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Minority carrier diffusion length measurements in 6H-SiC

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Minority carrier diffusion lengths were measured as a function of temperature and position along the growth axis of lightly nitrogen doped boules of 6H-SiC grown by the physical vapor transport technique. It is shown that the diffusion lengths increase from 1 to 2 microns in the seed portion of the boule to about 4 microns in the tail portion of the boules. Deep levels transient spectroscopy measurements revealed the presence of deep electron traps with the activation energies of 0.35 eV, 0.5 eV, 0.65 eV, and 1 eV. The densities of all these traps decrease when moving from seed to tail of the boules. A good correlation between the change of the lifetime values and the density of the 0.65 eV and 1 eV electron traps was observed. The measured lifetimes show an increase with temperature following a power law that suggests that the hole capture could be determined by cascade capture process. © 2005 American Institute of Physics. [DOI: 10.1063/1.1853501]

I. INTRODUCTION

Silicon carbide is an important semiconductor material with a variety of applications in high-power/high-temperature electronics.¹ For many applications, such as power *p-i-n* rectifiers, power thyristors, bipolar transistors, the control of minority carriers lifetimes, and diffusion lengths is of utmost importance. However, at present the understanding of the recombination mechanisms in SiC is incomplete.

The techniques most widely used to determine the lifetime values in SiC include the measurements of the switching characteristics of the SiC diodes,²⁻⁵ studying their current-voltage characteristics,²⁻⁵ measurements of the relaxation time of photoluminescence or photoconductivity.⁶⁻⁹ Diffusion lengths were most commonly calculated by fitting the dependence of the electron beam induced current (EBIC) signal on electron energy in SiC Schottky diodes and *p-n* junctions.^{9,10} In Refs. 9 and 10 a variant of this method allowing local diffusion length measurements near defect sites was described. Also, Anikin *et al.*⁵ measured the diffusion lengths from the bias dependence of Schottky diodes photocurrent taking into account the known absorption coefficient of the used light.

The results of the measurements show a strong scatter, but some trends are consistent. It appears that for samples grown by the same technique the lifetime values are considerably higher for the 4H polytype than for the 6H polytype.⁶⁻⁸ Also, the lifetimes measured in good quality thick films prepared by chemical vapor deposition (CVD) are by at least an order of magnitude higher than in bulk crystals grown by physical vapor transport (PVT) technique.⁵⁻⁹

The lifetimes of holes in *n*-type material were observed to increase with temperature for temperatures above 300 K.⁵⁻⁸ The diffusion lengths of minority carriers were

shown to decrease dramatically near dislocations and micropipes.^{9,10} The highest room temperature hole lifetimes reported were close to 1 μ s for CVD grown epitaxial layers of 4H-SiC and about 0.4 μ s for 6H-SiC.⁶⁻⁸ For bulk crystals the hole lifetimes were usually lower, from several nanoseconds to some tens of nanoseconds.^{4,5,9,10} The measured diffusion lengths of holes in *n*-SiC vary from below 1 μ m to about 10 μ m.^{2,9,10} For *p*-type samples the lifetimes of electrons are usually quite short, close to 1 ns, and the diffusion lengths are close to 1 μ m.¹⁰

The nature of recombination centers in SiC crystals is not well understood. There is general agreement that recombination proceeds via deep centers in the gap. It has been observed that, for CVD grown material, the lifetimes decrease with increased nitrogen concentration and with increased density of compensating shallow acceptors suggesting that the formation of deep recombination centers could be facilitated by increased concentration of shallow dopants.⁶⁻⁸

The correlation of lifetime data and deep levels spectra [measured by deep levels transient spectroscopy (DLTS)] is not yet complete. Anikin *et al.*⁵ suggested that the dominant recombination centers in 6H-SiC crystals grown by either PVT or container-free liquid phase epitaxy could be the traps located near 0.4 eV and 1.3 eV from the conduction band edge. Combined DLTS and lifetime measurements on CVD grown 4H-SiC epilayers indicate an existence of a correlation between the lifetime values observed and the density of deep electron traps located at 0.65 eV (Refs. 11 and 12) and 1.6 eV below the conduction band.¹¹

