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# ELECTRICAL PROPERTIES OF (Zn,Cu)O:Mn SUBMICRON WIRES

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Arrays of multisegment Pd/(Zn,Cu)O:Mn/Pd submicron wires have been grown electrochemically into the pores of nuclear track polycarbonate membranes. Their transport properties were investigated, by measuring current-voltage (I-V) characteristics in a temperature range from 300 K down to 40 K. I-V characteristics of Pd/(Zn,Cu)O:Mn/Pd wires exhibited a symmetric, non-linear shape on applied bias voltage ranging from -20 V to +20V. The ohmic region corresponds to polarization voltage under 3.5V. Comparatively, I-V characteristics of Pd/ZnO/Pd array of wires with diameter about 500 nm are linear in the entire range of applied voltages (-20 V to +20V).

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## 1. Introductiom

Zinc oxide, as direct and wide bandgap material, has attracted in the last decade intense experimental and theoretical attention for its potential applications in nanoelectronics and optoelectronics. Undoped ZnO with a wurtzite structure naturally becomes an n-type semiconductor due to the presence of intrinsic defects, which were generally attributed to native defects, such as the Zn interstitial or O vacancy [1,2]. On the other hand, hydrogen [3-6] is a common impurity in ZnO that strongly influences its electrical and optical properties. Diluted magnetic semiconductors (DMS) such as Mn-doped ZnO are attractive materials for the field of spintronics because both their electric and magnetic properties could be used for applications. Dietl et al. [7] predicted a Curie temperature $T_C$ of about 310 K for ZnO doped with a few percent of Mn. In this model ferromagnetism is supposed to be mediated by holes in the valence band. On the other hand, Sato and Katayama-Yoshida [8] have predicted also the possibility that high-Curie-temperature ferromagnetic materials could be realized also in n-type ZnO. Since $Mn^{2+}$ is an isovalent impurity in the ZnO matrix, no change in the carrier concentration can be expected. Co-doping with $Cu^{+}$ could facilitate the control of free charge carriers density.

ZnO is one of the few dominant nanomaterials for nanotechnology; it exhibits most of the configurations of nanostructures that one material can form [9-13]. Electrodeposition of ZnO films and nanorods in the presence of metal ions has been discussed by various groups [14-19].

Here, we report on our results on transport properties of multisegments submicron wires Pd/(Zn,Cu)O:Mn/Pd, prepared electrochemically by template method. The paper is organized as follows: experimental details on the deposition procedure of the wires are given in the next section. In the third section, the results of the investigation of transport properties are presented and discussed.

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## 2. Experimental details

Multisegments submicron wires Pd/ZnO/Pd and Pd/(Zn,Cu)O:Mn/Pd have been grown electrochemically by template method in polycarbonate membranes (pore diameter 500 nm, pore density $10^6$ $cm^{-2}$, membrane thickness 30 μm) covered with a copper/gold layer on one side, playing the role of cathode; its surface area was 1.75 $cm^2$. The aqueous solutions used to prepare undoped and doped ZnO wires and palladium contacts by using an electrodeposition process are presented in the Table 1. (Zn,Cu)O:Mn and ZnO wires were obtained from solutions A and B, respectively. The deposition potential was -0.7 V vs. saturated calomel electrode (SCE) and the temperature of the electrochemical bath was kept at $70^0$C; in these conditions, the length of the semiconductors segments was about 5 μm. Palladium segments were grown at -1.2 V/SCE from solution C The electrochemical processes were conducted using an Autolab PGSTAT 30 potentiostat, controlled by a computer.

For the purpose of imaging the nanowires using a scanning electron microscope, after the electrodeposition process was completed, the polymer membrane was dissolved in dichloromethane. The microstructures of deposits were imaged using a FEY Quanta Inspect scanning electron microscope, equipped with an EDAX device, for chemical composition measurements. From EDX spectra we have estimated the ratios (at%) of the metallic ion contents in ZnO:Mn:Cu wires, as 69% Zn : 30% Cu : 1% Mn. The SEM image of Pd/(Zn,Cu)O:Mn/Pd multisegments is presented in Fig.1.

