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First principles study and variable range hopping conductivity in disordered Al/Ti/Mn-doped ZnO

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ABSTRACT

Based on first principles electronic structure calculations using the Coherent Potential Approximation (CPA) in the Blackman–Esterling–Berk (BEB) multiscattering formalism and the variable range hopping (VRH) model proposed by Mott, we evaluate the low temperature dc conductivity and its temperature dependence for n-doped wurtzite-type M:ZnO, with M = Al, Ti, Mn, at concentrations of 2, 5 and 10 at.% respectively. We theoretically determine the phenomenologic quantities in the expression of the hopping conductivity, as well as the temperature range in which the VRH model is applicable to the investigated compounds. We show that self-consistent CPA-BEB and LSDA+U calculations yield reasonable band gaps, dopant state localization and also spin magnetic moments for the Ti and Mn systems. These results are discussed in comparison with reported data obtained by supercell LSDA+U calculations for similar systems. The results in this study point to 2–5 at.% Ti and approximately 2 at.% Al codoping in wurtzite-type ZnO as an interesting option to obtain a material with an increased low temperature dc conductivity and ferromagnetic background.

1. Introduction

Over the past decade studies on transparent semiconductor oxides have brought considerable evidence leading to wurtzite-type zinc oxide (ZnO) as a promising candidate material for transparent electronics, sensors and solar cells [1–9]. The focus of experimental investigations has been on improving the control of both electrical [10] and spin-dependent conductivities [2], as well as the creation of an intrinsic stable ferromagnetic background above room temperature required in spintronic applications [11]. The real material shows a significant level of intrinsic n-doping to which the effects of dopant atoms sum up. Particularly, ZnO thin films and nanostructures show a great sensitivity of the targeted conduction and magnetic properties to dopant species used to tune their properties, a fact which also determines a large scatter in the reported measured data. Thus, an early review of experimental results obtained on doped and undoped ZnO thin films deposited by a wealth of methods was presented in Ref. [12], with the aim to establish the physical limits of electrical resistivity in this material. Based on the findings that: (i) the lowest resistivities in ZnO thin films are in the range of $1.4–2 \times 10^{-4}\,\Omega\,\mathrm{cm}$, independently of the deposition method, (ii) an upper limit of carrier concentration of about $1.5 \times 10^{21}\,\mathrm{cm}^{-3}$, corresponding to a dopant solubility limit of about 4 at.%, and (iii) an upper limit of the carrier mobility in the region $n > 5 \times 10^{20}\,\mathrm{cm}^{-3}$ of about $40\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$, the author suggests that resistivities less than $1 \times 10^{-4}\,\Omega\,\mathrm{cm}$ for doped polycrystalline zinc oxide films are hard to achieve, due to a general limitation by ionized impurity scattering.

Since then, a great effort has been undertaken to improve the electrical and optical properties of ZnO films by utilizing a diversity of material synthesis techniques, substrates, doping and processing routes. Controlling electrical conductivity by Al-doping has received a particular interest as a convenient way of carrier density and mobility changing [2,13], which also has useful effects on optical properties in the blue and UV regions of the spectrum [14,15]. Recently, resistivity values of the order 10^{-3}–$10^{-4}\,\Omega\,\mathrm{cm}$ were reported for Al-doped ZnO thin films with Al concentration between 0.25 and 3.5 at.% [16–19]. The investigations have proven that for a given Al concentration the film resistivity values strongly depend on the synthesis method and post-processing, which determine the nanostructure and the defective state. Also, some experiments underscore the fact that increasing Al concentration above approximately 4 at.% determines an increase in the resistivity [17,20].

Research work performed on Ti-doped (97% ZnO+3% Al_2O_3), (ZATO), and undoped, (ZAO), films showed that the lowest achievable resistivity is 7.96 and $8.7 \times 10^{-4}\,\Omega\,\mathrm{cm}$ for ZATO and ZAO as-processed films, respectively, whereas after annealing in air, the resistivity of both ZATO and ZAO films is higher than

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$10^5\ \Omega\,cm$ [21]. The authors attributed this behavior mainly to the increase of oxygen defect levels and the disorder promoted by impurities.

The properties of Ti-doped ZnO films deposited on Al_2O_3 (0001) substrates with varying temperature, T_S, were also investigated [22]. The Ti and carrier concentrations were found to increase with increasing T_S, whereas the band-gap increased for $T_S = 100$ and 200 °C from that of pure ZnO and decreased for $T_S = 300$ and 400 °C. These authors rationalize that the observed band-gap variation along with a large increase in carrier concentration between $T_S = 200$ and 300 °C are due to a merging of the donor band with the conduction band minimum, which determines a semiconductor-metal transition. The increase in the donor density was tentatively attributed to the increase of the defect density at higher Ti doping levels [22].

In another investigation of ZnO:Ti films, a resistivity value of $3.82 \times 10^{-3}\ \Omega\,cm$ was determined and a semiconductor-metal transition was also reported for Ti concentration of 1.3% [23]. The enhancement of conductivity and the semiconductor-metal transition are likely attributed to the increase in the free carrier concentration, along with band-gap shrinkage effects caused by Ti doping.

