

Dominance of deep over shallow donors in ZnO-based varistors

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Broadband admittance spectroscopy measurements of ZnO-based varistors are analyzed in terms of charge transport theory through double Schottky barriers, hence obtaining empirical evidence about the nonmajority of the shallow donor in *n*-type ZnO. The dominant defect species is found to be a deep donor, which agrees with recent first-principles calculations. This result consistently explains the observed frequency-domain non-Debye and time-domain nonexponential electrical response, and invalidates a key assumption underlying various electrical characterization studies of this material. We find two deep levels with fine structures. These fine structures are attributable to fluctuating chemical environments around the defects. © 2003 American Institute of Physics.

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Zinc oxide has attracted much attention in the last decade, as it presents a wide range of interesting applications: *n*-type polycrystalline ZnO is widely used in ceramic varistors,¹ transparent conductors,² gas sensors,³ or phosphors;⁴ the close ZnO lattice matching with GaN has recently led to its use as substrate for epitaxial GaN growth;⁵ advanced electro-optical applications for ZnO single crystals have been recently reviewed by Look.⁶ From a fundamental viewpoint all these applications rely heavily upon zinc oxide defect chemistry and electronic structure, which have been the subject of recent theoretical^{7–9} and experimental^{10,11} studies, most of which focus on shallow-donor-related properties. Therefore, as remarked by Auret *et al.*,¹² very little is known about the concentrations and electronic properties of deep levels in zinc oxide. Junction spectroscopic techniques such as deep level transient spectroscopy^{13,14} (DLTS) and admittance spectroscopy^{15,16} (AS) have been widely applied to single- and polycrystalline ZnO. However, as recently noted¹⁷ in relation with *C*–*V* measurements, the lack of connection between these techniques and the general theory of charge transport through junction barriers is disappointing. Reported DLTS studies rely upon the assumption of exponential trapping transients, which is known to be incorrect^{15,18} for ZnO hence yielding erroneous physical parameters.^{19,20} Reported AS studies suffer from the fact that values for physical parameters can always be extracted from admittance spectra but, as recognized by García-Belmonte *et al.*,¹⁶ there is no reason for these values to be meaningful for a non-Debye response (NDR). As noted by Omling *et al.*,²⁰ meaningful studies require the origin of the NDR/nonexponential transient (NET) to be known, the system to be carefully modeled,²¹ and the measurement techniques to be suitably extended, something that has not been done for ZnO. Frequency domain NDR^{5,16} and time domain NET^{12,14,18} have been reported for ZnO single- and polycrystals, but its origin has been systematically qualified as poorly understood,¹⁸ not presently known,¹³ or unsubstantiated by

any theoretical model.¹⁶ This unsatisfactory situation extends to many other materials currently under research (such as SnO₂-based varistors²²), where the risk exists of basing the initial stages of knowledge on unreliable and improperly interpreted experimental data.

The purpose of this letter is to present a meaningful electrical characterization of *n*-doped polycrystalline ZnO that fully accounts for the nonexponential/non-Debye nature of the electrical response and yields empirical evidence on the nonmajority of the shallow donor. The dominant defect is found to be a deep donor. This result agrees with recent first-principles calculations and invalidates the assumption of a dominant shallow donor (necessary for an exponential transient behavior²³). We also show how the theory of charge transport through electrically active grain boundaries^{24–26} (GBs) can be applied to obtain relevant, not previously found, results.

The transport theory^{24–26} through double Schottky barriers (DSBs) provides a set of equations where the densities, energies, and capture cross sections of deep levels appear as adjustable parameters, which can be used to fit the electrical response of any polycrystalline semiconductor (such as poly-Si, Ge, GaAs, or ceramic perovskites such as BaTiO₃). Despite this theory has been frequently quoted in the literature, the expressions for the GB electrical response have been barely used, hence preventing the theory to be conveniently exploited. To fix the notation,^{17,26} Fig. 1 depicts a DSB: $E_C(x) = -e \times \Phi(x)$ is the equilibrium geometry of the conduction band (CB), $\Phi(x)$ is the electrostatic potential, and $\Phi_B \equiv -\Phi(x)|_{x=0}$ is the barrier height. The carrier concentration in the CB is N_0 , corresponding to an everywhere ionized shallow donor of energy $E_0(x)$, and defining the Fermi level position in the bulk $E_F(-\infty)$ [with $\xi = E_C(-\infty) - E_F(-\infty)$]. Deep lying defects have densities N_α capture cross-sections σ_α and energies $E_\alpha(x)$ (crossing the Fermi level at points $-x_{L\alpha}$ and $x_{R\alpha}$), where $\alpha = 1 \dots d$ from shallower to deeper. The CB and the defect energies bend in parallel,²⁵ so $\xi_\alpha \equiv E_C(x) - E_\alpha(x)$ ($\alpha = 0 \dots d$) remains con-

