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Charge Transport in Nanoparticulate Thin Films of Zinc Oxide and Aluminum-doped Zinc Oxide

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ABSTRACT

In this work, we report on the electrical characterization of nanoparticular thin films of zinc oxide (ZnO) and aluminum-doped ZnO (AZO). Temperature-dependent current-voltage measurements revealed that charge transport for both, ZnO and AZO, is well described by the Poole-Frenkel model and excellent agreement between the experimental data and the theoretical predictions is demonstrated. For the first time it is shown that the nature of the charge-transport is not affected by the doping of the nanoparticle and it is proposed that the Poole-Frenkel effect is an intrinsic and universally limiting mechanism for the charge transport in nanoparticular thin films with defect states within the bandgap.

KEYWORDS

Zinc oxide, aluminum-doped zinc oxide, nanoparticles, Poole-Frenkel effect, charge transport, and temperature-dependent J-V characteristics

MANUSCRIPT TEXT

Zinc oxide (ZnO) – a II-VI compound semiconductor with a large band gap (3.37 eV)¹ exhibits an excitingly widespread range of potential applications², such as lasers¹, field-effect transistors³⁻⁵, transducers⁶, varistors⁷, sensors⁸, UV-detectors⁹ and also thin-film solar cells, where it can serve as active^{10,11} or interfacial^{12,13} or electrode material¹⁴.

Moreover, ZnO is a promising material for the field of transparent^{3,4,15} and flexible electronics^{15,16}, because large-area solution processing on flexible substrates using techniques like ink-jet printing appears feasible^{17,18}. The solutions for film deposition are either based on the sol-gel route or on nanoparticle synthesis. The latter has the advantage that the synthesis and the film deposition can be separated from each other. As pointed out earlier^{19,20}, this

allows cheap and high-throughput synthesis at elevated temperatures, while the film deposition is achieved at lower temperatures, which is a prerequisite for the use of flexible (often polymer-based) substrates.

The problem of nanoparticulate ZnO thin films deposited at low temperature is that they hardly reach the electric performance of zinc oxide films based on sputtering²¹ or spray pyrolysis²². Therefore, a better understanding of the electric conduction in these films is desired.

So far, most of the charge transport studies on ZnO nanoparticle films used the transistor device structure: Meulenkamp²³ and Roest et al.^{24,25} studied ZnO nanoparticles with small sizes (≈ 5 nm) permeated in electrolyte solutions and it was demonstrated that transport occurs via tunnelling between discrete electronic states with or without additional thermal activation depending on the characteristics of the electrolyte²⁵. Besides, space-charge limited conduction (SCLC) was shown for ZnO by Bubel et al.¹⁹ and by Caglar et al.²⁶ (sandwich device geometry). In these two cases^{19,26}, the sizes of the nanostructures were larger (above 25 nm) compared to the above-mentioned reports. This might partially explain the different findings.

Discrepancies between various transport investigations were also revealed for other nanoparticulate materials, e.g. for nanostructured films of silicon. Besides hopping^{27,28}, also SCLC²⁹, Poole-Frenkel effect^{30,31}, and tunnelling^{32,33} were reported for nano-Si (porous silicon or nanoparticles). These inconsistent results further emphasize the need for a detailed description of charge transport in nanoparticulate films.

In this work, the charge transport of nanoparticulate ZnO and AZO thin films was investigated. A dispersion of ligand-stabilized ZnO or AZO nanoparticles was deposited on top of an ITO substrate via multiple doctor blading^{34,35} steps. The resulting film thickness is 0.7-1 μm . Afterwards the sample was transferred to a vacuum chamber equipped with a

physical vapor deposition (PVD) system for deposition of a 100 nm thick Ag top contact (for further details see Supporting Information).