Several studies of Al-doped ZnO thin films [24,13,25,26] have suggested that the conduction mechanism below 220 K may be interpreted within the variable-range hopping (VRH) model proposed by Mott for the carrier transport in disordered systems [27,28]. For the proper carrier concentration range [29] the VRH regime was identified by measuring the film resistivity as a function of temperature and fitting the experimental data to the relation $ln(\sigma T^{1/2}) \propto T^{-1/4}$ in the low temperature limit. A straight-line fit establishes the VRH behavior for $T < T_0$, with the fitting parameter T_0 giving an indication of the hopping probability: a high value of T_0 corresponds to a low probability for hopping and to a low conductivity [27]. It has been suggested that the VRH mechanism is also effective in pulsed laser deposited films obtained in a nitrogen atmosphere [30]. The observed enhancement of the conductivity was assigned to both the nitrogen ions and nitrogen induced defects in the zinc oxide lattice, that behave as localized hopping centers, as well as carrier suppliers.

A much lower temperature range for the hopping conduction mechanisms was determined in Mn-doped ZnO, in the dilute Mn concentration range of 0.1, 0.3, and 0.6% Mn [31]. The electrical conduction was studied by analyzing the dc and ac conductivity data. The abrupt change in the temperature dependence of conductivity at approximately 18 K and a much lower activation energy for conduction below 18 K were attributed to a transition from band, above 18 K, to hopping conduction between 18 to 10 K [32]. Since Mn contributes with deep donor states at about 2.0 eV below the conduction band bottom at room temperature, an increase in Mn concentration determines a decrease of the shallow donor concentration and therefore of the conductivity. The calculated critical temperature for the transition from a nearest neighbor hopping (NNH) mechanism to the VRH regime was evaluated below approx. 2 K [31].

It is worth to note that under certain conditions the experimental investigations may also be hindered by the formation of an electron accumulation layer near the surface which can alter the measured conductivity values in the underlying bulk or film (see [2] and references cited therein).

A systematic, clear cut study of the relationship between conductivity and magnetism in Mn, Co, Al -doped ZnO films with a wide range of carrier densities was presented in [33]. These authors identify three conductivity regimes which have a critical role on the magnetic behavior also, as follows: (1) an insulating phase, at low carrier densities, in which the low temperature conductivity arises from a variable range hopping process. In this regime, the least conducting films are the most magnetic at room temperature due to the interaction of the localized spins with static localized states; (2) an intermediate carrier concentration regime, where the samples satisfy neither the conditions for VRH at low temperatures nor for metallic behavior at room temperature. In this case, magnetism is quenched, due to carriers in the localized states becoming mobile; (3) a metallic phase at high carrier densities, in which free carrier-mediated exchange determines ferromagnetism, as predicted by theory [34].

In another investigation of the electrical transport and magnetoresistance in Co heavily doped TiO_2 and ZnO [35] it has been highlighted that, due to significant Coulomb interaction between localized carriers at high doping levels, both the spin–spin exchange between the carrier spins and the Coulomb interaction should be taken into account in the same frame. A linear relation of $\ln\rho$ versus $T^{-1/2}$ in the low temperature range was observed experimentally, in agreement with the theoretical model in [36,37] and a quantitative explanation in a spin-dependent variable range hopping model was proposed in [35].

Several first principles studies have approached the physical aspects involved in the description of the electronic conduction mechanisms in defective/doped ZnO. Extensive analyses of the details of the electronic structure in defective and/or doped ZnO have attempted to find justifications for the intrinsic n-type conductivity, the role of defects and dopants, as well as the difficulty in achieving the p-type conductivity (see, e.g., [2,10,38,9]). Although there is a conceptual agreement of these studies as regards the role of defects on the electrical and optical properties, no quantitative evaluation of the electrical conductivity is made based on calculation results, as a function of doping or temperature. Thus, one may not draw specific conclusions of practical relevance for the control of conductivity in the real material unless establishing, by experiment and theory, an unambiguos relationship between the sources – dopant and/or defect – and the electronic effect they produce.

In this contribution we present electronic structure results obtained within the Coherent Potential Approximation (CPA) and Blackman–Esterling–Berk (BEB) multiscattering formalism implemented in the FPLO5 code, in wurtzite-type $Zn_{1-x}M_xO$ crystal, with M=Al, Ti and Mn. We calculate the low temperature dc conductivity in the regime where electron hopping on localized impurity levels is the dominating mechanism described in Mott's Variable Range Hopping (VRH) model [32]. We theoretically determine the phenomenologic quantities in the expression of the hopping conductivity, as well as the temperature range in which the VRH model is applicable to the investigated compounds. A discussion of the magnetism promoted by Ti and Mn, and a prediction of the best material for a dilute magnetic semiconductor is also included. The paper is organized as follows. In Section 2 we present the details of our calculations. Then, an account on the electronic structure results obtained in this work for the Al, Ti and Mn-doped ZnO systems is given in Section 3. We also contrast our present results obtained using the CPA-BEB-LSDA+U formalism with reported calculated data on similar systems. In Section 4 we use these results to discuss the dc conductivity in the underlying systems analyzed in the variable range hopping model. We establish the dopant concentration and temperature ranges that are adequate for the applicability of this model in $Zn_{1-x}M_xO$ systems. Section 5 summarizes the conclusions of this work and a prediction on a suitable semiconductor combining a high dc conductivity and magnetism is made.

2. Calculation method

We carried out self consistent calculations in the Local Spin Density Approximation (LSDA) using the FPLO5.00-20 band structure code [39,40]. The exchange and correlation potential was trea-