

Features of the hopping conductivity in gallium and cobalt doped ZnO thin films

V G Kytin^{1,a}, O V Reukova^{1,b}, V A Kulbachinskii^{1,c}, L I Burova², A R Kaul², A G Ulyashin³

¹Physics Faculty, M.V. Lomonosov Moscow State University, 119991, Moscow, Russia

²Chemistry Department, M.V. Lomonosov Moscow State University, 119991, Moscow, Russia

³SINTEF Materials and Chemistry, P.O. Box 124, Forskingsveien 1, Blindern, 0314 Oslo, Norway

E-mail: ^akytin@mig.phys.msu.ru; ^breukova@physics.msu.ru; ^ckulb@mig.phys.msu.ru;

Abstract. The effect of Ga and Co doping on the hopping transport of electrons in ZnO films was studied. All investigated films were deposited on monocrystalline substrates by water assisted metal organic chemical vapour deposition method. Temperature dependencies of the resistivity of all films obeyed the Mott's law at low temperatures. Both positive and negative magnetoresistance were observed in the temperature range of the Mott's law. The values of the localization length obtained from magneto transport data for ZnO and ZnO:Ga films are larger than the effective Bohr radii of a shallow donor state and are independent on the Ga content. These observations point to the localization of electrons in the random potential originating from the structural disorder. In Co doped ZnO films large positive magnetoresistance was observed in low magnetic fields at low temperatures. The value of positive magnetoresistance increases with an increase of Co content and decrease of temperature. Observed magneto transport properties of Co-doped films were interpreted by the decrease of electron hopping probability due to decrease of the density of localized states in magnetic field.

Introduction

Conducting properties of ZnO films are the subject of intensive investigation due to their importance for applications and understanding of electron transport mechanisms in disordered semiconductors. Electrophysical properties of doped and undoped ZnO films depend strongly on the structure of the films and can be essentially modified by doping with different impurities [1].

Gallium is group III element. Therefore it behaves as donor impurity substituting Zn in ZnO lattice. In interstitial position Ga can also supply electrons in conduction band. Cobalt can be solved in ZnO up to very high concentration [2-3]. According to X-ray diffraction and X-ray absorption data it preferably substitutes zinc in the lattice in the same charge state. Therefore it should be electrically inactive. However there are observations that doping of ZnO films with Co essentially changes the resistivity, galvanomagnetic and magnetic properties of the films [2-3]. At low temperatures large positive magnetoresistance was reported in ZnO films doped with Co and Mn [1-3]. The value of this magnetoresistance increases with an increase of magnetic impurity content. Therefore recent theoretical models consider this magnetoresistance as spin-related and suggest exchange interaction between d-electrons of impurity and conduction electrons. The presence of this interaction is



supported by an increase of band gap with an increase of Co content [4]. The resent models for spin related magnetoresistance were developed for hopping transport of electrons. Therefore investigation of hopping conductivity in ZnO films with and without magnetic impurity is important for understanding the effect of magnetic impurity on electron transport.

This work reports the investigation of hoping conductivity in thin ZnO films doped with Co and Ga in the wide range of temperatures and magnetic fields. Temperature dependence of resistivity and magnetoresistance of the films were compared and analyzed in frame of available models of hopping transport.

Experimental

Investigated films were synthesized by water-assisted chemical vapor deposition (MOCVD). The details of this modification of MOCVD deposition method are presented in [5-6]. Water assisted MOCVD allows the deposition at lower temperatures than oxygen-assited MOCVD. All films were deposited on monocrystalline substrates of R- and C-sapphire and Yttrium stabilized zirconia (YSZ). Gallium and cobalt content were determined by energy dispersive X-ray microanalysis. Structure of the films was studied by X-ray diffraction. It was found that all films were polycrystalline with chaotic orientation of crystallites. Surface morphology of the films was investigated by scanning electron microscopy (SEM). According to SEM images surface of the films was nearly smooth although some crystallites can be seen. This is consistent with X-ray diffraction data. Some parameters of investigated films are listed in Table.1.

