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Thermally Stimulated Spectroscopy of Defects and Inhomogeneities in 4H-SiC

Vaidotas KAŽUKAUSKAS*, **Vidmantas KALENDRA, Juozas-Vidmantis VAITKUS**

Semiconductor Physics Department and Institute of Materials Science and Applied Research, Vilnius University, Saulėtekio al. 9, bldg. 3, LT-10222, Vilnius, Lithuania

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We present investigation of carrier traps and their transport in 4H-SiC single crystals and high energy radiation detectors. SiC detectors have been produced from bulk vanadium-compensated semi-insulating single crystal 4H-SiC. They were supplied with a titanium ohmic contact on the back surface and a nickel Schottky contact on the front surface. The prevailing defect levels were revealed by means of the Thermally Stimulated Current (TSC) and Thermally Stimulated Depolarization (TSD) methods and their advanced modification – multiple heating technique. From *I–V* measurements of the samples a barrier height of ~1.9 eV was found. In 4H-SiC:V the following thermal activation values were deduced: 0.18 – 0.19 eV, 0.20 – 0.22 eV, 0.33 – 0.41 eV, and 0.63 eV. The maximum with activation energy of 0.33 – 0.41 eV appears below 125 K and most probably is caused by the thermal carrier generation from defect levels. In contrast, the first two maxima with lowest activation energies, which nevertheless appear at higher temperatures, are likely associated with material inhomogeneities causing potential fluctuations of the band gap. The existence of different polarization sources in different temperature ranges is also demonstrated by TSD.

Keywords: 4H-SiC, charge carrier transport and trapping, defects, inhomogeneities.

INTRODUCTION

SiC is an emerging semiconductor material that is undergoing rapid development for use in high-temperature, high power density applications. Moreover SiC electronics can have unique advantages in nuclear power applications. 6H-SiC and 4H-SiC have a wide bandgap (> 3 eV). Therefore their equilibrium carrier concentration and leakage current are low, specific resistivity at room temperature can be as high as 10^{11} Ωcm, and a breakdown field is up to 3×10^6 V/cm. 4H-SiC is more preferable because of its higher electron mobility. The SiC devices can operate at temperatures up to 700 °C. The response of SiC Schottky high-energy radiation detectors was shown to be linear with thermal neutron fluence rate and gamma dose to better than 5 % over nine orders of magnitude.

On the other hand SiC-based device yield and efficiency are significantly limited by relatively high defect density in material. Electron and hole traps in the forbidden energy gap usually deteriorate their effectiveness due to the trapping of free charge carriers generated by irradiation. Particularly, traps of large capture cross-sections might hinder detector performance. Usually many different levels with quite different parameters are reported by different investigators even in the samples produced and processed by the similar technological process. Therefore, it is essential to investigate such traps in various detectors and develop methods to examine and determine their parameters.

SAMPLES AND EXPERIMENT

We investigated bulk 4H-SiC crystals and radiation detectors on their basis. SiC detectors have been produced from bulk semi-insulating single crystal 4H-SiC, 550 μm thick. A vanadium compensation was used to give very high material resistivities, $\rho > 10^{11}$ Ωcm. The SiC detectors were made in a standard parallel plate configuration by depositing a titanium ohmic contact on the back surface and a nickel Schottky contact on the front surface [1]. To minimise surface leakage effects, a nickel guard ring was used to surround the top contact, coupled with silicon nitride passivation of remaining free SiC surfaces [2]. In so produced detectors the charge collection efficiency by irradiating the samples with α-particles was found to be only about 60 % at the reverse bias voltages up to 600 V [1]. This suggests the presence of defect levels that trap and recombine the charge before it can be collected. A study of the defects in native samples has been therefore carried out.