However, despite all the previous work it seems that much still has to be done to improve our understanding and control of recombination processes in SiC. For example, it would be very interesting to monitor changes in the minority

carriers diffusion length (MCDL) as a function of material stoichiometry. Such data would indicate whether native point defects such as vacancies and interstitials play an important role in recombination. This report attempts to address this problem by measuring MCDL as a function of position along the crystal growth axis in boules grown by PVT. It is well known that PVT boules are silicon-rich at the initial stages of growth and that crystal composition changes toward stoichiometric or even carbon-rich near the end of the run. Simultaneous measurements of diffusion length values and deep levels spectra on such set of samples could shed additional light on the nature of recombination processes in SiC.

In what follows we present the results of diffusion length measurements carried out using the EBIC technique based on measuring the dependence of the magnitude of the EBIC signal on the distance from the edge of a Schottky diode when moving the electron beam along the surface of the diode not covered with metal toward the edge of the Schottky contact.^{13,14} Deep levels spectra in these Schottky diodes were assessed by conventional DLTS.

II. EXPERIMENT

The studied samples were prepared by slicing two 2-in.-diameter boules grown by physical vapor transport PVT technique.¹⁵ To facilitate the measurements the boule was lightly doped with nitrogen to obtain the electron concentration higher than 10^{15} cm^{-3} along the entire length of the crystal (similarly grown undoped boules were at least in part semi-insulating). Three wafers were cut from different locations along each boule at positions corresponding to 11%, 32%, and 49% of the SiC source material transported for boule 1 and 16%, 25%, and 41% for boule 2 (for brevity in what follows corresponding samples will be called the seed, the middle and the tail samples). Samples for measurements, approximately $7 \times 7 \text{ mm}^2$, were cut from the central parts of the wafers. The samples were mechanically polished, degreased in acetone and methanol, etched for 10 min in 10% HF and rinsed in deionized water. Ohmic contacts were prepared by sputtering Ni and annealing at 950°C for 15 min in forming gas.

Schottky contacts were made by sputtering Ni (total thickness of about 75 nm) using a shadow mask. The diameter of the diodes was 0.75 mm. Current–voltage measurements were done at room temperature using an HP4155B semiconductor parameters analyzer. Capacitance–voltage measurements were performed at 1 MHz using an HP4175A low-frequency LCR-meter.

Deep levels spectra were measured by standard commercial DLTS spectrometer (Sula Technologies) in the temperature range from 80 K to 720 K.

The diffusion length of minority carriers was measured using electron beam induced current (EBIC) technique with the electron beam of the scanning electron microscope (SEM) scanned along the surface of the Schottky diode not covered with metal toward the edge of the Schottky contact.^{13,14} The diffusion length was deduced from the slope of the logarithmic plot of the EBIC signal as a function of the distance from the edge of the Schottky diode. The mea-

TABLE I. Electrical and recombination parameters of the PVT samples studied in this paper; concentration of uncompensated shallow donors $N_d - N_a$, diffusion length L_d , minority carriers lifetime τ , photocurrent at zero volts, I_{ph} .

Sample position in the boule	$N_d - N_a$ (cm^{-3})	L_d (μm)	τ (s)	I_{ph} (A)
Boule 1, seed	1.7×10^{16}	1	5×10^{-9}	6.8×10^{-10}
Boule 1, middle	4.6×10^{15}	1.05	5×10^{-9}	1.02×10^{-9}
Boule 1, tail	2.5×10^{15}	4.5	1×10^{-7}	2.6×10^{-9}
Boule 2, seed	2.1×10^{16}	2	2.1×10^{-8}	NA
Boule 2, middle	1.1×10^{16}	3.3	5.6×10^{-8}	NA
Boule 2, tail	3.5×10^{15}	3.9	7.9×10^{-8}	NA

