Electrical characterization of vapor-phase-grown single-crystal ZnO

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Gold Schottky-barrier diodes (SBDs) were fabricated on vapor-phase-grown single-crystal ZnO. Deep-level transient spectroscopy, using these SBDs, revealed the presence of four electron traps, the major two having levels at 0.12 eV and 0.57 below the conduction band. Comparison with temperature-dependent Hall measurements suggests that the 0.12 eV level has a temperature activated capture cross section with a capture barrier of about 0.06 eV and that it may significantly contribute to the free-carrier density. Based on the concentrations of defects other than this shallow donor, we conclude that the quality of the vapor-phase-grown ZnO studied here supercedes that of other single-crystal ZnO reported up to now. © *2002 American Institute of Physics.*
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During the past few decades, ZnO has been used in many, diverse products. Its applications, among others, include phosphors, piezoelectric transducers, varistors, alcohol synthesis catalysis, and gas sensing. In a recent review, however, where the properties of ZnO are summarized,[1] it was pointed out that ZnO can be used for several other, more advanced, electro-optical applications. Based on the fact that ZnO has a direct bandgap of 3.4 eV, it is expected to fulfill a similar role as GaN in optoelectronics, i.e., play an important role in realizing blue and ultraviolet light-emitting diodes and lasers, as well as daylight–blind UV detectors. Similar to that of GaN, its large band gap renders ZnO suitable for the fabrication of high-temperature, high-power devices with application, among others, in space where typical operating temperatures exceed 200 °C. High-quality single-crystal ZnO can be successfully grown in bulk.[2] A very important consequence of this is that owing to the relatively close match in lattice constants, single-crystal ZnO may be used as a substrate to grow epitaxial GaN that is well oriented with respect to the substrate and that has a reduced defect density.[3] Further practical advantages of ZnO include amenability to conventional wet chemistry etching, which is compatible with Si technology[4] (unlike the case for GaN).

An important issue in ZnO technology is establishing a technology for the fabrication of high-quality Schottky-barrier diodes (SBDs). SBDs are of key importance to probe defects in semiconductors by junction spectroscopic characterization techniques, such as deep-level transient spectroscopy (DLTS) (Ref. 5) and admittance spectroscopy (AS).[6] They are also important structures for metal–semiconductor field-effect transistors (MESFETs) and detectors. A limited amount of research regarding Schottky contacts to ZnO was carried out in the 1960s, where among other things the barrier height of some metal contacts to vacuum-cleaved ZnO was reported.[7] However, up to now, no systematic studies of surface characterization as a function of cleaning method have been performed; i.e., the influence of different cleaning methods on the surface quality of ZnO and the quality of Schottky contacts to ZnO have not been compared. Consequently, the fabrication of high-quality Schottky contacts to ZnO is still an art, and not yet a science.

Compared to other semiconductors, very little is known about defects in ZnO. In the few reports pertaining to electrical characterization of defects in ZnO using junction spectroscopic techniques, the focus was mostly on polycrystalline ZnO, though some data are available for single-crystal ZnO. Common to the majority of these reports for poly- or single-crystalline ZnO, is the presence of a defect, $L2$, with a level situated around 0.3 eV below the conduction band.[8–14] In addition, single-crystal ZnO grown by the hydrothermal technique contains a defect with a level estimated at $E_C - 0.34$ eV, from temperature-dependent Hall-effect measurements;[1] this defect is probably related to $L2$. Another defect, $L1$, with a level reported between 0.18 and 0.23 eV,[8,10,12,13] has only been observed in poly-ZnO, but little is known about its identity. Metal impurities were reported to introduce acceptor levels in the ZnO band gap at $E_C - 0.17$ eV for Cu (Ref. 15) and at $E_C - 0.23$ eV for Ag.[16] A defect, $L3$, with a broad DLTS peak and an estimated energy level/band at 0.2–0.3 eV, has been detected in poly-ZnO.[8,10] There is speculation that $L3$ is linked to multiple, closely spaced deep levels.[10]

In this letter, we report on the electrical characterization of defects in vapor-phase-grown single-crystal n-ZnO. We have used DLTS to show that four electron trap defects ($E1 - E4$) are present in this ZnO. The most prominent of these has an activation energy of 0.12 eV.