The commercially available ZnO / AZO dispersions from Nanograde Ltd were selected for the investigations. These nanoparticles were produced by flame spray synthesis³⁶⁻³⁸ and are expected to have high crystallinity and no adverse surface ligands. In a flame spray synthesis a precursor solution of Zn-acetate is fed (5 ml min⁻¹) to a spray nozzle, dispersed by oxygen (7 l min⁻¹) and ignited by a premixed methane-oxygen flame (CH₄: 1.2 l min⁻¹, O₂: 2.2 l min⁻¹). For the synthesis of AZO nanoparticles with a nominal composition of 2 wt% Al₂O₃ in ZnO, the same Zn-acetate precursor with additional Al-acetylacetonate 2-ethylhexanoic acid under the same process conditions was used. The nanoparticles were collected by air-filtration of the off-gas. In order to prepare stable suspensions of ZnO/AZO, 5wt% of nanoparticles were dispersed in ethanol by the use of a phosphonate-based ligand.

The ZnO/AZO nanoparticles are crystalline with a diameter of 10-15 nm (see Fig. 1). Due to the high temperatures within the flame spray synthesis and the precisely controlled process conditions, the nanoparticles exhibit high purity and controlled stoichiometric correlation between dopand material and the oxides.

Figures 2a and 3a depict the current density-voltage (*J-V*) characteristics for AZO (thickness of 950 nm) and ZnO (750 nm), respectively, at various temperatures. The *J-V* characteristics appear to be symmetric (within 5 %) with respect to the bias (see Figure S1). We tested different models to fit the *J-V* data of both materials. Consistent and precise results could only be obtained with a combination of Ohm's law for low voltages and the Poole-Frenkel (PF) effect for higher voltages (see Figure S2). The former is not unexpected, as Ohm's law is usually valid for the low-voltage – intrinsic – regime of a low-conductivity material³⁹. By contrast, the occurrence of PF effect⁴⁰⁻⁴² is rather surprising, as it was originally derived for band-like insulators, such as Si₃O₄⁴³ or Ta₂O₅⁴⁴, which contain traps limiting conductivity.

The PF effect describes the lowering of the trap barrier height Φ due to an external electric field E and conductivity σ follows⁴⁰⁻⁴²

$$\sigma = \sigma_{const} \cdot \exp\left(\frac{\beta\sqrt{E}-\Phi}{kT}\right). \quad (1)$$

Here, σ_{const} is the conductivity constant, k is the Boltzmann constant and T the absolute temperature. The factor β deserves special attention, because it only depends on fundamental physical constants and the dielectric constant ϵ_r of the material

$$\beta = \sqrt{\frac{e^3}{\epsilon_0\pi\epsilon_r}}, \quad (2)$$

where e is the electronic charge and ϵ_0 is the permittivity of vacuum.

For the determination of β_{exp} based on the J-V data of ZnO and AZO, we apply the natural logarithm to both sides of Equation 1 leading to

$$\ln(\sigma) = \frac{\beta}{kT}\sqrt{E} + \left\{\ln(\sigma_{const}) - \frac{\Phi}{kT}\right\}. \quad (3)$$

Following Equation 3, Figure 2b and 3b depict the natural logarithm of conductivity versus the square root of electric field for AZO and ZnO, respectively. Both graphs show broad linear regimes for the data sets for all considered temperatures. The slopes and the y-intercepts of these linear regimes are listed in Tables 1 and 2 in the Supporting Information together with the resulting values of β .

The experimentally derived values of β_{exp} are *not temperature dependent* with mean values of $\beta_{exp} = 2.64 \pm 0.06 \cdot 10^{-5} \text{ eVm}^{0.5}\text{V}^{-0.5}$ for ZnO and $\beta_{exp} = 2.42 \pm 0.11 \cdot 10^{-5} \text{ eVm}^{0.5}\text{V}^{-0.5}$ for AZO. This is in extraordinarily good accordance with the theoretical values of $\beta_{theo} = 2.57 \cdot 10^{-5} \text{ eVm}^{0.5}\text{V}^{-0.5}$ based on $\epsilon_r = 8.72$ for ZnO and of $\beta_{theo} = 2.43 \cdot 10^{-5} \text{ eVm}^{0.5}\text{V}^{-0.5}$ based on $\epsilon_r = 9.72$ for AZO. The respective dielectric constants were measured with an independent impedance measurement and are confirmed by results from literature⁴⁵.