The prevailing defect levels were identified by means of Thermally Stimulated Current (TSC) method and its advanced modification – multiple heating technique [3]. Samples were excited by white light or by different applied voltages. Such excitation enables one to fill selectively just a part of deep levels, thus enhancing their discrimination possibilities. To reveal influence of the single levels, we used the thermal emptying of the traps by fractional heating. This modification is a powerful tool for the discrimination of the single defect levels in materials with many levels in the band gap. The multiple heating enables the sequential emptying of the initially filled by light excitation shallower levels thus giving the information about the deeper ones in the repetitive temperature scans. In every heating cycle the shallower levels are emptied (fully or partially) from the initially captured electrons that produce an increasing current. The heating cycles were realized by heating and cooling the samples in 10 K steps. After emptying of the previous level the emptying of the next deeper level begins thus giving the information about this level. Defect activation energies were evaluated by numerically fitting experimental curves as demonstrated in more detail in [3]. To reveal the polarization effects we

*Corresponding author. Tel.: +370-672-40208; fax: +370-5-2366003.
E-mail address: *vaidotas.kazukauskas@ff.vu.lt* (V. Kažukauskas)

also investigated the short-circuit Thermally Stimulated Depolarization currents (TSD) of the samples initially excited and polarized by light in the presence of the applied electric field.

To analyse the TSC in a convenient analytical way, we suppose that thermally generated carriers escape fast from the layer when a high electric field is applied to it, so the recombination and re-trapping of the free carriers can be neglected. The kinetics of electron density at the traps may be described by the following differential equation [4]:

$$\frac{dn_t}{dT} = -\frac{vS_n N_c n_t}{\beta} \exp\left(-\frac{E_t}{kT}\right) , \qquad (1)$$

here n_t is electron density at traps of energy E_t below the conduction band, T is temperature, v is electron thermal velocity, S_n is a trap capture cross-section area, N_c is the effective density of states in the conduction band, β is a heating rate, k is Boltzmann constant. Assuming that the initial condition is $n_t(T_0) = n_{t0}$, an exact solution of Eq. (1) is:

$$n_t = n_{t0} \exp\left[-\frac{1}{\beta}\int_{T_0}^{T} vS_n N_c \exp\left(-\frac{E_t}{kT}\right) dT\right] \qquad (2)$$

and an approximate solution is [4]:

$$n_t \approx n_{t0} \exp\left[-\frac{vS_n N_c kT^2}{\beta(E_t + kT)} \exp\left(-\frac{E_t}{kT}\right)\right] , \qquad (3)$$

if vS_nN_c is temperature independent. This approximation enables one to obtain the informative analytical solution and does not give essential quantitative deviation from the exact numerical calculation as compared to experimental errors. Here T_0 is the initial temperature. The current caused by thermally generated electrons is [4]:

$$I = \frac{1}{2} qLAvS_n N_c n_{t0} \exp\left[-\frac{E_t}{kT} - \frac{vS_n N_c kT^2}{\beta(E_t + kT)} \exp\left(-\frac{E_t}{kT}\right)\right] ,(4)$$

here q is electron charge, L is a thickness of Schottky-barrier diode, A is a sample area. T_m denotes the temperature of maximum current. It may be seen from Eq. (4) that at low temperatures, the slope of current in the onset of TSC curve $I \sim \exp(-E_t/kT)$, when the second term of the exponential index is negligible.

RESULTS AND DISCUSSION

In Fig. 1 typical *I–V* curves of the investigated SiC Schottky diodes are presented in the dark and under the white light illumination. In the darkness obtained dependencies are nearly linear in both directions of the applied electric field. Most probably this is because of a very high sample resistivity that causes nearly all applied voltage to drop on the sample volume. Under illumination, as it could be expected, this effect is diminishes significantly and a diode behaviour becomes evident. Current through the device in this case is limited by the sample contacts. From these dependencies a barrier height of ~1.9 eV was found [1]. The TSC spectra of the investigated samples are presented in Fig. 2.