The ZnO used for this study was grown by a vapor-phase technique, making use of a nearly horizontal tube.[2] The ZnO samples were cleaned by rinsing them ultrasonically for 5 min periods in acetone, then in toluene, and then in DMSO. After each of these steps, the samples were rinsed in deionized water for 5 s and then blown dry in nitrogen.[4] Following this, circular Au contacts, 0.7 mm in diameter and

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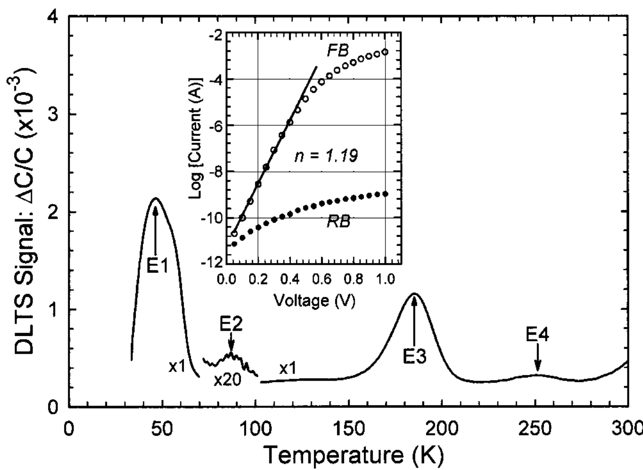

FIG. 1. Typical DLTS spectrum of a Au/ZnO SBD, recorded at a LIA frequency of 46 Hz, a quiescent reverse bias of 2 V, and a filling pulse amplitude of 2 V. In the inset we depict the $I-V$ characteristics of this diode, where FB and RB refer to the *forward bias* and *reverse bias* characteristics, respectively.

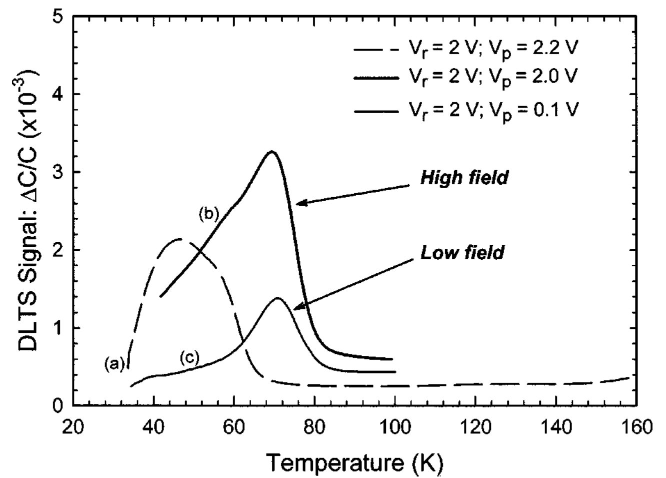

FIG. 2. DLTS spectra of the $E1$ defect. Curve (a), recorded at a LIA frequency of 46 Hz, depicts the asymmetric peak shape in the vicinity of the freeze-out region. Curves (b) and (c) were recorded at 2200 Hz at a high and low electric field, respectively, as per the indicated bias and pulse conditions.

200 nm thick, were resistively evaporated onto the $(000\bar{1})$ O face of the ZnO crystal through a mechanical mask. Thereafter, InGa Ohmic contacts were applied to the opposite side (Zn face) of the sample. The Au/ZnO Schottky-barrier diode structures were characterized by standard room temperature (297 K) current–voltage ($I-V$) and capacitance–voltage ($C-V$) measurements, and the defects in the ZnO by DLTS using a lock-in amplifier (LIA) based system in the temperature range 25–300 K.

$I-V$ measurements showed that the SBDs exhibited a high degree of rectification with a reverse current of about 10^{-9} A at a bias of 1 V (inset in Fig. 1). From $C-V$ measurements, the free-carrier density, N_D-N_A, was found to vary, from sample to sample, between $(4-6)\times10^{16}$ cm^{-3} in the first 0.2 μm below the surface, i.e., the region being probed by DLTS.