We emphasize that our results are in stark contrast to comparable transport studies investigating the PF effect in nanostructured silicon^{30, 31}. In those reports, the experimentally and theoretically derived values of ϵ_r , which directly correlate with β , were completely different. It was argued that the theory behind PF effect might not be adaptable to nanostructured films, because these films would not provide a straight-forward physical meaning of ϵ_r . Here, we show that β_{exp} and β_{theo} can indeed match remarkably and thus unambiguously prove the PF effect. We note that the values of β_{exp} at lower temperatures show a larger deviation from β_{theo} for AZO, but the plot of $\ln(\sigma)$ versus \sqrt{E} still provides broad linear regimes particularly for higher voltages. This rules out other transport mechanisms, such as tunneling or SCLC⁴⁶. Another possibility which should also be considered is Richardson-Schottky emission: it is the attenuation of a metal-insulator barrier arising from electrode image-force interaction with the field at the metal-insulator interface⁴⁷. Richardson-Schottky (RS) effect and PF effect are easily mixed up, as the J - V characteristics follow the same functional dependency on the electric field but the exponent for the RS effect is by a factor of 2 smaller. Therefore, our results clearly underline that transport in nanoparticulate ZnO and AZO follows the PF theory and not the RS theory. Moreover, the symmetry of the J - V characteristics despite the asymmetric contacts and the film thickness in the μm range clearly demonstrate that the conduction through the sandwich devices is bulk-limited (Poole-Frenkel), and not electrode-limited (Richardson-Schottky).

We sought to determine the barrier height Φ for AZO and ZnO. From Equation 1 it is evident that the conductivity at zero electric field (σ_0) is thermally activated. Figures 2c and 3c show an Arrhenius plot of (σ_0) for ZnO and AZO. Note that $\ln(\sigma_0)$ equals the y-intercept of the linear regimes in Figures 2b and 3b. The activation energies determined from the slopes in Figures 2c and 3c are $\Phi_{AZO} = 135\text{meV}$ and $\Phi_{ZnO} = 337\text{meV}$, respectively.

We emphasize that the activation energy of ZnO is by more than a factor of 2 higher than that of AZO but β_{exp} is practically the same for AZO and ZnO. This suggests that the nature of the charge transport mechanism is *equivalent* for intrinsic ZnO and AZO .

The question arises, why electron transport through these nanoparticulate thin films is so well described by the PF theory.

Due to the low post-deposition temperature, the thin films of AZO/ZnO can be considered as 3D assemblies of single nanoparticles (neck formation between neighboring nanoparticles is not expected at 80 °C²³). Electron conduction across the film requires that electrons are transferred from one nanoparticle to its next neighbor and so forth.

Practically such a hopping transport at higher temperatures is very likely to be thermally activated following $\sigma \propto \exp\left(\frac{-\Delta E}{T}\right)$. It is noted that a more complex temperature dependency is typically just observed in the limit of low temperatures and/or in amorphous systems^{48,49}.

On the other hand, the electric field often strongly influences charge transport in such systems^{50, 51}. However, to the best of the authors' knowledge, this is the first time that Poole-Frenkel-like charge transport was found in nanoparticulate thin films.

In order to experience PF effect, a trap is required to be positively *charged when empty* and *uncharged when filled*⁴¹. Consequently, the interaction between the positively charged trap and the trapped electron gives rise to a coulombic barrier. The question remains, what the origin of the observed activation energies in AZO ($\Phi_{AZO} = 135\text{meV}$) and ZnO ($\Phi_{ZnO} = 337\text{meV}$) is.

In literature, defects in ZnO (single crystal or sputtered film) with similar energy values have been observed in DLTS and impedance spectroscopy⁵²⁻⁵⁶. Reference 53 suggests that these defects might relate to the incorporation of oxygen in the crystal lattice. We emphasize that the origin of defects in ZnO is generally under debate in literature⁵²⁻⁵⁸ and that a direct comparison with literature needs to be done with caution, as the defect density is sensitively

affected by the growth method and annealing conditions. In addition, the flame spray synthesis utilized in this work is a new and novel production method.