*Table 1.Chemical compositions of the used solutions*

| Solution | Composition |
|---|---|
| A | 0.05 M $Zn(NO_3)_2$ + 0.01 M $Mn(NO_3)_2$ + 0.0005 M $Cu(NO_3)_2$ + 0.055 M lactic acid, pH 4.7 |
| B | 0.05 M $Zn(NO_3)_2$ |
| C | 0.0005M $PdCl_2$, 0.01M $NH_4Cl$, 0.1M $(NH_4)_2HPO_4$ |

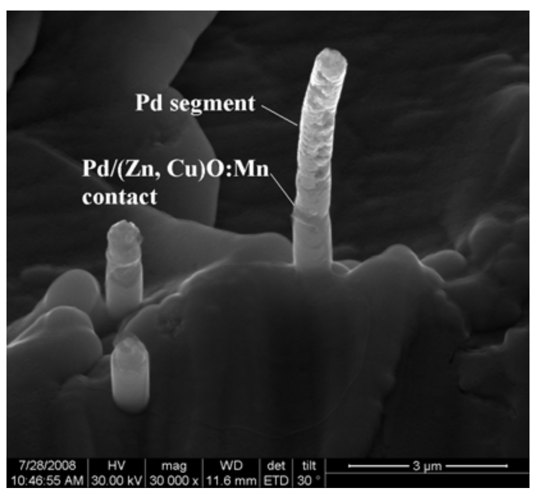


*Fig. 1.Pd/(Zn,Cu)O:Mn contacts for wires with diameter about 500 nm*

For electrical measurements, polycarbonate membranes containing multisegments wires were covered with a second gold film, thickened by electrochemical deposition with a copper layer.

Transport properties were investigated by using a Keithley 2400 SourceMeter and a Keithley 6517a electrometer, controlled by a computer. The samples were placed in a closed cycle helium cryostat, with sample in vacuum (residual pressure was below $10^{-3}$ Torr).

## 3. Results and discussion

In this study, "non-doped" samples, with Pd/ZnO/Pd wires, were used as a reference for those doped with Cu and Mn. Both types of samples were deposited in the same conditions, as described above. Next, we will start by discussing the transport properties of non-doped Pd/ZnO/Pd array of wires.

**Transport properties of Pd/ZnO/Pd**

I-V characteristics of Pd/ZnO/Pd array of wires with diameter about 500 nm are linear in the entire range of applied voltages covered during this experiment (Fig.2a), respectively -20 V, +20 V. The average current density through a wire, at 12 V and 290 K, is about 0.8 mA/cm$^2$, when the applied electric field is $8.3 \times 10^3$ V/cm. The fact that the ohmic regime is present at such values of the electric field is remarkable; it can be a proof of good crystalline quality of wires.

The temperature dependence of the electrical resistance of the samples, *R(T)*, is indicated in Fig.2b. At temperatures above 200 K a band conduction mechanism is determining the electrical conduction of the sample (it shows a n-type conduction, as obtained from thermoelectric measurements). The temperature dependence of the resistance of this sample is of activated type, described by the equation: $R(T) = R_0(T)\exp\left(\frac{E_a}{k_B T}\right)$(1)

where $E_a$ is the activation energy, $k_B$ is Boltzmann's constant and the pre-exponential factor $R_0\ (T)$ may have a weak temperature dependence, which is due to the dominant scattering mechanism of conduction electrons [20].

The value of the activation energy, obtained by numerical fit, was 0.064 eV; it can be related to the ionization energy of the main donor center, but the nature of this center remains unknown. *R(T)* dependence described by eq. (1) is induced primarily by the rapid decrease of the concentration of conduction band electrons, due to their recapturing on the main donor levels.
At temperatures below 200 K there is a gradual shift to another conduction mechanism, and below 90 K resistance varies very little with temperature. Data presented in Fig. 2b suggests a hopping transport mechanism in this range (between 90 K and 40 K).

**Transport properties of Pd/(Zn,Cu)O:Mn/Pd**

I-V characteristics of Pd/(Zn,Cu)O:Mn/Pd array of wires embedded in polycarbonate membrane with pore diameter around 500 nm were obtained at various temperature in the interval 40-300 K; they exhibited a clear nonlinear and symmetric dependence on the applied bias voltage, ranging from -20 V to +20 V (Fig.3a).

The ohmic region corresponds to applied voltages below 3.5 V and we have found only a small change of this limit in a temperature range from 300 K down to 40K.

