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Electronic properties of defects in pulsed-laser deposition grown ZnO with levels at 300 and 370 meV below the conduction band

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Abstract

We have used deep level transient spectroscopy (DLTS) to characterize defects in ZnO grown by pulsed-laser deposition (PLD). Using high resolution Laplace DLTS, we found that at the high temperature side of the commonly observed defect E3 (about 300 meV below the conduction band) another close lying peak (E3′ with thermal activation energy of 370 meV) is also observed. The concentration ratio of E3 and E3′ depends on the annealing history of the samples. It is most prevalent in as-grown samples and samples that had been annealed in an oxygen atmosphere. This suggests that E3′ may be related to the incorporation of oxygen in the lattice. Electron capture onto that E3′ defect strongly increases with increasing temperature.

Article Outline

1. Introduction
2. Experimental procedure

1. Introduction

ZnO is a semiconductor with a bandgap of 3.4 eV and has a number of properties that render it suitable for electro-optical applications [1]. It has recently become the focus of many studies, since a wide range of applications are possible due to its direct and large bandgap [2]. Devices such as detectors, lasers and diodes operating in the blue and ultraviolet (UV) spectrum have been reported [3], but are not very efficient yet. As in all semiconductors, defects play an important role in optimizing the characteristics of devices. Although the defects in bulk-grown ZnO have been studied in some detail by deep level transient spectroscopy (DLTS) [4] and [5], much less is known about the defects present in ZnO grown by pulsed-laser deposition (PLD).

In this contribution, we report the electronic properties of two defects, E3 and E3′, in PLD-grown ZnO with DLTS peaks in the 160–190 K temperature range. In the case of bulk-grown ZnO, only one of these defects, the E3 defect with an energy level at E_C=300 meV is present [4] and [5]. We show that electron capture onto the E3′ defect in PLD-grown ZnO, with an energy level at E_C=370 meV, increases strongly with increasing temperature.

2. Experimental procedure

High-quality Pd/ZnO Schottky diodes were realized on ZnO thin films grown heteroeptaxially on a-plane sapphire substrates by PLD. First, a 50 nm thick n^{++} ZnO:Al layer was deposited. The main layer, with a thickness of 1 μm, deposited on top of the n^{++} layer, is nominally undoped and was grown at a temperature of 650 °C at an oxygen partial pressure of 0.016 mbar. Some samples were annealed *ex situ* for 2 h at 750 °C, either in oxygen, nitrogen (700 mbar) or in vacuum prior to metal deposition. Circular

Schottky contacts, having areas ranging from 4×10^{-4} to 5×10^{-3} cm^2, were realized by thermal evaporation of Pd on the top, nominally undoped, ZnO layer. On part of the sample, the top, undoped layer was removed and the n^{++} ZnO:Al layer was contacted by sputtering Au onto it to serve as an ohmic back contact [6].

We have used DLTS as well as high-resolution Laplace DLTS [7] and [8] to characterize the defects in this ZnO. In this study, we concentrated on the defects that have DLTS peaks in the 160–190 K temperature range.

3. Results and discussion

In Fig. 1, we depict DLTS spectra of PLD-grown ZnO annealed under different conditions (curves (a)–(d)), as well as of bulk-grown ZnO (curve (e)). In the nomenclature used to index the peaks, "E" means that it is an electron trap and the subscript of "E" is the energy level of the defect below the conduction band, in meV. Note that, except the E3 (E_{300}), none of the seven defects observed for the PLD grown ZnO, are observed in bulk-grown ZnO. Here, the E_{300} defect is the same as the previously reported E3 defect for bulk-grown ZnO [4] and [5].
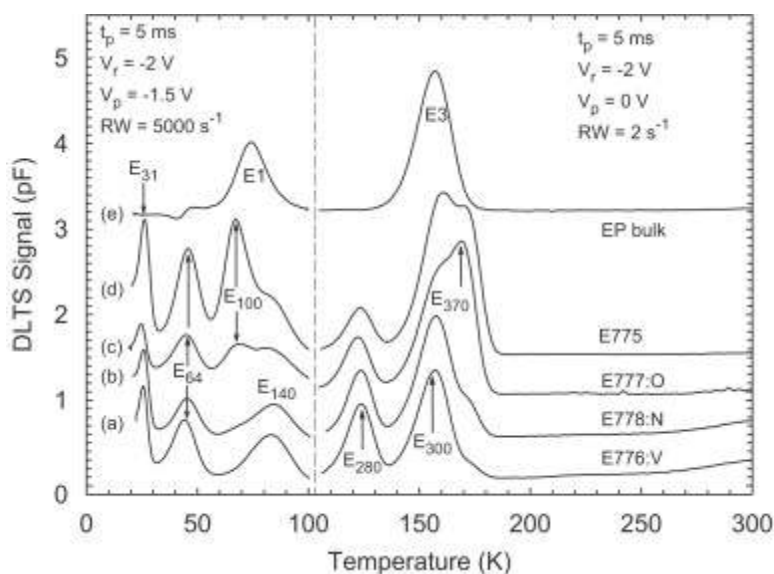

