

Dominance of deep over shallow donors and the non-Debye response of 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 on the non-majority of the shallow donor in *n*-type ZnO. The dominant defect species is found to be a deep donor, in agreement with recent first-principles calculations. This result consistently explains the observed frequency-domain non-Debye and time-domain non-exponential electrical response of these materials. Also, it invalidates several assumptions that have been made through the years in the study and characterization of polycrystalline ZnO. We find two deep levels with fine structures, which are attributable to fluctuating chemical environments around the defects.

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1 INTRODUCTION

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 lead 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 on the concentration and electronic structure of intrinsic/extrinsic point defects. It is for this reason that, in the last years, the electronic structure and formation energy of native point defects in ZnO have attracted a lot of attention, and have been calculated from first principles.⁷ One conclusion of these calculations is the lack of an abundant defect with shallow donor properties. This fact is relevant because several, widely applied, methods for the study of gap electronic states (such as deep level transient spectroscopy or admittance spectroscopy or capacitance-voltage techniques), assume a dominant concentration for the shallow donor and a comparatively small deep defect concentration, additionally neglecting any type of interaction among defects. Indeed, very little is known about the concentrations and electronic properties of deep levels in zinc oxide. Deep level transient spectroscopy^{8,9} (DLTS) and admittance spectroscopy^{10,11} (AS) have been widely applied to single- and polycrystalline ZnO but, as recently noted¹² 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^{10,13} for ZnO hence yielding erroneous physical parameters.¹⁴ 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.,¹¹ there is no reason for these values to be meaningful for a non-Debye response (NDR). Frequency domain NDR^{5,11} and time domain NET^{9,13} have been reported for ZnO single- and polycrystals, but its origin has been systematically qualified as poorly understood,¹³ not presently known,⁸ or unsubstantiated by any theoretical model.¹¹ This unsatisfactory situation extends to many other materials currently under research (such as SnO₂-based varistors¹⁵), where the risk exists of basing the initial stages of knowledge on unreliable and improperly interpreted experimental data.

The purpose of this paper is to present empirical evidence in favour of a non-majority shallow donor in polycrystalline ZnO and to show how the general theory of charge transport through charged interfaces in polycrystalline semiconductors can be used without unjustified assumptions.

2. METHODOLOGY

The general analytical framework for charge transport through semiconductor GB's was developed in a series of papers by Pike and Blatter and Greuter.¹⁷⁻¹⁹ By means of the double Schottky barrier (DSB) model, these authors were able to obtain useful and general expressions for the steady and non-steady state charge transport properties of such important materials as poly-Ge, poly-Si, GaAs, BaTiO₃ or ZnO. The theory provides a set of equations such that the densities, energies, and capture cross-sections of defect levels appear as fully adjustable parameters that can be used to fit the electrical response of any polycrystalline semiconductor. Despite the fact that these papers have been thoroughly quoted in the literature, the complete and correct expression for the GB admittance has been barely used. Yet the understanding and use of the proper equations is not a question of academic rigor devoid of physical sense: much on the contrary, it leads to interesting new results, and it can help gaining new insights on all those materials to which the DSB model can be applied. Indeed, as very recently noted,¹² most characterization procedures applied to GB's in semiconductors have relied upon expressions borrowed from the well known theories of p-n junctions and one-sided Schottky barriers in metal semiconductor contacts, neglecting the many (and extremely relevant) features associated with the presence of charged (electrically active) GB's, field-dependent electrostatic barriers (DSB's) and coupling phenomena among the various defect-induced energy levels.