Conventional lock-in amplifier based DLTS in the temperature range 30–300 K (using the same SBDs) revealed the presence of at least three levels (solid curve in Fig. 1, recorded at 46 Hz). During the experiment we have noted that the capacitance decreases by about 90% from 50 to 30 K, due to carrier freeze-out. The peak of the most prominent defect, $E1$, therefore occurs in the freeze-out region. This implies that an accurate analysis of its emission kinetics or concentration is not possible in this temperature region. Curve (a) of Fig. 2 more clearly illustrates the asymmetric DLTS peak shape of defect $E1$, recorded at a LIA frequency of 46 Hz. In an attempt to move out of the freeze-out regime, DLTS spectra were recorded at a higher lock-in amplifier frequency (2200 Hz). From these measurements [curve (b) in Fig. 2], we observed that the $E1$ peak is still quite asymmetric. This indicates either that the $E1$ peak is the superposition of more than one peak, from closely spaced energy levels, or that it is the consequence of a strong electric-field-enhanced emission.[17]

Using the lowest possible electric field that still yields a strong enough signal for DLTS measurements [$V_r=2$ V and $V_p=0.1$ V, curve (c) in Fig. 2], we determined the activation energy and apparent capture cross section of $E1$ as 0.12 ± 0.02 eV and $(2.7\pm1.0)\times10^{-13}$ cm^2, respectively (Table I and Fig. 3). This is the lowest value of an energy level reported for DLTS or AS measurements on ZnO. Based on its energy level, $E1$ may be the same level as the 0.14 eV level reported by Tuller for a defect in ZnO.[18] Fixed bias–variable pulse DLTS profiling was used to determine the concentration of $E1$ and indicated that the $E1$ concentration approaches 10^{16} cm^{-3} in the region probed by DLTS. This, together with the fact that the $E1$ signal is observed in the freeze-out region, indicates that it significantly contributes to the shallow donor concentration in ZnO.

The peak position of the second most prominent level, $E3$, exhibited very little dependence on the electric field. We have determined its activation energy and apparent capture cross section as 0.29 ± 0.01 eV below the conduction band, and $(5.8\pm1.0)\times10^{-16}$ cm^2, respectively (Table I and Fig. 3). The concentration of $E3$, determined by DLTS profiling, was found to be about 10^{14} cm^{-3}. A third, less prominent defect, $E4$, is present in a concentration of $10^{13}-10^{14}$ cm^{-3}.

TABLE I. Electronic properties of defects detected by DLTS in vapor-phase-grown n-type ZnO.

Defect label	E_T (eV)	σ_a (cm^2)	N_T (cm^{-3})	T_{peak}[a] (K)	Similar defects and references
$E1$	0.12 ± 0.02	$2.7\pm1.0\times10^{-13}$	$\approx10^{16}$	70[b]	$D2$? (Ref. 2)
$E2$	0.10 ± 0.03	$8.4\pm4.0\times10^{-18}$	$10^{12}-10^{13}$	92	⋯
$E3$	0.29 ± 0.01	$5.8\pm1.0\times10^{-16}$	10^{14}	184	$L2^+$ (Ref. 12), $D3$ (Ref. 1)
$E4$	0.57 ± 0.02	$2.0\pm0.5\times10^{-12}$	$10^{13}-10^{14}$	249	⋯

[a]Peak temperature at a lock-in amplifier frequency of 46 Hz (emission rate of 109 s^{-1}).
[b]Peak temperature at a lock-in amplifier frequency of 2200 Hz (emission rate of 5200 s^{-1}).

