On the temperature dependence of the electron capture cross-section of the E3 deep level observed in single crystal ZnO

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Abstract. We report on the temperature dependence of the capture cross-section of the E3 deep level defect observed in single crystal ZnO samples. Temperature dependent deep level transient spectroscopy reveals an increase in the DLTS peak height with an increase in the rate window frequency for the E3 level which is a proof that the E3 deep level has a temperature activated capture cross-section. However the observed capture rate is not constant during the filling pulse but depends on the occupancy of the defect itself. This phenomenon is in contradiction with what is expected of an ideal deep level.

1. Introduction

ZnO is a wide and direct bandgap semiconductor with experimental bandgap energy of about 3.4 eV. Deep level transient spectroscopy (DLTS) measurements performed on differently grown ZnO crystals reveal the presence of the E3 deep level defect with an activation enthalpy of between 0.29 eV and 0.31 eV and an apparent capture cross-section of 5×10^{-16} cm^2 to 10^{-14} cm^2 [1, 2, 3, 4, 5, 6]. However its ionisation energy as well as its energy barrier for electron capture is not known yet, whereas in established semiconductors such as GaAs and Si, capture barrier energies for most defect levels are well known. The capture barrier is usually obtained using emission rate DLTS scans and varying the filling pulse width as suggested by Henry and Lang [7]. A second method which uses DLTS rate window scans with short filling pulses (less than 10 μs) has been employed by Zhao *et al.* [8], Criado *et al.* [9], Telia *et al.* [10] and Cavalcoli *et al.* [11]. In this paper, we report on the electronic properties of the E3 deep level in a bulk single crystal ZnO sample obtained from Cermet Inc.

2. Sample preparation

In preparation of the DLTS measurements, crystal cleaning was performed as in reference [12]. Ohmic contacts with a composition of Al/Au were deposited on the O-polar face using the resistive evaporation technique at a pressure of approximately 10^{-6} Torr. Finally, Iridium Schottky contacts with a diameter of 0.5 mm and thickness of 100 nm were electron beam deposited onto the Zn-polar face under vacuum at a pressure of approximately 10^{-7} Torr.

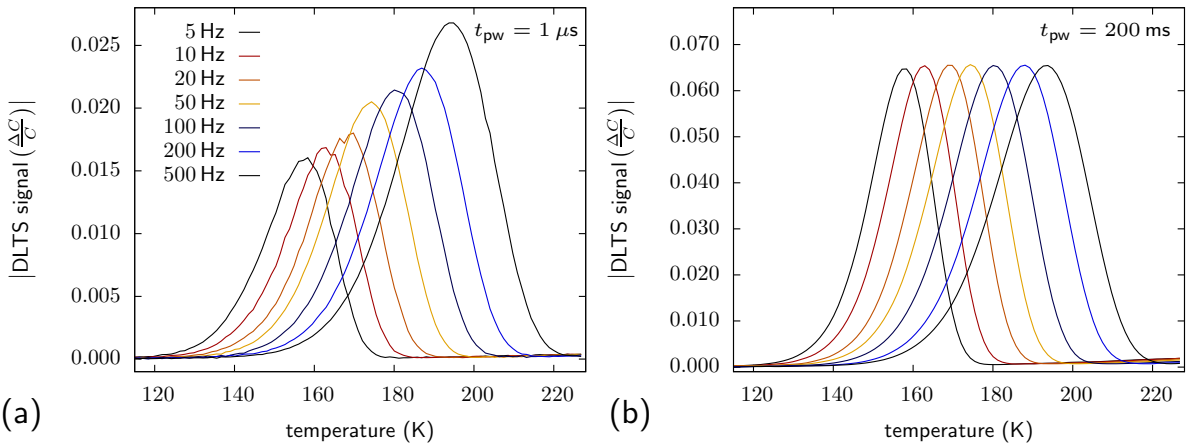

Figure 1. The E3 peak in deep level transient spectroscopy temperature scans conducted at different rate window frequencies using 1 μs filling pulses (a) and 200 ms filling pulses (b) that flattened the bands. During the recording of the capacitance transients the sample was reverse biased at 2 V.

Current voltage measurements at room temperature confirmed that the sample was suitable for DLTS measurements and a net doping density of $N_{\mathsf{net}} = 4.6 \times 10^{16}\,\mathrm{cm}^{-3}$ was obtained from CV measurements using the van Opdorp analysis [13].

3. Results and discussion

Emission DLTS rate window scans were performed in the dark in a closed cycle helium cryostat and revealed the presence of the E3 deep level, as shown in Figure 1. Arrhenius analysis[1] of the temperature dependence of the thermal emission rate of the E3 level yielded an activation enthalpy of 0.30 eV and an apparent capture cross-section of $10^{-14}\,\mathrm{cm}^2$. It was observed that the spectra differ depending on the filling pulse width (t_{pw}). For $t_{\mathsf{pw}} = 1\mu$s filling (Figure 1(a)), the DLTS peak height increases with an increase in rate window frequency, whereas for long enough filling pulse widths (Figure 1(b)), the peak height was constant for all rate window frequencies. The variation of the DLTS peak height with chosen rate window frequency for the E3 deep level has previously been observed but to the best of our knowledge, no explanation was given. In the following we are going to shed some light on this observed effect. The DLTS experiment allows one to prepare an initial probability to find a defect state occupied by an electron, q_{in}. This is achieved by the application of a filling pulse and monitoring the capacitance transient afterwards. The DLTS signal peak height, $\Delta C/C$ is related to the trap concentration N_{t} and the difference in the occupancy probabilities by,

$$\frac{\Delta C}{C} = -\frac{N_{\mathsf{t}}}{2N_{\mathsf{net}}}\left(q_{\mathsf{fin}} - q_{\mathsf{in}}\right) \tag{1}$$

where q_{fin} is the final occupation probability. The differential equation for the time evolution of the occupancy probability $q(t)$ of a defect state is [14]

$$\frac{\mathrm{d}q(t)}{\mathrm{d}t} = c_{\mathsf{n}}\left[1 - q(t)\right] - e_{\mathsf{n}}^{\mathsf{th}} q(t). \tag{2}$$