The lower observed activation energy for the AZO thin films is due to the higher free electron concentration. Al is a shallow donor in ZnO (in Reference 59, it was shown that Al is even substitutionally shallow) and by the increased free charge-carrier concentration the Fermi-energy is closer to the “transport-band”. Consequently the thermal activation energy for the charge transport is reduced. In either case the nature of the charge transport remains unaffected by the Al doping and is limited by the inter-particle charge transport. We suggest that this might be attributed to surface defects, which always occur due to unsaturated bonds on the surface, but further investigations are needed to test this hypothesis.

CONCLUSION

In this work, the conduction through nanoparticulate ZnO and AZO thin films was investigated. While the J-V characteristics at low voltage obey Ohm’s law, transport in the high voltage data regime is dominated by Poole-Frenkel effect. It is outlined that the occurrence of the Poole-Frenkel effect is related to coulombically-bound electrons, which have to overcome a field-dependent barrier to the next nanoparticle. It is demonstrated that the conduction mechanism is equivalent for the AZO nanoparticles, where Al acts as a shallow donor. To the best of our knowledge, this is the first time that Poole-Frenkel effect was unambiguously demonstrated as the dominant transport mechanism in a nanoparticulate thin film.

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SUPPORTING INFORMATION AVAILABLE

Supplementary details are available on the experimental procedure, the symmetry of the J-V data of AZO and ZnO, the fitting of the AZO J-V plot and tables containing the data related to Figures 2b and 3b.

FIGURES

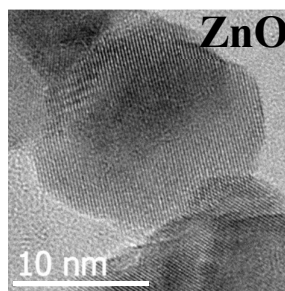
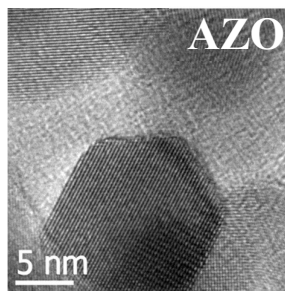


Figure 1: Transmission electron microscopy images for AZO and ZnO nanoparticles.