First of all their complicated character has to be pointed out. Moreover, though qualitatively comparable,

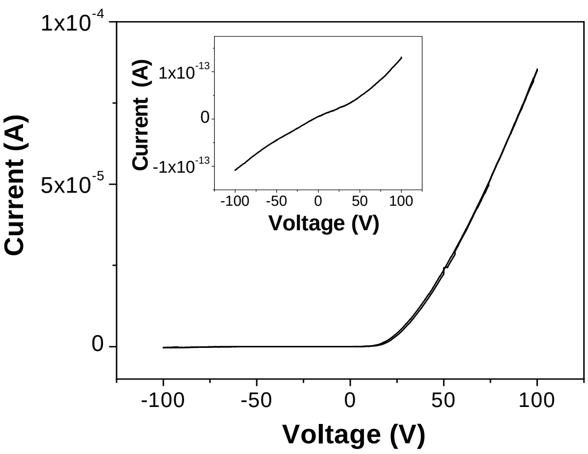

Fig. 1. Typical *I–V* curves of the investigated SiC radiation detectors in the dark (inset) and under the white-light illumination

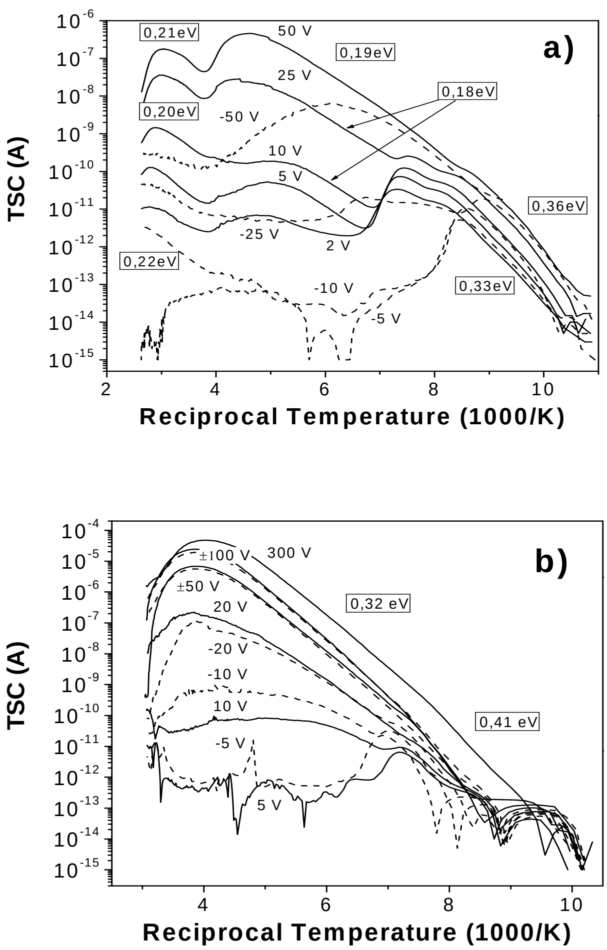

Fig. 2. TSC spectra in two SiC samples at different applied voltages. Solid lines indicate forward biases, and dashed curves mark voltages applied in reverse direction. Nearby the curves the effective thermal activation energy values are indicated

the spectra were nevertheless different even in unirradiated detectors. Meanwhile the dark currents measured in unexcited samples remained significantly lower, as it is indicated in Fig. 3. These differences evidence complex defect structure in investigated crystals, which is significantly influenced by the charge state of the defects. A prominent feature is that in excited samples the form of the TSC curves itself as well as the maxima positions and the effective activation energy values were dependent on the applied voltage polarity and its value. From Fig. 2, a it can be seen that several maxima can be discriminated in the total spectra that behave differently depending on the bias. First of all in the low temperature region of approx. 110 – 140 K a maximum appears, which has an effective activation energy of about 0.33 – 0.36 eV. In the second sample (Fig. 2, b)) similar maximum with activation energy of about 0.41 eV appears at slightly higher temperature on the background of other thermally activated processes. These activation energy values remain unchanged independent on the voltage value and polarity. Meanwhile the height of this maximum is directly proportional to the bias. All these facts are indicators of the thermal carrier generation from the trap level, according to the Eqs. (1) – (4). Similar activation energy values of 0.32 eV for the maximum observed at 118 K and of 0.39 eV for the maximum at 135 K are reported in [5]. They are attributed to the localized dislocation. The 0.32, and 0.39 eV activation energies are close to the 0.35 eV value reported for uncompensated boron dopant activation in SI SiC [6].

