Electronic properties of shallow level defects in ZnO grown by pulsed laser deposition

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Abstract. We have used deep level transient spectroscopy (DLTS) to characterise four defects with shallow levels in ZnO grown by pulsed laser deposition (PLD). These defects all have DLTS peaks below 100 K. From DLTS measurements and Arrhenius plots we have calculated the energy levels of these defects as 31 meV, 64 meV, 100 meV and 140 meV, respectively, below the conduction band. The 100 meV defect displayed metastable behaviour: Annealing under reverse bias at temperatures of above 130 K introduced it while annealing under zero bias above 110 K removed it. The 64 meV and 140 meV defects exhibited a strong electric field assisted emission, indicating that they may be donors.

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 large, direct band gap [2]. Devices such as detectors, lasers and diodes operating in the blue and ultra-violet (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) [4,5], 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 defects with DLTS peaks below 100 K in PLD grown ZnO. We show that one of these defects is metastable and that emission from two others is strongly enhanced by an electric field.

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 (thickness: 1 µm) deposited on top was 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 2h 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 ZnO layer. The n^{++} ZnO layer was contacted by sputtering Au onto it as an ohmic back contact [6].

We have used deep level transient spectroscopy (DLTS) to characterise the defects in this ZnO. In this study we concentrated on the defects that have DLTS peaks below 100 K, to which we shall refer as shallow level defects.

3. Results

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 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 none of the defects observed for the PLD grown ZnO are observed in bulk grown ZnO. The defects E_{31}, E_{64} and E_{140} are found in all PLD samples studied here, regardless of the annealing conditions. E_{100} on the other hand, is only clearly observed in unannealed samples and samples that had been annealed in oxygen. This may mean that it is 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) [7].

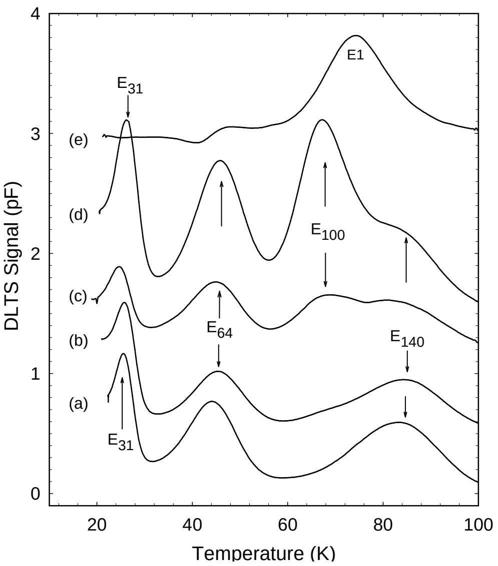

Figure 1. DLTS spectra of ZnO grown by PLD (curves (a) – (d)), and bulk ZnO (curve (e)). Curves (a), (b) and (c) are for PLD grown ZnO annealed in vacuum, nitrogen and oxygen, respectively, under conditions specified in the experimental procedure. All curves were recorded at a reverse bias of –2 V, a filling pulse amplitude of 2 V, a pulse width of 5 ms and a rate window of 5000 s^{-1}.

The DLTS "signatures" (energy levels and apparent capture cross sections) were determined from the Arrhenius plots in Fig. 2. For all defects the electric field during these measurements was kept as low as possible to prevent electric field enhanced emission that leads to incorrect "signatures". This was especially important for E_{64} and E_{140}, as will be discussed below. The estimated error in the

Table 1. Electronic properties of shallow level defects in PLD grown ZnO determined by DLTS

Defect	E_T (meV)	σ_a (cm^2)	T_{peak} [a] (K)
E_{31}	$E_C - (31 \pm 10)$	$(4.5 \pm 1.0) \times 10^{-14}$	22
E_{64}	$E_C - (64 \pm 5)$	$(1.8 \pm 0.2) \times 10^{-14}$	50
E_{110}	$E_C - (100 \pm 5)$	$(2.3 \pm 0.2) \times 10^{-14}$	67
E_{150}	$E_C - (140 \pm 5)$	$(1.0 \pm 0.2) \times 10^{-13}$	83

[a] Peak position at a rate window of 5000 $s^{-1.}$

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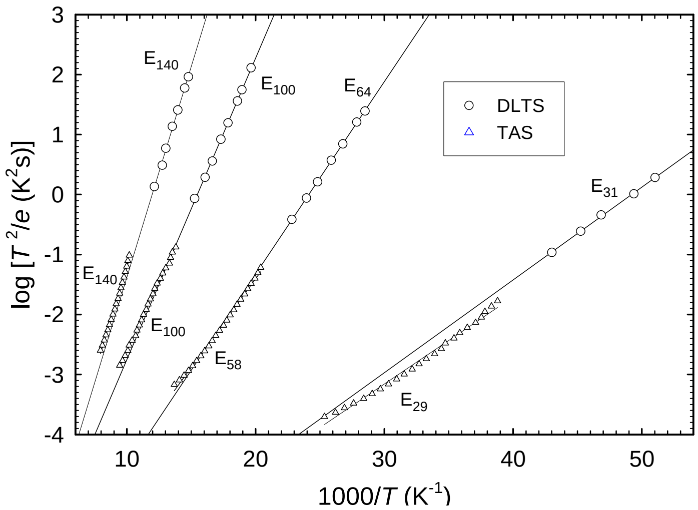

Figure 2. DLTS and TAS Arrhenius plots of the shallow level defects in PLD grown ZnO. The regression lines shown are fitted to the DLTS data. The DLTS data used for the construction of these plots were obtained under low-field conditions. Typically this would be a quiescent reverse bias of –2 V with a filling pulse ampli–tude of 0.3 V superimposed on it. The filling pulse width was 5 ms. The TAS data was obtained using dc bias of 0 V and an HF amplitude of 100 mV [7].

energy level of E_{31} are rather large as some measurements were carried out just above and below 20 K where the temperature stability in our cryostat was not very good. The electronic properties of these defects are summarized in Table 1. For comparison the TAS data are included in Fig. 2 [7].