Fig. 1. DLTS spectra of ZnO grown by PLD (curves (a)–(d)), and bulk ZnO (curve (e)). Curves (a)–(c) are for PLD-grown ZnO annealed in vacuum, nitrogen and oxygen,

respectively, under conditions specified in the experimental procedure. All curves were recorded at a reverse bias of 2 V, and a filling pulse amplitude and width of 2 V and 5 ms, respectively. Spectra below and above 100 K were recorded at rate windows of 5000 and 2 s^{-1}, respectively.

The defects E_{31}, E_{64}, E_{140}, E_{280} and E_{300} are found in all PLD samples studied here, regardless of the annealing conditions. E_{100} and E_{370}, on the other hand, are only clearly observed in unannealed samples and samples that had been annealed in oxygen. This may mean that they are related to the presence of oxygen because the samples were grown under a partial oxygen pressure. Similar results have been reported after analyzing the same samples by thermal admittance spectroscopy (TAS) [9].

We have previously shown that E_{100} displayed metastable behavior [10]. Annealing under reverse bias at temperatures above 130 K introduces it while annealing under zero bias above 110 K removes it. These introduction and removal processes are completely reproducible. We have determined the introduction and removal kinetics of this defect by isothermal and isochronal annealing cycles. We have found that the introduction and removal processes follow first and second order kinetics, respectively [10].

We have also found that emission from E_{64} and E_{140} was strongly enhanced in the presence of an electric field [10]. In particular, they displayed typical Poole–Frenkel behavior [11] in an electric field, suggesting that E_{64} and E_{140} may be donors. In this regard, it is noteworthy that E_{64} is most likely the Al_{Zn} donor because it is most clearly detected by DLTS in the highest concentrations where the ZnO layer is grown on a heavily Al-doped layer on the sapphire. The Al can then diffuse into the undoped ZnO layer during growth and subsequent annealing. This identification is supported by Meyer et al. [12] that report the donor binding energy of the Al_{Zn} donor as 51.55 meV. Next, we focus on the defects E_{300} and E_{370}. With conventional DLTS, it is possible to distinguish between their peaks only for specific combinations of the filling pulse width, t_p, and rate window, RW. In Fig. 1, this is shown for t_p=5 ms and RW=2 s^{-1}. If t_p is kept constant and RW increased, we have found that E_{370} increased but that E_{300} remained

about the same size. This means that the ($E_{300}+E_{370}$) peak appeared to be a single, slightly asymmetric peak consisting primarily of E_{370}. On the other hand, if the RW was decreased while the pulse width remained the same, the height of E_{300} again remained the same but the height of E_{370} decreased. This again rendered a single-looking DLTS peak, but this time containing mostly E_{300}. If the RW was kept constant at 2 s^{-1} and the pulse width was decreased, the combined peak consisted mostly of E_{300}. Conversely, if the pulse width was increased while the RW was kept at 2 s^{-1}, the combined peak consisted primarily of E_{370}. These observations depended critically on the choice of the values of the pulse width and RW because of the limited ability of conventional DLTS to distinguish between closely lying energy levels.