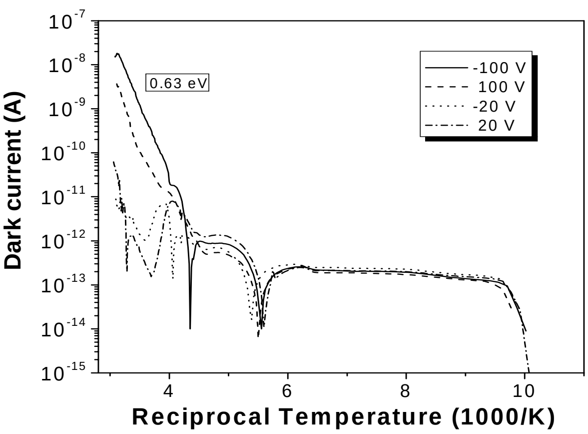

Fig. 3. Temperature dependencies of the dark current in the second sample

The existence of different polarization sources in different temperature ranges is being demonstrated by depolarization current data in Fig. 4. The recharge of the above described level is also causing sample polarization as it is evidenced by the thermal depolarization spectra.

It can be seen that in the temperature region of 110 – 140 K depolarization current depends on the value of the polarizing voltage. Such behaviour seemingly supports the idea, that the defect is not a point-like, but extended in space, as it is in case of dislocations.

At the higher temperatures (above 130 – 140 K) dependence of the depolarization current on the polarizing voltage disappears. Nevertheless TSD spectra still demonstrates a rich structure, though it can be hardly resolved and analyzed in detail. Usually appearance of TSD is associated with spatial inhomogeneities of electrical properties, which can either be introduced upon excitation, or to be a characteristic of material itself. The character of the TSC spectra changes as well (Fig. 2). Their prominent feature at higher temperatures is a highly nonlinear dependence of the current on the applied voltage: the height of the maximum observed at the temperatures of 205 – 220 K changes by up to 7 orders of magnitude by changing the applied voltage from 2 V up to 50 V. The effective activation energy does not remain the same either – it increases with applied voltage up to approx. 50 V, i.e., until the electric field strength becomes about 1 kV/cm.

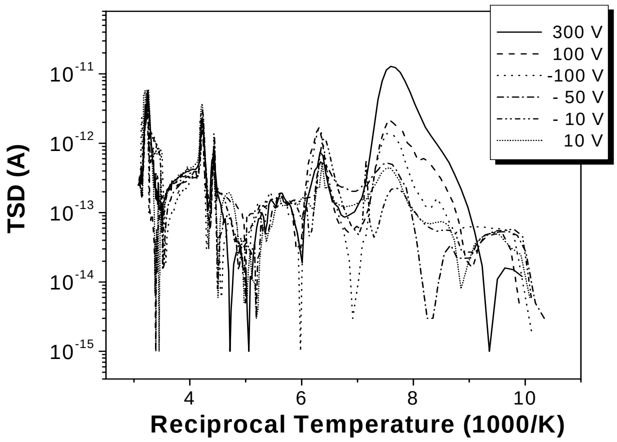

Fig. 4. Thermal depolarization current dependencies on temperature after excitation of the sample by light and applied electric field