Fig. 1 depicts a DSB: $E_C(x) = -e\Phi(x)$ is the equilibrium geometry of the conduction band (CB), $\Phi(x)$ is the electrostatic potential, and $\Phi_B = -\Phi(x)|_{x=0}$ 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,¹⁸ so $\xi_\alpha = E_C(x) - E_\alpha(x)$ ($\alpha = 0 \dots d$) remains constant 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.¹⁹ 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 $G_{ac}(\omega)/\omega = [G_{tot}(\omega)/\omega] - (G_{dc}/\omega) = (-1/2)\text{Im}[C_L(\omega)]$, where

$$C_L(\omega) = \epsilon_0 \epsilon_r \frac{\sum_{\alpha=0}^d r_\alpha(\omega)}{\sum_{\alpha=0}^d x_{L\alpha} r_\alpha(\omega)} \quad (1),$$

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

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

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

where A is Richardson's constant and g_{α} is the degeneracy factor. 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 equations (1)-(3) do indeed fulfill the requirements pointed by several authors,²⁰ who emphasized the inappropriateness of usual assumptions for dielectric analysis, which involve distributions of uncoupled relaxation times describing parallel, independent processes.

3. EXPERIMENTAL RESULTS

The experiments were done over disc-shaped ($\varnothing 11\text{mm}$ and 1.6mm thickness) samples of sintered, n -doped, ZnO-based varistor materials. Chemical composition was 94mol% ZnO, 2mol% Bi₂O₃ (which is known not to be soluble in the ZnO grains), and the remaining quantity formed by various n -type dopants (MnO, CoO, Al₂O₃); SEM microscopy, grain EDAX, and X-ray analysis, showed a very homogeneous microstructure (average grain size equal to $7.5\mu\text{m}$ and very narrow grain size distribution), and the usual distribution of phases at the inter-grain triple junctions, as repeatedly reported in the literature.¹ Our experiments were done over disc-shaped samples of sintered, n -doped, ZnO-based varistors. The free-electron density and shallow donor activation energy were measured as reported in Ref. 21, obtaining a typical value of $(2.1 \pm 0.1) \times 10^{17} \text{cm}^{-3}$. 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: $(N_{\alpha}, \xi_{\alpha}, \sigma_{\alpha})$], which were used to fit the experimental data through about five orders of magnitude (10^{-5}Hz – 1Hz). 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.¹⁷ Hence, for a given set of deep trap parameters, we do not need a detailed knowledge of the interface parameters. We model $N_S(E)$ 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.

4. RESULTS AND DISCUSSION

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 has been found by Kohan et al.⁷ to be robust under variable doping and growth conditions.

Other 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. This result points to a widely recognized effect, first discussed by Levinson et al.:²² 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,²³ where it introduces a fine structure in the energy levels, particularly broad for vacancy-type point defects and for defect complexes/clusters.²² The same effect should be expected in heavily doped polycrystalline semiconductors, where local stoichiometric fluctuations are abundant, and different nearest-neighbour shells can appear around each kind of defect.²⁴ Indeed, activation energy differences of 40-50 meV (similar to those in Table 1) have been reported, for example, between fine structure peaks of substitutional Fe in GaAsP alloys.²⁴ 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 1 (0.56-0.6eV below the conduction band) lie within the ab-initio predicted range for the oxygen vacancy.⁷ Also, the small measured capture cross sections are consistent with the fact that the oxygen vacancy has been predicted to be a negative-U defect,⁷ which precludes it from appearing as V_O^\bullet , and forces the possible charge states for this defect to be (0) and (++) : this implies the simultaneous transfer of two electrons at the edge of the ionization region under non-steady state transport regime. We have verified that all the arguments and calculations carry on unmodified to this case, provided the corresponding capture cross-section σ_v is properly interpreted as that for a two-electron capture event: it is reasonable for this capture cross-section to be smaller than the usual cross sections for non-radiative recombination at Coulomb-attractive centers. 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 clear identification of the chemical nature of the dominant defect.