surements were done by performing line scans in a Phillips XL30 TMP scanning electron microscope SEM. The EBIC signal was processed using a Perkin Elmer 7225 DSP lock-in amplifier. The results presented below are the average over 3 Schottky diodes on each sample. For each Schottky diode the value of the diffusion length was obtained by averaging over 5 linear scans. The temperature of the samples in these measurements could be varied from room temperature to 200°C by varying the temperature of the hot stage on which the samples were placed within the SEM. The surface recombination velocities usually measured in SiC [about $10^3 - 10^4 \text{ cm/s}$ (Refs. 2 and 16)] do not preclude correct determination of bulk MCDL from EBIC.^{13,14}

However, in order to verify the consistency of the obtained results current–voltage characteristics of the Schottky diodes were measured in the dark and under illumination with an UV light source (a fluorescent UV lamp with a filter, model UVL-56, fabricated by Ultra Violet Products, Inc., USA). The light intensity of that source was peaked at 362 nm. That wavelength corresponds to the absorption coefficient of about 10^3 cm^{-1} .¹⁷ The space charge region thickness for the samples used in this study would be below $1 \mu\text{m}$ for applied voltages below 10 V. Hence the photocurrent at low voltages should be proportional to the diffusion length value in the Schottky diode base material.

III. RESULTS

A. I – V and C – V measurements

All Schottky diodes showed good rectification and reverse current values at room temperature below 1 nA at -2 V . The ideality factors in the forward direction were between 1 and 1.1. The reverse current decreased when moving from the seed wafer to the tail wafer, which reflects the change in the concentration of uncompensated shallow donors along the growth direction.

$1/C^2$ versus voltage plots were linear with the voltage intercept value between 1.4 and 1.6 V for all studied samples. This is consistent with the Schottky barrier heights reported for Ni/SiC Schottky diodes.¹⁸ The uncompensated shallow donor concentrations $N_d - N_a$ deduced from the $1/C^2(V)$ plots are presented in Table I (N_d is the concentration of shallow donors, N_a the concentration of all compensating acceptors). It can be seen that, despite the presence of intentional nitrogen doping, the concentration decreases sig-

FIG. 1. Room temperature diffusion lengths measured in the seed, middle and tail portions of the two studied boules (closed squares for boule 1, open squares for boule 2; the ordinate axis presents the portion of the SiC charge transported by the time the studied portion of the boule was grown).

nificantly from seed to tail. This could reflect the change in the number of *C* vacancies available for nitrogen incorporation during growth as the stoichiometry changes from Si-rich at the seed end to C-rich at the tail end of the crystal.^{19,20}

B. Room temperature diffusion length measurements

The results of room temperature diffusion length measurements performed on the seed, middle and tail samples cut from the two boules are presented in Fig. 1. It can be seen that the diffusion length measured in the tail portion of either crystal is higher by a factor of 2–4 than in the seed portion of the crystal. To convert the measured diffusion length values to the minority carriers lifetimes one needs to know the hole mobilities. Analysis in Ref. 21 for *p*-type 6H-SiC samples suggests that the room temperature hole mobility in the material with the ionized centers concentration between 10^{16} cm^{-3} and 10^{17} cm^{-3} (which is the case for the samples studied in this paper) should be close to $80 \text{ cm}^2/\text{V s}$. Using this value the lifetimes of the minority carriers τ were calculated and are shown in Table I.

C. Room temperature photocurrent measurements

The diffusion lengths measurements by EBIC were supplemented for samples from boule 1 by the photocurrent measurements performed on the same Schottky diodes (see Fig. 2 where both the dark current and the photocurrent $I-V$ data are presented). The UV light with $\lambda=362 \text{ nm}$ used in this experiment penetrates at least 10 μm into the 6H-SiC. The total length from which the photocarriers are collected in a Schottky diode in the case of weakly absorbed light is equal to the sum of the thickness of the space charge region and the diffusion length. The measured photocurrent at a given voltage is proportional to this charge collection length. Hence if the ratios of the photocurrents measured in different samples come close to the expected ratios of the charge collection lengths estimated from the known space charge thickness and the measured diffusion lengths this would indicate that the diffusion lengths were measured correctly and the effects of surface recombination velocity were not dominant.