In order to more clearly illustrate this RW/temperature-dependent peak size of E_{370}, we have applied high resolution Laplace DLTS [7] and [8] to the E_{300} and E_{370} peak combination. Note that Laplace DLTS is an isothermal technique. The results of measurements at temperatures of 165, 175 and 185 K are depicted in Fig. 2. For all three temperatures, the individual contributions of E_{300} and E_{370} are clearly separated after performing the inverse Laplace transform. The small feature to the right of the E3 peak in the 175 and 185 K spectra is a measurement artifact related to noise.
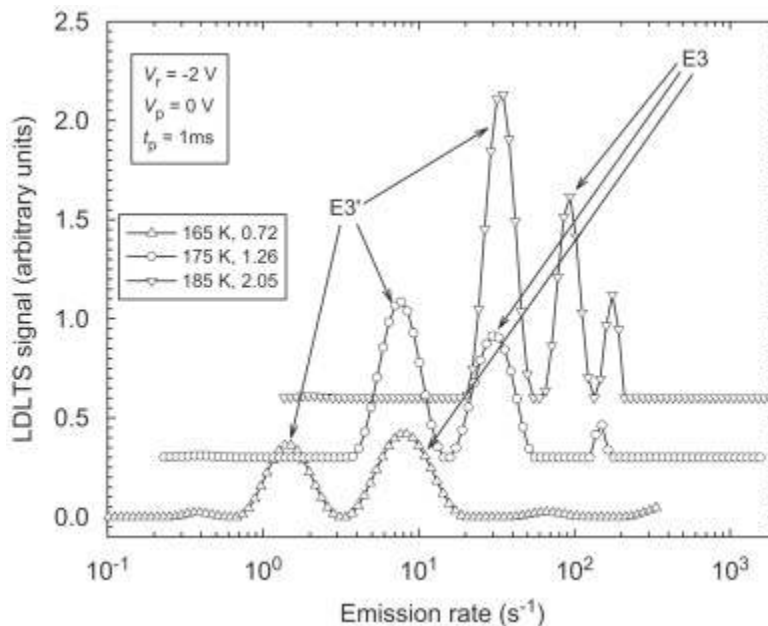
Fig. 2. Laplace DLTS spectra of the E3 (E_{300}) and E3′ (E_{370}) defects in PLD-grown ZnO at temperatures indicated in the inset. The second column in the inset gives the ratio of the peak heights of E3′ to E3 at different temperatures.

In the inset of Fig. 2, we have also tabulated the ratio of the peak heights of E_{370} to E_{300} next to the temperature. It is clear from this table that this ratio increases with increasing temperature, from 0.72 at 165 K to 2.05 at 185 K. It was found from these measurements that this increase is mainly due to an increase in the height of E_{370}; the height of the E_{300} remained essentially constant for these three measurement temperatures.

The Laplace DLTS measurements also allowed for the construction of accurate Arrhenius plots for E_{300} and E_{370} as shown in Fig. 3. Note that for all temperatures between 160 and 190 K, the DLTS peaks could clearly be separated, yielding accurate values for the activation energy and apparent cross-section, as tabulated in Table 1. The E3 (E_{300}) level measured here is the same as that of the E3 defect measured in bulk-grown ZnO [4] and [5]. The E3′ (E_{370}) defect has not been reported for any bulk-grown ZnO and has only been seen in PLD-grown ZnO.
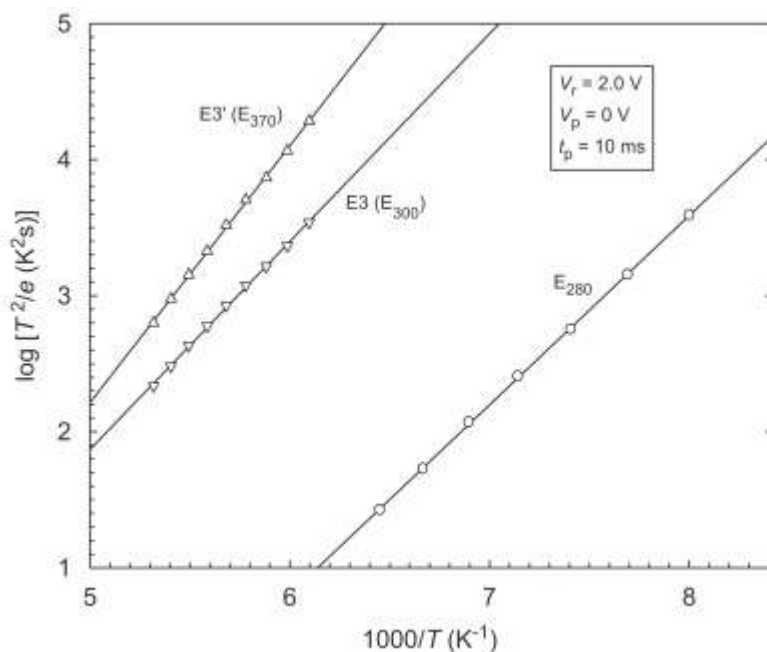

Fig. 3. Arrhenius plots of the E_{300} and E_{370} levels, together with the E_{280}, constructed using Laplace DLTS with conditions as indicated in the inset.