5. CONCLUSIONS

Most of the previous studies on polycrystalline ZnO and other grain boundary semiconductors either completely neglect the deep defect density [17] or use methods that are only valid in certain specific limits of GB properties [19] and defect concentrations [20]. We have presented here empirical evidence in favour of a non-majority shallow donor in polycrystalline ZnO. Also, we have shown how the general theory of charge transport through charged interfaces in polycrystalline semiconductors can be applied without unjustified assumptions in order to devise 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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References

- ¹ Clarke, D. R., Varistor Ceramics. *J. Am. Ceram. Soc.*, 1999, **82**, 485-502.
- ² Minami, T., Sato, H., Nanto, H., and Takata, S., Group III Impurity Doped Zinc Oxide Thin Films Prepared by RF Magnetron Sputtering. *Jpn. J. Appl. Phys.*, 1985, **24**, L781- L784.
- ³ Lin, F.-C., Takao, Y., Shimizu, Y., and Egashira, M., Zinc oxide varistor gas sensors. I. Effect of Bi₂O₃ content on the H₂ sensing properties. *J. Am. Ceram. Soc.*, 1995, **78**, 2301-2306.
- ⁴ Vanheusden, K., Warren, W. L., Seager, C. H., Tallant, D. R. Voight, J. A. and Gnade, B. E., Mechanism behind green luminescence in ZnO phosphor powders. *J. Appl. Phys.*, 1996, **79**, 7983-7990.
- ⁵ Hamdani, F., Botchkarev, A. E., Tang, H., Kim, W. and Morkoç, H., Effect of buffer layer and substrate surface polarity on the growth by molecular beam epitaxy of GaN on ZnO. *Appl. Phys. Lett.*, 1997, **71**, 3111-3113.
- ⁶ Look, D. C., Recent advances in ZnO materials and devices. *Mater. Sci. Eng. B*, 2001 **80/1-3**, 383-387.
- ⁷ Kohan, A. F., Ceder, G. Morgan, D. and Van de Walle, C. G., First-principles study of native point defects in ZnO. *Phys. Rev. B*, 2000, **61**, 15019-15027.
- ⁸ Wang, H., Li, W., and Cordaro, J. F., Single Junctions in ZnO Varistors Studied by Current-Voltage Characteristics and Deep Level Transient Spectroscopy. *Jpn. J. Appl. Phys.*, 1995, **34**(4A), 1765-1771.
- ⁹ Wang, Y.-P., Lee, W.-I., and Tseng, T.-Y., Degradation phenomena of multilayer ZnO-glass varistors studied by deep level transient spectroscopy. *Appl. Phys. Lett.*, 1996, **69**, 1807-1809.