In the first sample the saturation value of the effective activation energy is about 0.19 eV, and in the second one – 0.32 eV. Notably, that in both samples these values differ significantly, and, furthermore, that they remain lower than that of the first maxima, observed at lower temperatures. Behaviour of the TSC, described above, cannot be explained within a classical model of homogeneous semiconductor according to Eqs. (1) – (4). Therefore it is plausible that indeed effect of material inhomogeneities leading to the potential relief of the band-gap makes its influence in the observed phenomena. An appearance of different type inhomogeneities is indeed highly plausible in different samples of SiC, because of the complicated structure of the material itself. It is well known, that in SiC, besides its complicated energy band structure, several polytypes can co-exist, depending on technology [7]. Furthermore, compensation usually introduces additional local deviations from stoichiometry due to temperature variation during crystal growth. Because of this energy band relief, excited charge carriers are trapped in potential wells and cannot take part in electrical conductivity. The applied electric field can activate electrical conductivity by capacitating carriers to overcome potential barriers. Otherwise potential relief can be screened by injected carriers. Thermal carrier generation acts alongside, and, therefore, effective thermal generation value does not remain constant. It saturates when at high electric fields transport conditions become favourable for the thermally generated carriers. This model explains the described above decrease of activation energy values with increasing temperature. Indeed, though in principle even in a classical model defect level with lower activation energy can appear at higher temperature due to significant differences in a capture cross section, but in practice such probability is low, because capture cross section appears as a pre-exponential multiplier in Eqs. (1), (4), meanwhile activation energy stands in exponent. Therefore difference in capture cross section should be very large. In the proposed inhomogeneity model such situation be realised because of the different generation and transport mechanisms. E.g., in the case of inhomogeneities which are formed by a large number of atoms, multiple re-trapping can take place that results in a shift of the TSC maxima towards higher temperatures [8]. The model explains also significant scatter of the thermal activation energy values in different samples – from 0.18 eV up to 0.35 eV. This could be due to different average amplitude of the potential relief in different samples.

The TSD curves at the higher temperatures can also be associated with potential inhomogeneities (Fig. 4). Indeed different spatial polarization is possible in inhomogeneous material because of the filling of potential wells. Therefore a complicated character of TSD curves, which cannot be explained within the model of homogeneous semiconductor, most probably reflects not a recharge of single defect levels, but rather is caused by thermal modulation and carrier redistribution in the wells of potential relief. On the other hand the amplitude of TSD current variation, which is up to 10^{-13} – 10^{-12} A, equals or exceeds TSC values, measured at low applied voltages. This causes that TSCs in such conditions are significantly influenced namely by thermal depolarization of the samples.

In order to test the last issue about the influence of potential inhomogeneities we applied the repetitive heating technique. The scans are presented in Fig. 5. It can be seen that during successive thermal cycles effective activation energy values do not change even by the reduction of the TSC current by up to 6 orders of magnitude. This result confirms that indeed the effective activation energy values are given not by a number of carriers flowing along the sample, but rather by the applied voltage, which changes carrier percolation conditions in a network of potential barriers. It might be assumed that applied voltage should change the effective barrier height by a value that is similar to that of its thermal activation value. If all the barriers are supposed to be connected in series, than such evaluation gives that in a sample of about 0.5 mm thick there should be approximately 130 – 290 barriers, i.e., the mean dimensions of inhomogeneous regions should be 1.5 – 3.8 μm, what is close to the real values [9].

Different properties of different defect types observed at lower and at higher temperatures are evidenced also by photocurrent temperature dependencies (Fig. 6). These dependencies were measured using white light illumination with different intensities. It can be seen, that in the low temperature region, photocurrent does not change at low intensities. Afterwards it starts growing proportionally to the light intensity. In contrast, at higher temperatures the steep photocurrent increase takes place namely at the lowest light intensities; afterwards it saturates. Such behaviour confirms that carrier generation and transport conditions are different in different temperature regions. It can be assumed that at higher temperatures photoconductivity increases because light-generated carriers smooth the potential relief, improving carrier percolation conditions.