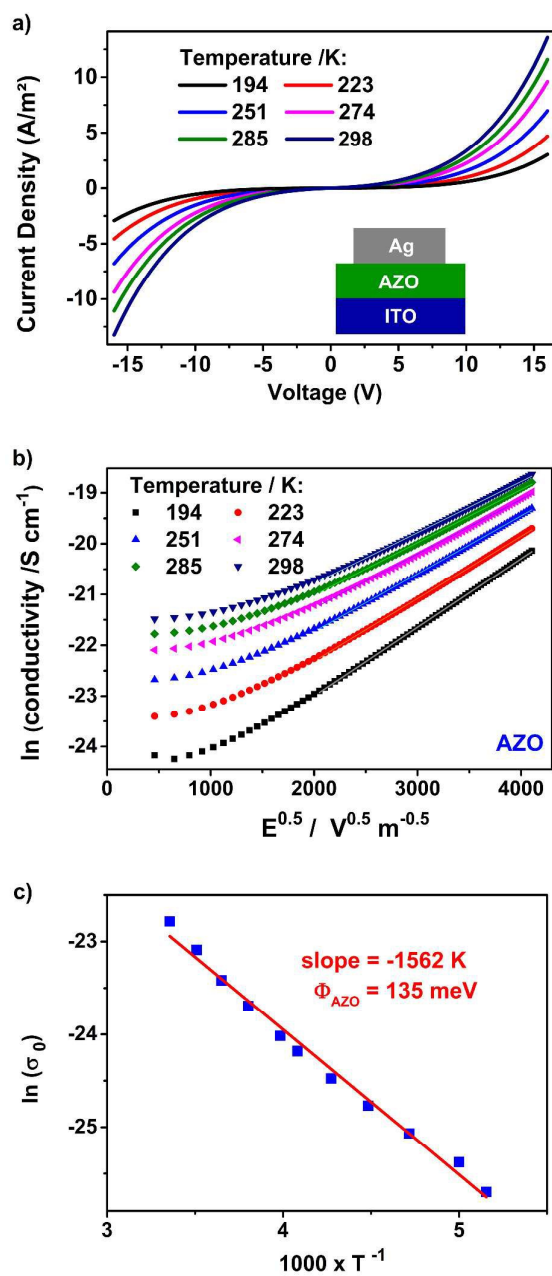


Figure 2: **a)** Current density-voltage (J-V) characteristic of AZO (950 nm) recorded at different temperatures. The inset shows the device setup. **b)** Natural logarithm of conductivity determined for the J-V data of AZO versus the square root of the applied electric field. This plot corresponds to Equation 3. **c)** The y-intercepts of the linear fit functions ($\ln\sigma_0$) in Figure 2b are plotted versus the inverse of temperature to determine the trap barrier height.

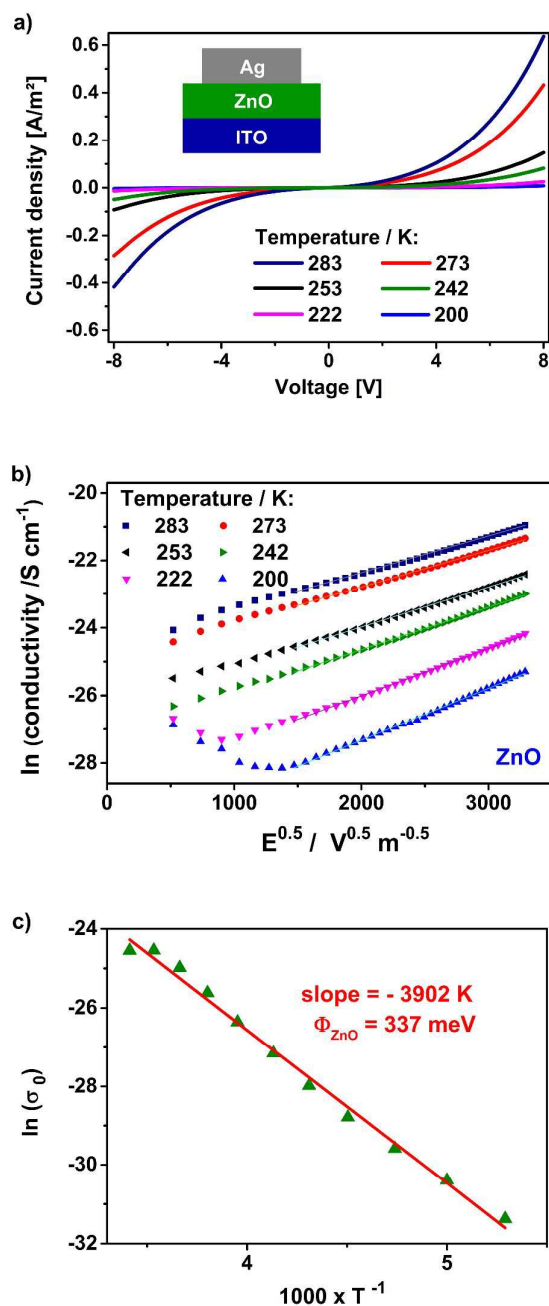


Figure 3: **a)** Current density-voltage (J-V) characteristics of ZnO (740 nm) recorded at different temperatures. The inset shows the device setup. **b)** Natural logarithm of conductivity determined for the J-V data of ZnO versus the square root of the applied electric field. This plot corresponds to Equation 3. **c)** The y-intercepts of the linear fit functions ($\ln\sigma_0$) in Figure 3b are plotted versus the inverse of temperature to determine the trap barrier height.

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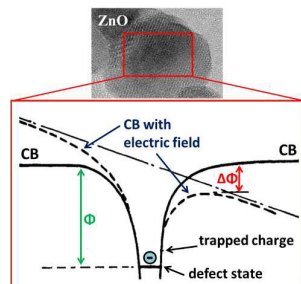
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