FIG. 2. Room temperature current voltage characteristics measured in the dark (solid lines) and with an UV lamp illumination (dashed lines) for various studied samples, curves 1, 1' are for the tail sample, 2, 2'-for the middle sample, 3, 3'-for the seed sample.

The space charge region thickness at a given voltage can be calculated from the known $N_d - N_a$ values (Table I). At 0 V the space charge thickness (w_d) was $w_d=0.32 \text{ μm}$ for the seed sample, $w_d=0.61 \text{ μm}$ for the middle sample, and $w_d=0.82 \text{ μm}$ for the tail sample. By adding the diffusion lengths measured by EBIC one should obtain the photocurrent values at 0 V normalized to the photocurrent in the seed sample as 1, 1.26, and 4.05 for the seed, middle, and tail samples, respectively. The measured values of photocurrent at 0 V (again, normalized by the value in the seed wafer) were 1, 1.3, and 3.8 in agreement with the EBIC results. This agreement indicates that the impact of the surface recombination velocity is not so strong as to seriously affect the results.

D. The temperature dependence of diffusion lengths and lifetimes

The temperature dependence of the diffusion length measured in the seed, middle and tail samples cut from boule 1 is shown in Fig. 3. The diffusion lengths increased with increasing temperature in all samples. This temperature dependence cannot be due to mobility because the mobility of

FIG. 3. The temperature dependence of the diffusion length in the seed (closed circles), middle (open squares), and tail (closed squares) samples cut from boule 1.

FIG. 4. The temperature dependence of the minority carriers lifetime calculated from the measured diffusion length values for the seed sample (open circles), middle sample (open squares), and tail sample (closed squares), β is the exponent in the temperature dependence of the lifetime ($\tau \sim T^\beta$).

holes in this temperature range decreases with temperature. Hence the effect comes from the increase of the lifetime with temperature.

To determine this dependence one has to make certain assumptions regarding the temperature dependence of the hole mobility. The hole mobility in *p*-SiC for temperatures *T* above room temperature decreases with temperature and can be approximated by power law dependence of the form $\mu \sim T^{-\alpha}$ with α values between 2.5 and 3.3.^{22,23} (For Ref. 22 the quoted value is our estimate based on the data published in the paper.) However, hole scattering in *n*-type material could be rather different than in *p*-type material. Direct measurements of the temperature dependence of the ambipolar diffusion coefficient in 4H *n*-SiC samples suggest a somewhat weaker temperature dependence with the exponent $\alpha = 2$ and the room temperature mobility close to 100 cm²/V s.¹⁶ The structure of the valence band and the effective masses of holes in 4H and 6H SiC are quite similar.²⁴ Based on the above, we assumed that the temperature dependence of the hole mobility is the same as reported by Grivickas *et al.*¹⁶ and that the room temperature hole mobility is 80 cm²/V s (as corrected for the known difference in effective masses between the 4H and the 6H polytypes). The hole mobility μ_h will then be given by the expression

$$\mu_h = 80(T/300)^{-2}. \quad (1)$$

To convert the measured diffusion lengths at different temperatures to the minority carriers lifetime values one can use the standard expression,¹³

$$\tau = L_d^2/D, \quad (2)$$

where *D* is the ambipolar diffusion coefficient that for *n*-type material reduces to $D = \mu_h k_B T / e$. Here k_B is the Boltzmann constant, *e* is the elementary charge, and the hole mobility is given by expression (1). The results are shown in Fig. 4. It can be seen that the double-logarithmic dependence of the calculated lifetimes on temperature is linear with the exponent β in the expression $\tau \sim T^\beta$ close to $\beta = 3-4$.

FIG. 5. DLTS spectra measured on the seed (dashed curve), middle (dashed-dotted curve), and tail (solid curve) samples of boule 1; measurements at reverse bias of -5 V, forward bias pulse of 1 V, 50 ms-long, emission rate window 46.5 s⁻¹.

