work the electrical activity should be mainly induced by Si_i -related clusters.

The electrical properties of such Si_i -related clusters would depend strongly on the conditions in the surrounding of the precipitates and secondary defects, i.e. on the induced strain field.

The analysis of the deep level defects in a point-defect model has revealed that the properties of the deep level, as energy position $E_T - E_V$ in the band gap and capture cross section σ_p^* , depend in certain limits on the actual stage of volume defect formation. A longer ht would result in stronger strain in the surrounding of the precipitates with the beginning of secondary defect formation, leading to the broadening of the dl energetic distribution, but on the other hand, also to a locally increased dl concentration causing mainly barrier-limited capture of holes.

A strong secondary defect formation (mainly dislocation loops) is accompanied by a band-like energetic distribution of dl from the characteristic dl with $E_T - E_V = (0.4 \text{ to } 0.6) \text{ eV}$ toward the valence band, this might have been due to the result of the interaction of Si_i -related clusters with dislocation loops or their transformation due to the formation of dislocation loops.

It is necessary to consider that in the case of heat-treated Cz-Si the dislocation induced dl observed for plastically deformed silicon [16, 20] has not been detected. This fact might be a further argument for the proposed origin of dl in heat-treated Cz-Si.

A quantitative analysis of the band-like energetic distribution and the capture cross section of the dl in the case of strong secondary defect formation is difficult due to the fact that DLTS measurement gives only an integral information for the volume under the Schottky contact.

But, TEM investigations have shown that in most cases different stages of secondary defect formation are simultaneously present after longer ht leading probably to energetically different local dl distributions.

It turns out that the formation of a band-like dl energetic distribution appears also in the case of strong secondary defect formation with mainly stacking faults, as recent investigations have shown [33]. Therefore, it is suggested that the electrical properties of Si_i-related clusters measured by means of DLTS in the case of strong secondary defect formation account mainly for the strongly inhomogeneous distribution in the silicon matrix.

The results of the present paper given above might establish a basis for further work in the field of oxygen precipitation induced deep levels toward a better microscopic understanding.

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