The super-ohmic behaviour registered at voltages higher than 5 V is probably due to a phonon-assisted tunneling mechanism (Fig.3b). Ganichev et al. argued in [21] that a super-ohmic dependence of the current on the applied electric field of the type $\log I \propto E^2$ is a signature for such a mechanism. At this point, it is worth mentioning that contact effects, associated to Schottky barriers, are to be rejected as being responsible for the observed super- ohmic behavior, as they result in unphysically small values of the dielectric constant of the material.

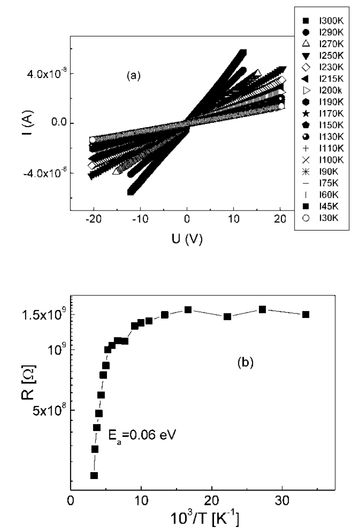


*Fig. 2. Electrical characteristics of Pd/ZnO/Pd array of wires with diameter about 500 nm a) I-V characteristics registered at various temperatures from the interval 40 K-300 K; b) electrical resistance in Arrhenius representation in the temperature range 40 K-300 K*

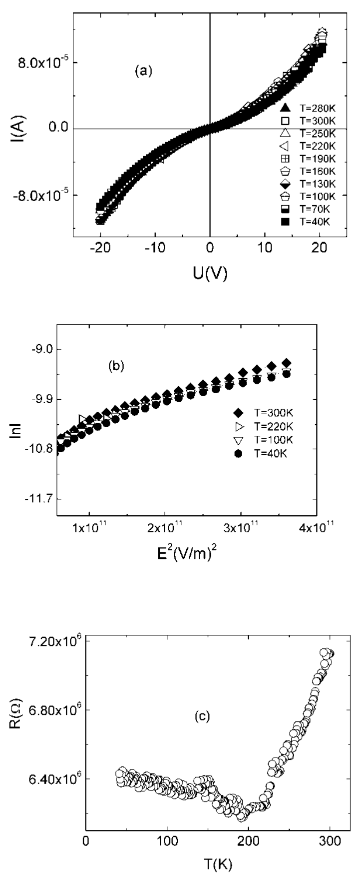


*Fig. 3. a) I-V characteristics of Pd/(Zn,Cu)O:Mn/Pd array of wires with diameters of about 500 nm, recorded at various temperatures in the range 40 K – 300 K; b) current-field dependence in the super-ohmic region of I-V curves; c) temperature dependence of the electrical resistance*

The temperature dependence of the electrical resistance, measured in the ohmic region of I-V characteristics, at an applied voltage of 0.8 V, is presented in the Fig.3c. For this sample, the resistance only changes by a factor of 1.2. The temperature coefficient of the resistance is positive at temperatures higher than 200K, becoming negative at lower temperatures. These results can be explained as follows: the wires in the array act as parallel resistances, the overall resistance of the sample being determined by those wires with the smallest values of their individual resistance. These wires show a metallic behavior, probably induced by regions containing a degenerate ZnO:Cu semiconductor or, less probable, precipitated Cu, percolating through the wire. The observed linear temperature dependence of the resistance above 200 K is then induced by free carriers scattered by phonons. With increasing the applied electric field, more wires, in which degenerate regions are not percolating, being separated by semiconducting ZnO, become conductive through the above mentioned phonon-assisted tunneling mechanism.

## 4. Conclusions

Transport properties of arrays of multisegment wires (500 nm diameter) of types Pd/ZnO/Pd and Pd/(Zn,Cu)O:Mn/Pd, produced by electrochemical deposition, at the same temperature and deposition potential, in the pores of a nuclear track polymer template, were investigated. While Pd/ZnO/Pd wires show a semiconducting behavior, the array of Pd/(Zn,Cu)O:Mn/Pd wires shows a temperature dependence of the electrical resistance typical for degenerate electronic systems. This was related to a degenerate ZnO:Cu phase or precipitated Cu, percolating through some of the wires, which then determine the overall resistance of the sample.

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