E. Deep level spectra measurements

Figure 5 shows DLTS spectra measured on the Schottky diodes cut from the seed, middle and tail portions of the SiC boule 1. The ordinate presents the $2(N_d - N_a)\Delta C_{\max}/C$ value which, for the temperatures corresponding to the peaks, represents the concentration of the traps without the so called λ -correction^{25,26} (here $\Delta C_{\max}$ is the spectrometer correlator output corrected for the spectrometer correlator function,^{25,26} *C* is the steady-state capacitance at the given reverse bias, $N_d - N_a$, the concentration given by *C*-*V* measurements). Five electron traps with the activation energies of 0.35 eV, 0.5 eV, 0.65 eV, 0.7 eV, and 1 eV can be clearly seen in the seed and middle samples. In the tail sample only the 0.7 eV and the 1 eV traps could be observed. The concentrations of all the traps were more than an order of magnitude lower in the tail sample compared to the seed and middle samples.

Figure 6 shows similar measurements performed for the seed, middle and tail wafers of boule 2. In all three samples one could observe the electron traps with the activation energy of 0.35 eV, 0.5 eV, 0.65 eV, and 1 eV. The concentration of all detected traps was steadily decreasing when moving from seed to tail.

FIG. 6. DLTS spectra measured on the seed (dashed curve), middle (dashed-dotted curve), and tail (solid curve) samples of boule 2; measurements at reverse bias of -5 V, forward bias pulse of 1 V, 50 ms-long, emission rate window 46.5 s⁻¹.

IV. DISCUSSION

It is well known that the dominant vapor phase species forming upon sublimation of SiC source material in PVT growth are Si and Si₂C molecules.¹⁹ Hence at the beginning of the growth run the PVT grown material is expected to be strongly Si-rich. Toward the end of the process, the source is usually depleted of Si and often partially graphitized indicating that the tail portion of the PVT grown boules should be closer to stoichiometric composition or even C-rich. Hence the concentrations of point defects associated with the Si-rich growth conditions, such as C vacancies and their complexes, should be greatly diminished in the tail portion of the PVT crystals compared to the seed portion.

The minority carriers lifetimes measurements described above invariably show that the lifetimes in the seed portion of the crystal are much lower than in the tail portion of the crystal. The observed changes occur exactly in the same manner as would be expected if the lifetime killer centers were excess-silicon-related defects. This strongly suggests that the defects responsible for recombination of minority charge carriers in 6H *n*-SiC are related to such "Si-rich" defects.

At the same time, the results presented above show that the concentrations of all deep electron traps detected in DLTS measurements decrease dramatically in the tail portion of the boules compared to the seed portion (Figs. 5 and 6). This indicates that the traps seen in DLTS could also be related to Si-rich growth conditions.

Two groups have suggested the Z_{1,2} centers located 0.65 eV below the conduction band to be the dominant recombination centers in CVD SiC material.^{11,12} These defects are known to be so called negative *U* acceptors so that the peak observed in DLTS spectra corresponds to the emission of two electrons and transition between single negatively charged state and single positively charged state $\pm$.^{27,28} The capture of holes to the negatively charged acceptor centers would be expected to follow the cascade capture mechanism that has been shown to have the temperature dependence of the capture cross section for the holes σ_h of the form $\sigma_h \sim T^{-\beta}$, with the exponent $\beta=1-3$.²⁹ From the general expression of the lifetime in the Shockley–Hall–Read model (see, e.g., Ref. 30) one expects the lifetime τ in *n*-type material to be close to $\tau=\tau_{p0}=1/(N_t v_t \sigma_h)$ (N_t here is the density of the traps, v_t is the thermal velocity of holes). It is easy to see that the temperature dependence of the lifetime in that case would be similar to the one shown in Fig. 4. Therefore, the Z_{1,2} traps would be good candidates for the role of major lifetime killers in SiC. The 0.65 eV traps observed in Figs. 5 and 6 above are most likely similar to the Z_{1,2} traps as reported in Refs. 11 and 12. If these traps were indeed the dominant recombination centers one would expect that the hole capture cross section deduced from the measured lifetime values and the measured traps concentration in different parts of the boule would be approximately constant for all samples. Figure 7 presents such a plot of the estimated hole capture cross section versus the position in the boule for boule 2. The cross section was estimated as $1/(\tau N_t v_t)$. The τ values were taken from Table I, the concentration N_t was