Table 1.

Electronic properties of the E3–E3′ defect pair in PLD-grown ZnO measured by Laplace DLTS

Defect	E_T (meV)	σ_a (cm^2)	T_{peak}[a] (K)
E3/E$_{300}$	300	2×10^{-16}	182
E3′/E$_{370}$	370	7×10^{-15}	190

[a] Peak position at a RW of 80 s^{-1}.

Next, we have performed high resolution Laplace DLTS on the E$_{300}$ and E$_{370}$ using variable pulse widths. The results of these measurements are shown in Fig. 4 for the E3 (E$_{300}$) and E3′ (E$_{370}$) defects at temperatures of 165, 175, 185 and 195 K. Because the peak heights of the E3 for these temperatures are the same within the measurement accuracy, only the trend for 165 K is shown for E$_{300}$. It can be seen that there is little variation in the peak height of E$_{300}$ with temperature for changes in the filling pulse between 2×10^{-5} and 8×10^{-1} s. Also, for a given filling pulse width, there is little variation in the pulse height of E$_{300}$ with changing temperature. This is typical for a point defect with a temperature independent capture cross-section.
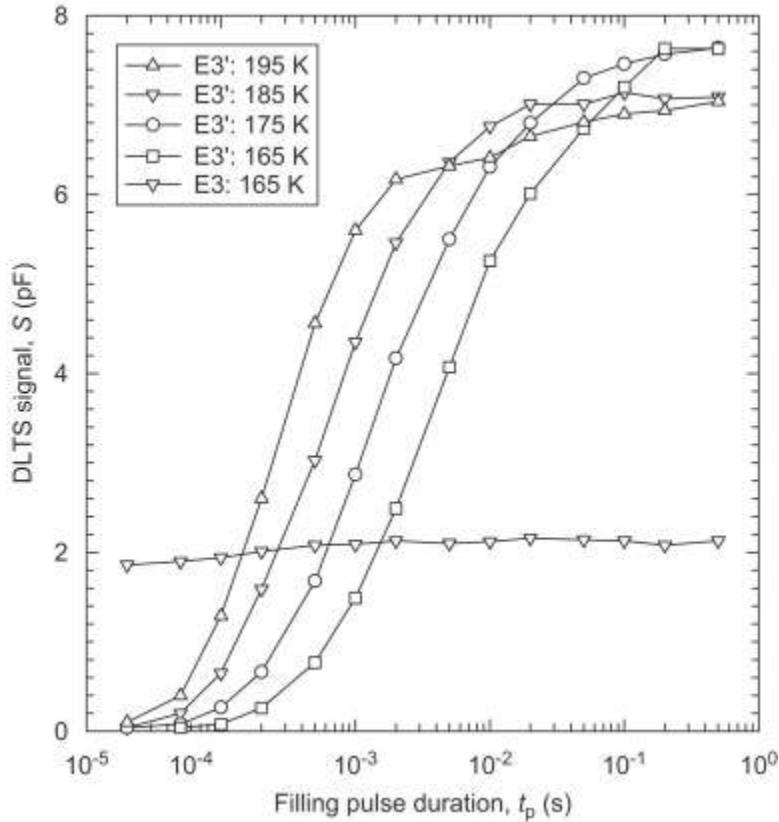
Fig. 4. Peak heights of the E3 (E_{300}) and E3′ (E_{370}) peaks measured by Laplace DLTS as a function of filling pulse duration for different temperatures as indicated in the inset. The defect E3′ (E_{370}) on the other hand, displays a strong dependence on filling pulse duration and temperature. For a given pulse filling width, the peak height of E_{370} increases strongly with increasing temperature (Fig. 4). For example, at a temperature of 165 K (which more or less corresponds to the peak temperature of E_{370} in Fig. 1), its height increases by a factor of about 40 if the pulse width is increased from 200 μs to 200 ms, i.e. in the typical range of pulse widths used for DLTS. Also, for a typical DLTS pulse width of 1 ms, the E_{370} peak height increases from 1.6 to 6 pF if the measurement temperature increases from 165 to 195 K.