[1] ZnO effective mass: 0.27 m_{e}

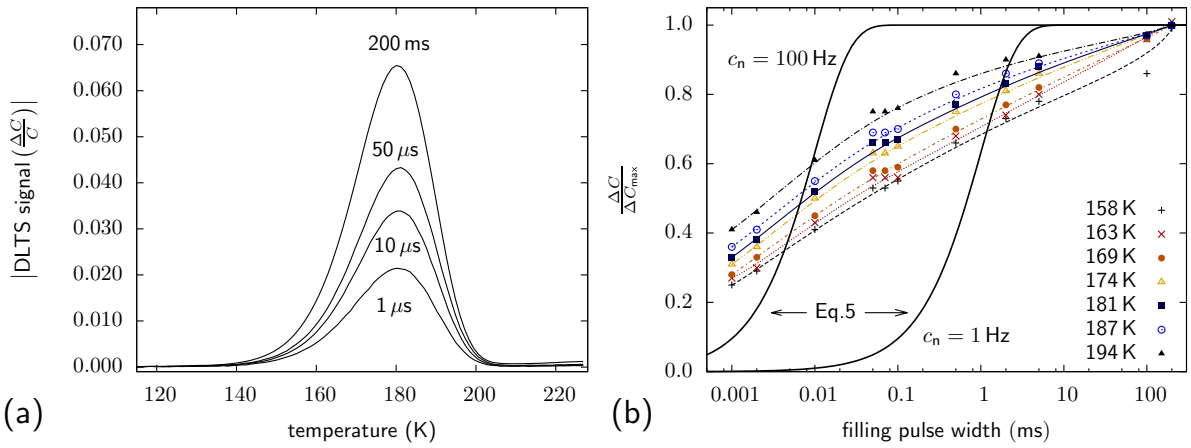

Figure 2. a) Dependence of the E3 DLTS peak height on filling pulse width t_{pw} at a rate window frequency of 100 Hz. b) Symbols represent the variation of the measured, normalised DLTS peak height with filling pulse width and sample temperature. The black solid lines are the graphical representation of equation 5 assuming a constant capture cross-section during the filling process.

c_n denotes the thermal capture rate for electrons and its temperature-dependence is given by

$$c_n(T) = \sigma_n(T) \langle v_{th} \rangle (T) n(T) = \sigma_n^{\infty} \exp\left(-\frac{E_b}{k_B T}\right) \langle v_{th} \rangle (T) n(T) \tag{3}$$

where E_b is the barrier for electron capture, $\langle v_{th} \rangle (T)$ is the thermal velocity of electrons and n is the free electron concentration available for capture. Since at a particular temperature, c_n is considered to be a constant and assuming that during the filling process, $e_n^{th} \ll c_n$, the solution of equation 2 is given by

$$q(t) = 1 - \exp(-c_n t). \tag{4}$$

Thus, equation 1 can be written as,

$$\frac{\Delta C}{C} = \frac{N_t}{2N_{net}} (1 - \exp[-c_n t_{pw}]) \tag{5}$$

since for the maximum DLTS peak height, $q_{fin} \approx 0$.

In the light of this, we studied the filling process of E3 by varying the filling pulse width at fixed rate window frequency. The results are presented in Figure 2(a). As expected, the DLTS peak height increases with increasing filling pulse width as well as increasing temperature, Figure 2(b). However this increase is not in accordance with equation 5 and therefore the Henry and Lang approach [7] cannot be applied. In particular, the slope of the measured, normalised DLTS peak height versus filling pulse width plot is less steep compared to the one predicted by equation 5. A suggestion of this is as follows.

Since every solution of equation 2 must be exponential if c_n and e_n^{th} are constant, only a change of c_n during the filling process can explain our observations. According to equation 3, this change can be attributed to either a decrease in σ_n (at the same temperature) or a decrease in n in the vicinity of the defect while it is being filled. The first possibility might originate from defect-defect interaction which cannot be excluded at doping levels of $N_{net} = 4.6 \times 10^{16}\,\mathrm{cm}^{-3}$. The latter, which to our opinion might be more probable, is due to the charging up of grain

boundaries. This results in a double Schottky barrier and therefore a depletion region which lowers the local electron density [15]. Further investigations and analysis are required and will be performed.

4. Conclusions

In conclusion, the electron capture of the E3 deep level in ZnO was studied in detail by DLTS. The capture process cannot be described by a single exponential filling of the defect state, as would be the case for a simple capture barrier of an isolated point defect. Due to this difficulty, the capture barrier could not be obtained from emission DLTS rate window scans with varying pulse widths without employing a more involved analysis. Furthermore there is a high uncertainty associated with the high temperature limit of the capture cross-section obtained from standard Arrhenius analysis which is frequently reported.

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