FIG. 7. Effective hole capture cross section of the 0.65 eV traps or 1 eV traps calculated as $1/(\tau N_t v_t)$; closed squares and open squares are respectively the results for the 0.65 eV and 1 eV traps in the seed, middle and tail samples of boule 2; if the traps in question are indeed the main recombination centers one expects the cross section to be approximately the same for all samples.

taken from Fig. 5 and multiplied by 2.2 which is the λ -correction for the center near 0.65 eV at -5 V bias,^{25,26} v_t was taken equal to 10^7 cm/s. It can be seen that the capture cross section thus estimated is in fact high, close to 10^{-14} cm², and is, as expected, virtually constant for all three samples. This result is in agreement with Refs. 11 and 12.

However, we should point out that all traps observed in the SiC samples studied in the present paper show similar behavior and most of them would provide similar correlation with the lifetime values (in Fig. 7 we show such data for the 1 eV electron traps for different samples cut from boule 2). Moreover, DLTS measurements performed for various electric field strengths in the space charge region show that the activation energies of the 0.35 eV, 0.5 eV, 0.65 eV, and 1 eV electron traps change very little with applied electric field indicating that all these traps could be acceptors³⁰ (detailed results will be presented in a separate paper). Hence all of these traps could give rise to the observed power-law increase of the lifetimes with temperature and have a high capture cross section for holes.

At the same time, if one considers the results of lifetime and deep trap measurements in different crystals one would have to assume that the capture cross sections for holes should be considerably different for boule 1 and boule 2 (mind also that there are no Z_{1,2} traps in the tail sample of this crystal). This suggests that more than one center could be involved in recombination of nonequilibrium charge carriers in *n*-SiC. The question clearly needs more study. And it should be stressed that DLTS measurements with electrical injection performed on Schottky diodes can only provide information about the upper half of the band gap, whereas the traps in the lower half of the band gap could prove to be equally important. To probe the lower half of the band gap one has to do DLTS measurements with optical injection.²⁶ Such studies are currently underway in our laboratory.

V. CONCLUSIONS

We have shown that the diffusion lengths of minority charge carriers in lightly doped 6H *n*-Si boules grown by PVT increase quite substantially from the seed portion to the

tail portion of the boule. The concentration of the major deep electron traps at 0.35 eV, 0.5 eV, 0.65 eV, 1 eV strongly decreases in the tail portion of the boules. Both effects appear to be related to defects predominant under Si-rich growth conditions. There is a correlation between the density of the major electron traps with the apparent activation energy of 0.65 eV, so-called $Z_{1,2}$ traps, and the measured lifetimes, as suggested in some recent publications (Refs. 11 and 12).

However, a definitive identification of the 0.65 eV traps as the major lifetime killer defects is not possible because other traps observed in DLTS show the same trend in the traps concentration change along the growth direction as the 0.65 eV traps. Experimental results also suggest that more than one center could be involved in recombination of non-equilibrium charge carriers. The measured lifetimes of holes increase with temperature as $\tau \sim T^\beta$ with the exponent β close to $\beta=3-4$ which suggests cascade capture mechanism for holes and indicates the dominant recombination centers to be acceptors. The values of the hole lifetimes measured in the tail portions of the boules are on the order of 0.1 μ s. Since the electron concentration in these samples was in the low 10^{15} cm^{-3} range, such material has a potential for high-voltage devices. It has been noted in the Introduction section above that the lifetimes are generally higher in 4H-SiC. It would be interesting to perform similar measurements on lightly doped PVT grown *n*-SiC of that polytype.

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