The data above indicates that electron capture onto E_{370} is strongly temperature dependent. This behavior is often associated with a defect that has a capture barrier for carrier capture. This barrier can be calculated by determining the capture cross-section, $\sigma(T)$, as a function of temperature and then constructing an Arrhenius plot of $\log[\sigma(T)]$ vs $1/T$. Then the capture barrier follows from the slope of this plot.

When determining the capture cross-section, σ, it is first necessary to determine the capture constant, c, from the equation

$$S(t)=S_{\text{inf}}(1-\exp(ct)), \qquad (1)$$

where S_{inf} is the saturation value of the DLTS signal and $S(t)$ is the signal height for a filling pulse of duration t. This is achieved by measuring $S(t)$ as a function of pulse width, t. After determining the capture rate, the capture cross-section, σ, is calculated using

$$c=v_{\text{th}}\sigma n, \qquad (2)$$

where v_{th} is the electron thermal velocity and n is the free electron concentration. However, in the case of E_{370}, Eq. (1) could not be satisfied for all pulse widths at a given measurement temperature. Filling of the E_{370} occurred over a too long filling pulse range—about five orders of filling pulse width—before saturation was achieved. Therefore, it was not possible to calculate a well-defined capture cross-section for E_{370} at any given temperature. This, in turn, meant that we could not compute the capture barrier for carrier capture onto E3′. This slow filling of E_{370} may mean that it is not a well-defined point defect but that it may have a somewhat extended nature onto which multiple charges can be captured, thus leading to a Coulomb barrier, somewhat like carrier capture onto a dislocation [13].

4. Conclusions

We have used DLTS to characterize the defects in ZnO grown by PLD. Using high resolution Laplace DLTS we found that at the high temperature side of the commonly observed defect E3 (300 meV below the conduction band) another close lying peak (E3′ with a level at 370 meV below the conduction band) is also observed. The concentration ratio of E3′ to E3 was found to depend on the annealing history of the samples. It is most prevalent in as-grown samples and samples that had been annealed in an oxygen atmosphere, suggesting that E3′ may be related to oxygen incorporation in the lattice.

Finally, the E3′ defect has a capture rate that strongly increases with increasing temperature.

References

[1] D.C. Look, *Mater. Sci. Eng. B* **80** (2001), p. 383.

[2] C. Kligshirn, *Phys. Status Solidi (b)* **71** (1975), p. 547.

[3] T. Aoki, Y. Hatanaka and D.C. Look, *Appl. Phys. Lett.* **76** (2000), p. 3257.

[4] F.D. Auret, S.A. Goodman, M. Hayes, M.J. Legodi, H.A. van Laarhoven and D.C. Look, *J. Phys.: Condens. Matter* **13** (2001), p. 8989.

[5] F.D. Auret, J.M. Nel, M. Hayes, L. Wu, W. Wesch and E. Wendler, *Superlattices Microstruct.* **39** (2006), p. 17.

[6] H. von Wenckstern, G. Biehne, R.A. Rahman, H. Hochmuth, M. Lorenz and M. Grundmann, *Appl. Phys. Lett.* **88** (2006), p. 092102.

[7] L. Dobaczewski, P. Kaczor, I.D. Hawkins and A.R. Peaker, *J. Appl. Phys.* **76** (1994), p. 194.

[8] L. Dobaczewski, A.R. Peaker and K. Bonde Nielsen, *J. Appl. Phys.* **96** (2004), p. 4689.

[9] H. von Wenckstern, et al., unpublished.

[10] F.D. Auret, et al., unpublished.

[11] J. Frenkel, *Phys. Rev.* **54** (1938), p. 647.

[12] B.K. Meyer *et al.*, *Phys. Status Solidi (b)* **241** (2004), p. 231.

[13] W. Schröter, J. Kronewitz, U. Gnauert, F. Riedel and M. Seibt, *Phys. Rev. B* **52** (1995), p. 13726.

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