Table 1. Deposition parameters of studied films

Film	Substrate	T _{deposition} (°C)	Thickness (nm)	Impurity content at%
GaC	C-sapphire	350	900	7 (Ga)
GaR	R-sapphire	350	750	21 at% (Ga)
GaY	Zr ₂ O ₃ (Y ₂ O ₃)	350	900	25 wt% (Ga)
Co1	R-sapphire	500	70	0.4 (Co)
Co2	R-sapphire	500	80	1.9 (Co)

Resistivity and magnetoresistance of the films were measured by the conventional four probe method. Samples for measurements were prepared in rectangular shape with typical dimensions 5×3 mm. Contact plates were made by vacuum deposition of gold and copper wires were soldered to the plates. For the measurements samples were mounted in the cryostat where the temperature was varied from 4.2 to 293 K. Magnetic fields up to 6 T for magnetoresistance measurements was created by superconducting solenoid. The presence of CoO or other phases was not detected

Results and discussion

For all investigated films significant increase of resistivity with the decrease of temperature was observed in the in all studied temperature range. Observed temperature dependencies of resistivity can be well described by Mott's law [7] at sufficiently low temperatures:

$$\rho = \rho_0 \exp \left[\left(\frac{T_0}{T} \right)^{1/4} \right] \quad (1)$$

where ρ and T is the resistivity and the temperature, ρ_0 and T_0 are parameters. This is illustrated in figure 1. Mott's law was derived for variable range hopping conduction in disordered semiconductors. Parameter T_0 depends on the density of localized states at Fermi energy $g(E_F)$ and localization length r_{loc} of electron wave function [7]:

$$T_0 = \frac{\beta}{k_B g(E_F) r_{loc}^3}, \quad (2)$$

where $\beta=21,2$ is the digital coefficient, k_B is the Boltzmann constant.

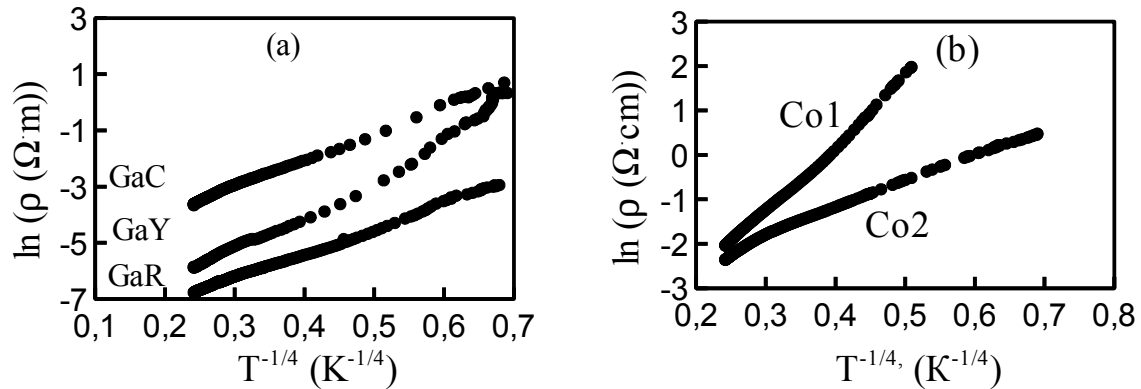


Figure 1. Dependencies of $\ln(\rho)$ on $T^{-1/4}$ for ZnO:Ga (a) and ZnO:Co (b) films

All investigated films exhibited positive and negative magnetoresistance depending on temperature and magnetic field range. Magnetoresistance of some Ga and Co-doped film is shown in figure 2. In low magnetic fields magnetoresistance of ZnO:Ga films is negative while in higher magnetic field it is positive. At low temperatures magnetoresistance of ZnO:Co films was strong and positive. In higher magnetic fields the saturation or change the sign of magnetoresistance from positive to negative was observed for these films. These observations suggest different origin of magnetoresistance for Ga and Co-doped films.