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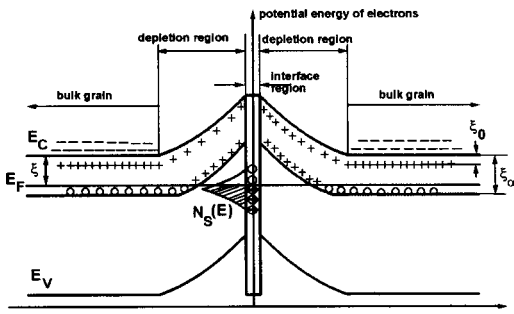


FIG. 1. Schematic energy band diagram of a DSB at a GB in a polycrystalline semiconductor.

stant everywhere. An interface density of states $N_S(E)$ exists at the boundary. The equations determining the band geometry and the $2d+3$ unknowns $x_{L\alpha}$, $x_{R\alpha}$ and Φ_B ($\alpha=0,\dots,d$) were written and solved by Blatter and Greuter.²⁶ Upon application of a small time-dependent signal $\Delta V(t) = V_0 e^{i\omega t}$ ($eV_0 \ll k_B T$), and subtraction of the dc-transport component, one gets the true ac loss $G_{ac}(\omega)/\omega = [G_{tot}(\omega)/\omega] - (G_{dc}/\omega) = (-1/2)\text{Im}[C_L(\omega)]$, where²⁶

$$C_L(\omega) = \varepsilon_0 \varepsilon_r \frac{\sum_{\alpha=0}^d r_{\alpha}(\omega)}{\sum_{\alpha=0}^d x_{L\alpha} r_{\alpha}(\omega)}, \quad (1)$$

with the recursive definition $r_0(\omega) \equiv 1$ and

$$r_{\alpha}(\omega) = \frac{1}{1 + i\omega\tau_{\alpha}} \frac{\sum_{\mu=0}^{\alpha-1} (x_{L\mu} - x_{L\alpha}) r_{\mu}(\omega)}{\sum_{\mu=0}^{\alpha-1} (x_{L\mu} - x_{L\alpha}) (N_{\mu}/N_{\alpha})}, \quad (2)$$

$$\tau_{\alpha} = \frac{e}{AT^2\sigma_{\alpha}(1 + g_{\alpha})} e^{\varepsilon_{\alpha}/k_B T}, \quad (3)$$

where A is Richardson's constant and g_{α} is the degeneracy factor²⁷ ($g_{\alpha} = 1/2$). The r_{α} s are complex functions, so the quotient in Eq. (2) mixes real and imaginary parts in an involved way that does not lend itself to simplifications: the deep levels couple among themselves, and one has to resort to a global fitting in order to obtain any reasonably accurate quantitative information. In this sense, the set of Eqs. (1)–(3) do indeed fulfill the requirements pointed by several authors,²⁸ who emphasized the inappropriateness of usual assumptions for dielectric analysis, which involve distributions of uncoupled relaxation times describing parallel, independent processes.

Our experiments were done over disk-shaped samples of sintered, n -doped, ZnO-based varistors. The free-electron density and shallow donor activation energy were measured as reported in Ref. 29, obtaining a typical value of N_0 (2.1 ± 0.1) $\times 10^{17}$ cm^{-3} . At each temperature, the zero-bias small signal response was measured and the true ac loss $G_{ac}(\omega)/\omega = (-1/2)\text{Im}[C_L(\omega)]$ was obtained. As shown by Eqs. (1)–(3), this quantity contains the information about the DSB electronic structure in form of adjustable parameters [three per trap: (N_{α} , ξ_{α} , σ_{α})], which were used to fit the experimental data through about five orders of magnitude (10^{-5} –1 Hz). There are no unknown parameters related to the interface states because the only interface parameter that enters the zero-bias admittance is the barrier height, which is an experimental input at each temperature.²⁴ Hence, for a given set of deep trap parameters, we do not need detailed knowledge of the interface parameters. We model $N_S(E)$

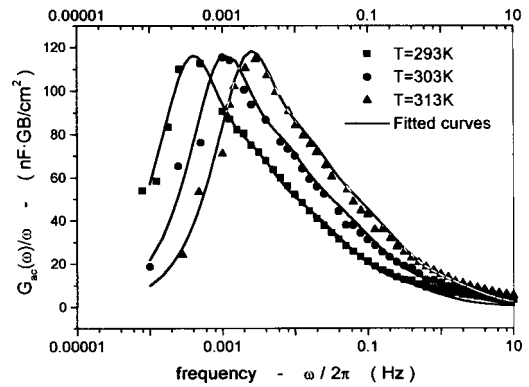


FIG. 2. Measured and calculated (parameters from Table I) true-ac loss curves at various temperatures.

with a Gaussian and, at any given temperature, we sweep trap parameters in order to obtain a best fit to the experimental data. For each set of trap parameters, we use the measured barrier height as an input and begin our calculation by adjusting the parameters of $N_S(E)$ (area and energy position) so as to reproduce, at that temperature and with those deep traps, the experimental barrier height. Within the explored frequency range, we found an optimum fitting with five levels. Examples of measured and fitted curves at various temperatures are shown in Fig. 2. The results are summarized in Table I.