Next, consider an interesting property of E_{100}. This defect displayed metastable behaviour. Annealing under reverse bias at temperatures of above 130 K introduced it while annealing under zero bias above 110 K removed it. These introduction and removal processes were 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 [8].

Finally, consider the effect of an electric field on the emission of electrons from the shallow levels. This is illustrated in Fig. 3 where curve (a) was recorded with a small filling pulse of 0.5 V, i.e. a low electric field. Following this, curves (b), (c) and (d) were recorded under increasing electric field strengths as the filling pulses were increased from 1 V to 1.5 V to 2 V, respectively. From this it is clear that whereas E_{31} was totally unaffected by the field, E_{64} and E_{140} are strongly influenced by the field. Not shown (to allow a clear observation of the E_{140} peak) is that the metastable defect E_{100} was also not significantly affected by the field. To quantify the influence of the field on these defects we have plotted in Fig. 4 the log of the emission rate vs the square root of the electric field. These plots are straight lines for both the E_{64} and E_{140} defects. Such a relationship is characteristic of the Poole-Frenkel model whereby emission from a coulombic potential well is enhanced due to a reduction of the well depth / barrier height under an applied electric field [9]. This type of emission enhancement is

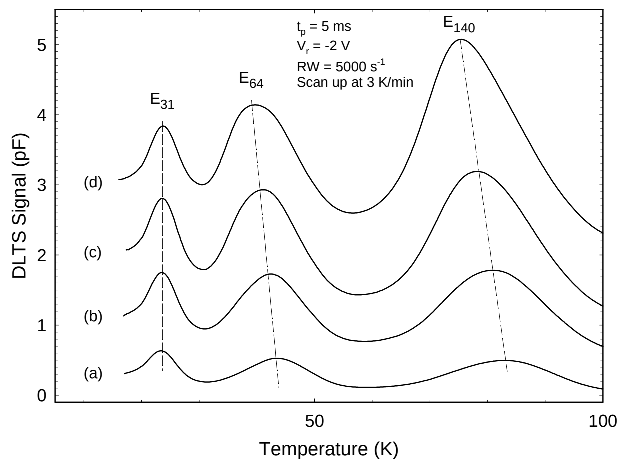

Figure 3. The effect of an electric field on emission from shallow level defects in ZnO grown by PLD. The quiescent reverse bias for all four scans was –2 V. The amplitude of the filling pulse was 0.5V, 1.0 V, 1.5 V and 2.0 V for curves (a), (b), (c) and (d), respectively. E_{31} was unaffected by the electric field while a significant effect was seen on the DLTS peak shapes of E_{64} and E_{140}.

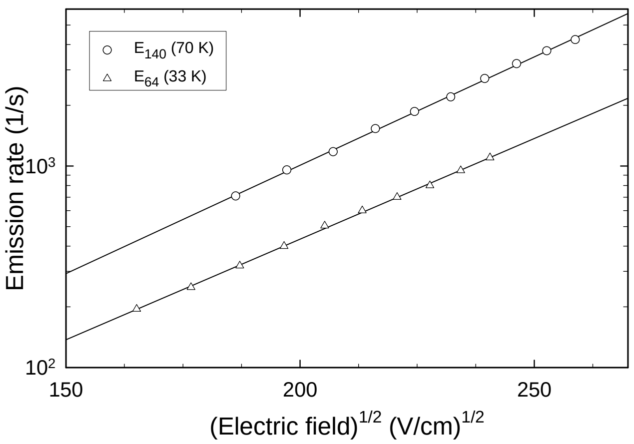

Figure 4. Poole Frenkel plots for the E_{64} and E_{140} defects that suggest their donor-like behaviour. These measurements were performed at a fixed temperature in double DLTS mode with V_{p1} = 0 V and V_{p2} = – 0.1 V. The reverse bias was stepped between – 0.8 V and – 2.6 V to vary the electric field. The electric field strengths were calculated using free carrier densities of 1×10^{16} cm^{-3} and 9×10^{15} cm^{-3} at 70 and 33 K, respectively, as calculated from capacitance-voltage measurements.

typical of a donor-like defect in an n-type semiconductor. From this it is tempting to conclude that E_{64} and E_{140} are donors. However, the slopes of both graphs are more than a factor of two smaller than what would be expected for single donors [9]. The reason for this is not clear at present. Despite this, it is worth while pointing out 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* [10] that report the calculated donor binding energy of the Al_{Zn} donor as 51.55 meV.

4. Conclusion

The shallow level defects (with DLTS peaks below 100 K) in PLD grown ZnO exhibit some interesting properties. The E_{31} level is unaffected by an electric field, suggesting that it is an acceptor. E_{100} is metastable and can be removed by annealing above 110 K under zero bias and re-introduced by annealing above 130 K under reverse bias. Emission from E_{64} and E_{140} shows evidence of a typical Poole-Frenkel behavior in an electric field, suggesting that these defects may be donors.

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