- ¹⁰ Alim, M. A., Seitz, M. A., and Hirthe, R. W., Complex plane analysis of trapping phenomena in zinc oxide based varistor grain boundaries. *J. Appl. Phys.*, 1988, **63**, 2337-2345.
- ¹¹ García-Belmonte, G., Bisquert, J., and Fabregat-Santiago, F., Effect of trap density on the dielectric response of varistor ceramics. *Solid-St. Electron.*, 1999 **43**, 2123-2127.
- ¹² Fernández-Hevia, D., de Frutos, J., Caballero, A. C., and Fernández, J. F., Mott–Schottky behavior of strongly pinned double Schottky barriers and characterization of ceramic varistors. *J. Appl. Phys.*, 2002, **92**, 2890-2898.
- ¹³ Modine, F. A., Major, R. W., Choi, S. I., Bergman, L. B., and Silver, M. N., Polarization currents in varistors. *J. Appl. Phys.*, 1990, **68**, 339-346.
- ¹⁴ Robert Thurber, W., Forman, R. A., and Phillips, W. E., A novel method to detect nonexponential transients in deep level transient spectroscopy. *J. Appl. Phys.*, 1982, **53**, 7397-7400.
- ¹⁵ Bueno, P. R., Oliveira, M. M., Bacelar-Junior, W. K., Leite, E. R., Longo, E., García-Belmonte, G., and Bisquert, J., Analysis of the admittance-frequency and capacitance–voltage of dense SnO₂-CoO-based varistor ceramics. *J. Appl. Phys.*, 2002, **91**, 6007-6014.
- ¹⁶ Phillips, W. E. and Lowney, J. R., Analysis of nonexponential transient capacitance in silicon diodes heavily doped with platinum. *J. Appl. Phys.*, 1983, **54**, 2786-2791.
- ¹⁷ Pike, G. E., Semiconductor grain-boundary admittance: Theory. *Phys. Rev. B*, 1984, **30**, 795-802.
- ¹⁸ Pike, G. E., Diffusion-limited quasi Fermi level near a semiconductor grain boundary. *Phys. Rev. B*, 1984, **30**, 3274-3276.
- ¹⁹ Blatter, G. and Greuter, F., Carrier transport through grain boundaries in semiconductors. *Phys. Rev. B*, 1986, **33**, 3952-3966.
- ²⁰ Queisser, H. J., Nonexponential Relaxation of Conductance near Semiconductor Interfaces. *Phys. Rev. Lett.*, 1985, **54**, 234-236.
- ²¹ Fernández-Hevia, D., de Frutos, J., Caballero, A. C., and Fernández, J. F., Bulk-grain resistivity and positive temperature coefficient of ZnO-based varistors. *Appl. Phys. Lett.*, 2003, **82**, 212-214.
- ²² Levinson, M. and Temkin, A., Defect states in electron irradiated InGaAsP. *Appl. Phys. Lett.*, 1983, **42**, 605-607.
- ²³ Zhan, H. H., Kang, J. Y., Wu, Z. Y., and Huang, Q. S., Fine structure of DX(Sn) centers in Al_xGa_{1-x}As. *J. Appl. Phys.*, 1998, **84**, 2497-2500.
- ²⁴ Kang, J. Y., Zhan, H. H., and Huang, Q. S., Laplace defect spectroscopy for recognition of deep-level fine structures. *J. Crystal Growth*, 2000, **210**, 247-250.

FIGURE CAPTIONS

FIG. 1. Schematic energy band diagram of the double Schottky barrier at a grain boundary in a polycrystalline semiconductor

FIG. 2. Measured and calculated (with the parameters of Table 1) true-ac loss curves at various temperatures.

Table 1: Physical parameters obtained by fitting the measured true-ac loss to the double Schottky barrier model equations.

Level	Density	Energy	Capture cross-section
(" α ")	N_α (cm ⁻³)	ξ_α (eV)	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}

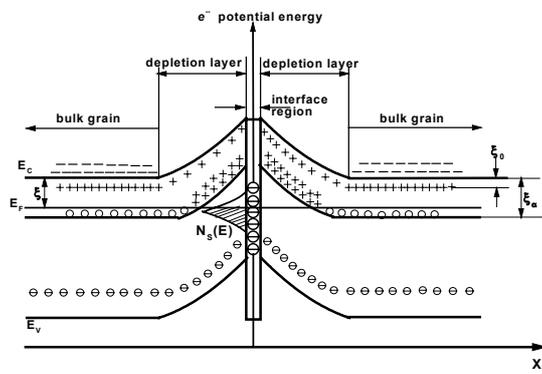


FIG. 1.

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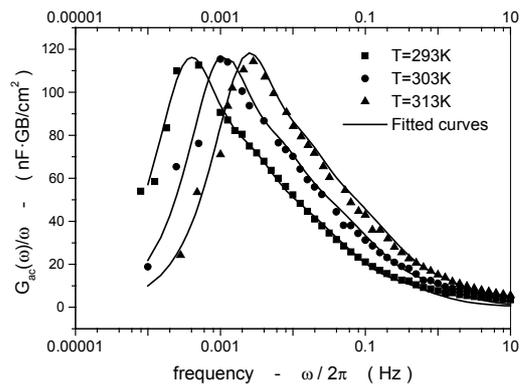


FIG. 2

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