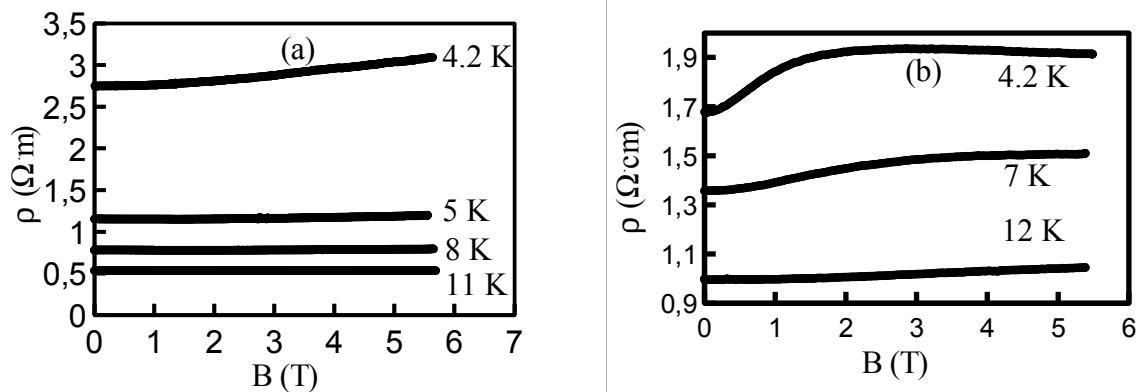


Figure 2. Magnetoresistance of GaC (a) and Co2 (b) films

Several mechanisms of magnetoresistance were proposed for hopping transport of electrons. Some of them consider the effect of magnetic field on the localization length of electron wave function. In sufficiently strong magnetic field the localization length of electrons decreases in the directions perpendicular to magnetic field. This is the origin of positive magnetoresistance for hopping conduction [7]. The value of this positive magnetoresistance is significant when magnetic length ($l_B = \sqrt{\hbar/eB}$) is comparable or smaller than localization length in zero magnetic field. Expressions for this type of positive magnetoresistance were presented in [7]. For example in low magnetic field ($l_B \gg r_{loc}(B=0)$):

$$\rho = \rho_0 \exp \left[\alpha \frac{e^2 r_{loc}^4 B^2}{\hbar^2} \left(\frac{T_0}{T} \right)^{3/4} \right] \quad (3)$$

In this expression $\alpha=5/2016$ is the digital coefficient, B is the magnetic field, e is the elementary charge, \hbar is the Plank constant. In low magnetic field logarithm of magnetoresistance is proportional to the square of magnetic field while in high magnetic field it is proportional to the square root of magnetic field. In figure 3 (a) logarithm of resistivity is plotted versus square of magnetic field for ZnO:Ga films. Taking a slope of linear parts of the plots and using expressions (2) and (3) we calculated the localization length and density of electronic states at Fermi energy. Obtained values are listed in table 2.

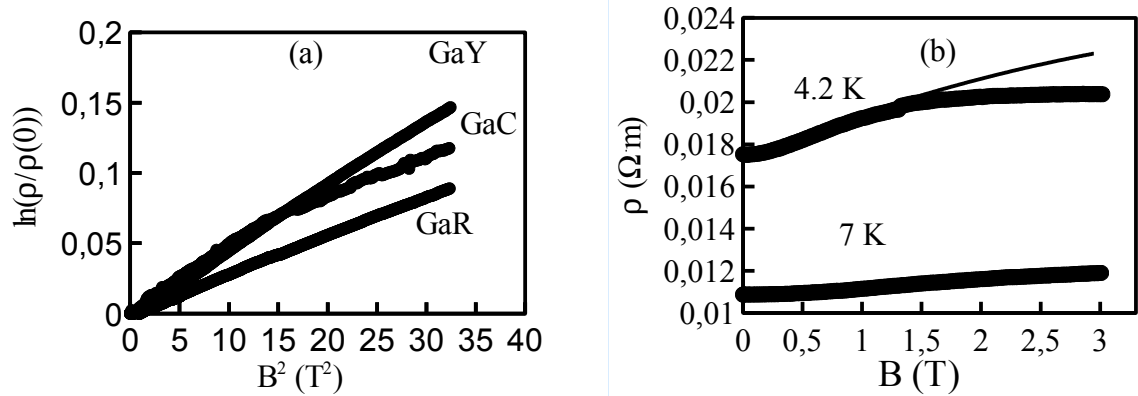


Figure 3. Dependencies of $\ln(\rho)$ on B^2 for ZnO:Ga films at 4.2 K (a) Magnetoresistance fitting for Co2 film by expressions (4-5) (b) Points are experimental data, Solid lines are fitting by expressions (4-5)