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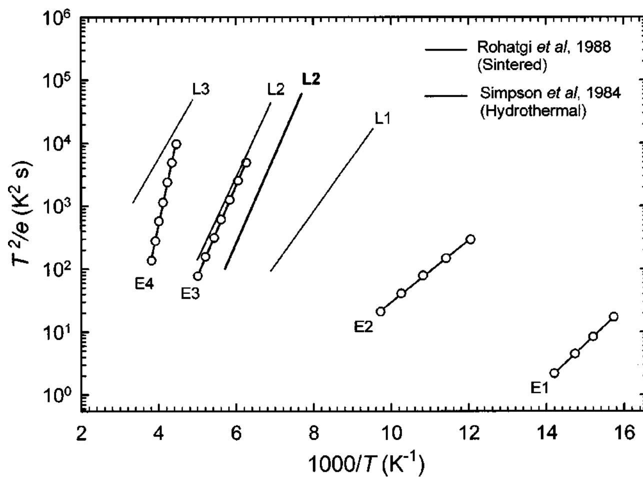

FIG. 3. Arrhenius plots of defects ($E1$–$E4$) observed in vapor-phase-grown ZnO (open symbols), and those of defects reported by other authors for single-crystal ZnO (thick line) and polycrystalline ZnO (thin lines).

Its concentration varied from sample to sample. We have determined the activation energy and apparent capture cross section of $E4$ as 0.59 ± 0.02 eV below the conduction band, and $(2.0\pm0.5)\times10^{-12}$ cm^2, respectively (Table I and Fig. 3). The unrealistically high value of its apparent capture cross section suggests that $E4$ may not be a simple point defect. No defect with a similar energy has yet been reported in the literature. Another minor peak, $E2$, not observed in all samples, was found to have an activation energy and apparent capture cross section of 0.10 ± 0.03 eV below the conduction band, and $(8.4\pm4.0)\times10^{-18}$ cm^2, respectively.

Some insight into the possible origin of these defects can be gained by noting, for example, that $L1$ has thus far only been detected in polycrystalline ZnO, and not in single-crystal ZnO. It, therefore, seems that $L1$ is characteristic of polycrystalline ZnO. $L2$ ($E3$ in our work), on the other hand, has been observed in both single-crystal and polycrystalline ZnO. This implies that $L2$ is a structural defect or impurity that can occur in both crystal types. It has been proposed that $L2$ is the oxygen vacancy (V_0) (Ref. 11) or the zinc interstitial (Zn_I).[10] From two, recent theoretical calculations,[19,20] based on the local density approximation (LDA), it appears that the V_0 model for $L2$ may be correct, but not the Zn_I model. That is, both calculations agree that Zn_I is a shallow donor, and V_0, a deep donor, about 0.6 or 0.7 eV from the conduction band. Considering the errors inherent in the LDA theory, it is entirely possible that $L2$ is related to V_0. $L3$,[8,10] too, has not been detected in the ZnO studied here or in hydrothermally grown ZnO,[11] indicating that it may occur only in poly-ZnO.

The activation energy of the main shallow level observed here, $E1$, is 0.12 eV. The two main shallow donor levels observed by Look *et al.* using Hall measurements in the same material have levels at 31 and 61 meV, respectively, below the conduction band.[2] Whereas Look *et al.* did not observe any level close to 0.12 eV, they did detect a level at 0.34 eV, similar to the $E3$ in the same material.[1] The question that thus arises is why they detected two levels shallower than $E1$ and a level at about the $E3$ position, but not the prominent level at 0.12 eV. A possible explanation is that $E1$ is a defect with a temperature-activated capture cross section. If the barrier for this process is about 59 meV, the true level of $E1$ would correspond to the 61 meV level ($D2$) of Look *et al.* A similar situation was found in GaN in which the energy levels of the main shallow radiation-induced defects observed by Hall measurements and DLTS were very different.[21] In both these cases it has to be assumed that a donor defect has a capture barrier, which is difficult to reconcile with the picture of a simple Coulombic center.

In summary, we have fabricated SBDs with low-leakage currents on ZnO, allowing accurate DLTS measurements. Our DLTS results have revealed that the main defect in vapor-phase-grown ZnO is a shallow-level defect close to the conduction band with an activation energy of 0.12 eV, and possibly a capture barrier for electrons of about 60 meV. This defect has not been observed with any junction spectroscopic technique. Based on the concentrations of defects other than this shallow donor, we conclude that the quality of the vapor-phase-grown ZnO studied here, supercedes that of other single-crystal ZnO material reported.

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