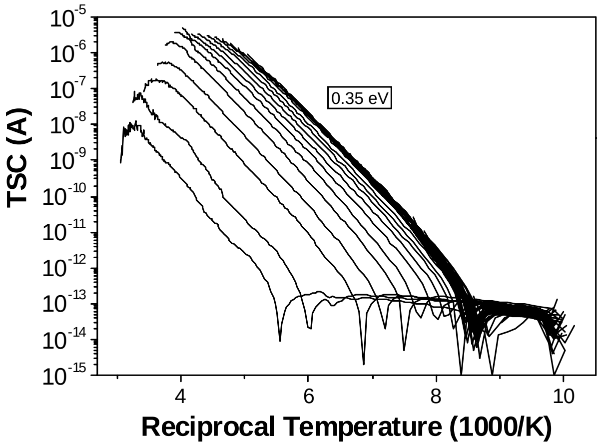

Fig. 5. Results of the TSCs in the repetitive heating regime at 50 V applied voltage

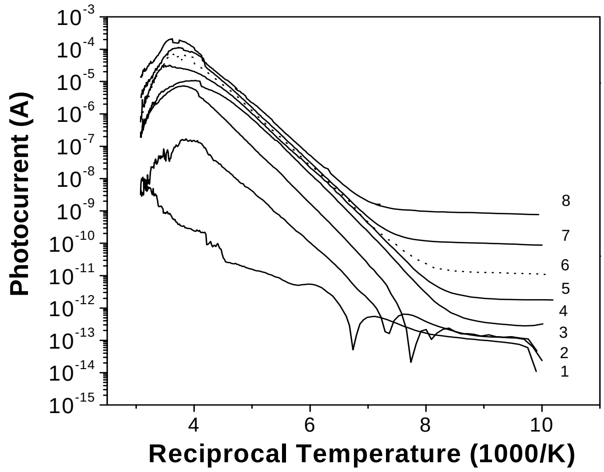

Fig. 6. Dependence of the photocurrent on temperature at different incident light intensity. The relative light intensity increases by a factor of approx. 9 starting from the lowest curve numbers

And, finally, near the room temperature, a growth of the dark current is observed (Fig. 3), which has thermal activation energy of about 0.63 eV. It can be attributed to the carrier generation from the defect level with similar activation energy. A level with similar activation energy was reported in [10]. It was attributed to Carbon vacancy [5], Carbon interstitial-nitrogen complex, or Silicon vacancy [10]. Pintilie et al. [10] discuss a defect with activation energy at 0.66 eV; this is a comparable energy to the 0.63 eV defect observed here. They have attributed this primarily to a carbon interstitial-nitrogen defect which is influenced heavily by the concentration of nitrogen and the C/Si ratio in the growth process. Many other defects have been reported for Semi-Insulating SiC which we did not observe in our samples [11, 12]. E.g., in [12] at 260 K a level at 0.92 eV was reported, and it was attributed to Vanadium activation.

CONCLUSIONS

Investigations of 4H-SiC:V crystals and ionising radiation detectors by means of thermally stimulated current spectroscopy and current-voltage techniques had proven the simultaneous effect of several physical phenomena on material transport and trapping properties.

The deduced thermal activation energy values of current (0.18 – 0.19 eV, 0.20 – 0.22 eV, 0.33 – 0.41 eV, and 0.63 eV) could be related either to the thermal generation of carriers from deep traps or to potential fluctuations of the band gap modifying carrier transport. The TSC maximum having effective activation energy of 0.33 – 0.41 eV might be ascribed to the thermal carrier generation from defect levels. Therefore it appears at relatively low temperature below 125 K. Meanwhile the first two maxima with lowest activation energies are likely associated with material inhomogeneities causing potential fluctuations of the band gap. As a result they are observed at higher temperatures. This conclusion is based on the fact that the current value as well as the form of the TSC spectrum markedly and nonlinearly depend on applied voltage. The observed peculiarities of TSCs could not be explained by a homogeneous semiconductor model, confirming significant influence of spatial inhomogeneities. The existence of different polarization sources in different temperature ranges was also proved by TSD.

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