The value of localization length is significantly larger than the effective Bohr radii in ZnO (1.3 nm). Thus the localization of electrons most probably occurs due to polycrystalline structure of structure and random potential caused by disorder and random distribution of donors. Then localization can be partially caused by interference of electron waves scattered by separated donors and/or grain boundaries. Magnetic field destroys the interference introducing additional phase shift between scattered electron waves. This mechanism of negative magnetoresistance for variable range hopping conduction was proposed in many publications [8-10]. Therefore the observation of negative magnetoresistance is consistent with the large value of localization length listed in table 2.

Large positive magnetoresistance observed in Co-doped films should be somehow related to the presence of magnetic impurity. There are several models for spin-related magnetoresistance and hopping conduction of electrons. The recent and detailed interpretation of positive magnetoresistance in magnetically doped semiconductors was presented in [11]. The authors of this work showed that the density of electronic states at Fermi energy can be reduced in magnetic field. They proposed the method for determination of the relative variation of width σ of the density of localized states assuming Gaussian form of density of states. The method is based on the following expressions:

$$\frac{\rho}{T} = f\left(\frac{\sigma}{\sigma_0 T}\right) \quad (4)$$

$$\frac{\sigma(B)}{\sigma_0} = \sqrt{1 - \gamma_1^2 + \left(\gamma_1 + \gamma_2 BF\left(\frac{g\mu_B B}{k_B T}\right)\right)^2} \quad (5)$$

where σ – is width of the energy distribution of donor levels, f is the universal function, BF is the Brillouin function, μ_B and g is Bohr magneton and factor Lande. The fitting of magnetoresistance of Co2 film by expressions (4-5) is shown in figure 3 (b). Fitting parameters were γ_1 and γ_2 . Expressions (4-5) describes the experimental magnetoresistance quite well for intermediate magnetic fields. For low and especially for high magnetic fields theoretical dependence is stronger than the experimental one. The deviation can be due the difference between BF and real magnetization. Negative

magnetoresistance (NMR) observed at 4.2 K can originate from bound magnetic polarons [12]. This type of NMR can also decrease the total MR in smaller magnetic field.. Parameters γ_1 and γ_2 are related to the localization length of donor states via expressions [11]:

$$r_{loc} = \left(\frac{d E_c / dx}{y x^{1/2} N^{3/2}} \right)^{2/9} \quad (6)$$

$$y = \alpha J \frac{\gamma_1}{2 \gamma_2} \quad (7)$$

where N is the Zn concentration, x is the Co content, α is the exchange energy, E_c is the bottom of conduction band, J is angular momentum of Co ion.

Table 2. Density of states at Fermi energy and localization length for ZnO:Ga films

Film	$g(E_F)$, ($10^{19} \text{ eV}^{-1} \text{ cm}^{-3}$)	r_{loc} (nm)
GaC	7.1	7.3
GaR2	4.2	5.5
GaY1	13	6.9

Taking α and dE_c/dx from [4] we got an estimate of 1.2 nm for localization length in Co2. This value is close to effective Bohr radii of shallow donors in ZnO (1.3 nm).

Summary

Thus the hopping transport of electrons in ZnO films doped with Ga and Co was investigated and compared. Density of localized states at Fermi energy and localization length was estimated for ZnO:Ga films by analysis of temperature dependencies of resistivity and magnetoresistance data. Obtained values of localization length are essentially larger than effective radii of shallow donors and nearly independent on Ga content. Magnetoresistance of ZnO:Co films was interpreted by reduction of electron density of states at Fermi energy in magnetic field due to Zeeman effect and exchange interaction between conduction electrons and magnetic impurity.

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