The main result is the presence of a dominant deep level, with a concentration above that of the shallow donor. Note that, even when the total defect concentrations can be lower in bulk single crystals or polycrystalline thin films, the relative abundances of native point defects are expected to be similar because the lack of a majority defect with shallow donor properties in n -type ZnO was found by Kohan *et al.*⁷ to be robust under variable doping and growth conditions. Notice that the calculated curves are very sensitive to changes in the parameters of the denser levels: Figure 3 shows the curve obtained with the parameters of Table I, along with curves obtained by slightly varying the parameters of the denser trap ($\alpha=5$ in Table I). The N_{α} , ξ_{α} , and σ_{α} for the two denser traps ($\alpha=4$ and $\alpha=5$ in Table I) can be resolved within $\pm 4\%$, $\pm 1\%$, and $\pm 8\%$, respectively. Variations in the parameters of the more diluted traps are not so easily perceptible by sight, but they are still significant enough to resolve N_1 , ξ_1 , and σ_1 within $\pm 40\%$, $\pm 3\%$, and $\pm 45\%$, respectively.

Another salient feature of Table I is the presence of several thermal activation energies associated with a single capture cross section and, therefore, with a single defect.^{20,30} This result points to a widely recognized effect, first dis-

TABLE I. Trap parameters deduced from a best fit of the measured true-ac loss to the DSB equations.

Lever (" α ")	Density N_{α} (cm^{-3})	Energy ξ_{α} (eV)	Cross section σ_{α} (cm^2)
1	4.8×10^{16}	0.41	1.2×10^{-18}
2	8.5×10^{16}	0.47	2.5×10^{-18}
3	2.0×10^{17}	0.51	2.5×10^{-18}
4	5.0×10^{17}	0.56	1.4×10^{-18}
5	3.6×10^{18}	0.60	1.4×10^{-18}

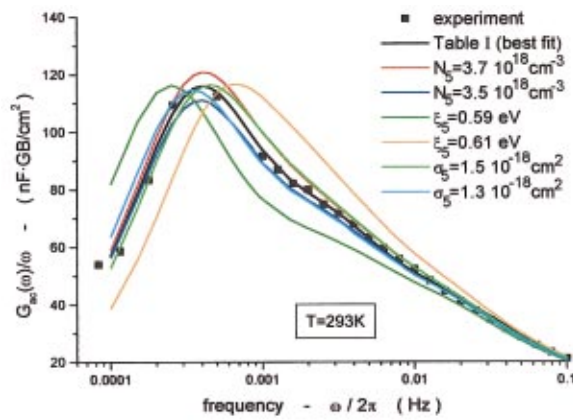


FIG. 3. (Color) Calculated true-ac loss curves at 293 K with slightly varying parameters for the denser trap. For each curve, the remaining 14 parameters are exactly those appearing in Table I.

cussed by Levinson *et al.*³⁰ and studied in deep by Omling *et al.*²⁰ the broadening of the emission activation energy of a single defect level due to its fluctuating chemical environment. This effect has been widely studied for DX centers in semiconductor alloys,³¹ where it introduces a fine structure in the energy levels, particularly broad for vacancy-type point defects and for defect complexes/clusters.³⁰ The same effect should be expected in heavily doped polycrystalline semiconductors, where local stoichiometric fluctuations are abundant, and different nearest-neighbor shells can appear around each kind of defect.³² Indeed, activation energy differences of 40–50 meV (similar to those in Table I) have been reported, for example, between fine structure peaks of substitutional Fe in GaAsP alloys.³² Regarding the chemical identities of the three kinds of defects appearing in Table I, it is worth pointing out that the thermal activation energies of the levels $\alpha=4$ and $\alpha=5$ in Table I (0.56–0.6 eV below the conduction band) lie within the *ab initio* predicted range for the oxygen vacancy.^{7–9} However, neither the data reported in this work, nor the present understanding and knowledge of the physical parameters of the main intrinsic defects in ZnO, allow for any identification on the basis of the energy level position only.

In conclusion, we have provided empirical evidence on the minority of the shallow donor and the majority of a deep donor species in ZnO-based varistors. In doing so, we have shown that the theory of charge transport through double Schottky barriers, when applied in its full generality and without unjustified assumptions, accurately reproduces the spectral behavior and temperature variation of the zero-bias electrical response of *n*-doped polycrystalline ZnO, hence yielding a powerful spectroscopic technique. By using this technique we have found two deep levels with fine structure

features, a property attributable to the effect of fluctuating chemical environments. These results provide a consistent qualitative and quantitative explanation to the observed and hitherto unexplained frequency-domain non-Debye and time-domain nonexponential responses of this material.

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