

Electron Paramagnetic Resonance in Transition Metal Doped ZnO Nanostructures

A.O. Ankiewicz^{*1}, W. Gehlhoff², A.S. Pereira³, S. Pereira³, A. Hoffmann²,
E.M. Kaidashev⁴, A. Rahm⁴, M. Lorenz⁴, M. Grundmann⁴,
M.C. Carmo¹, T.Trindade², N.A. Sobolev¹

¹Departamento de Física e I3N, Universidade de Aveiro, Campo de Santiago, 3810-193 Aveiro, Portugal

²Institut für Festkörperphysik, Technische Universität Berlin, D-10623 Berlin, Germany

³CICECO, Universidade de Aveiro, Campo de Santiago, 3810-193 Aveiro, Portugal

⁴Institut für Experimentelle Physik II, Universität Leipzig, D-04103 Leipzig, Germany
*amelia@fis.ua.pt

ZnO based diluted magnetic semiconductors attract increasing attention of the scientific community due to their potential applications in spintronics [1]. Electron paramagnetic resonance (EPR) spectroscopy is a powerful characterization tool for this kind of materials. In this work, we studied two types of samples doped with Co and Mn during the growth, ZnO nanowires (NWs) and colloidal ZnO quantum dots (QDs). Extensive simulations of the experimental EPR spectra have been performed to extract information on the incorporation of the ions in the lattice.

The ZnO NWs were synthesized on *a*-plane sapphire substrates by high-pressure pulsed laser deposition. The EPR measurements were carried out in the X-band. For the lowest nominal doping contents in the NWs, we detect the anisotropic EPR spectra of substitutional Mn²⁺ ($3d^5$, 6S) and Co²⁺ ($3d^7$, 4F) on Zn sites. Furthermore, for the sample doped with Co it was possible to identify two different components, A and B, of the reported spectra. We found from the temperature dependence of the EPR intensity that both of these components exhibit paramagnetic behaviour and are present in a concentration ratio of $N_B/N_A=1.4$. In the case of the Mn-doped ZnO NWs, the linewidth increases with increasing Mn concentration due to the dipole-dipole interaction of the paramagnetic ions. At the highest used nominal concentration, an additional broad single line is observed, probably stemming from local regions with higher concentrations of the Mn ions.

We also present detailed analysis of Mn- and Co-doped colloidal ZnO quantum dots (QDs) by simulations of the experimental powder EPR spectra measured in the X- and Q-bands. The doped ZnO QDs were prepared using a colloidal method [2] which consists in the growth of ZnO nanoparticles in the presence of Mn(II) or Co(II) in homogeneous solution. These colloids were isolated as powders, which exhibit EPR spectra stemming in part from the isolated Mn²⁺ ($3d^5$, 6S) and Co²⁺ ($3d^7$, 4F). The excellent agreement between experimental and simulated spectra, using the spin Hamiltonian parameters for bulk material [3,4], reveals that these transition metal (TM) ions were successfully incorporated in the QDs. Furthermore, the EPR spectra show that the TM ions occupy substitutional Zn sites in the wurtzite crystal structure of ZnO, in accordance with complementary X-ray diffraction measurements. The other part of the Mn EPR spectra has a broader linewidth and a larger hyperfine splitting of approximately 90 G. In Ref. [2] this signal was ascribed to Mn bound to the surface. A sound interpretation of the second part of the Co-related spectra is more difficult to

achieve. The tentative interpretation of the part of the spectra that cannot be ascribed to substitutional Co is as coming from a different location of Co in the QDs.

In conclusion, using EPR analysis we have been able to identify the location of the doping Mn and Co ions in ZnO NWs and QDs.

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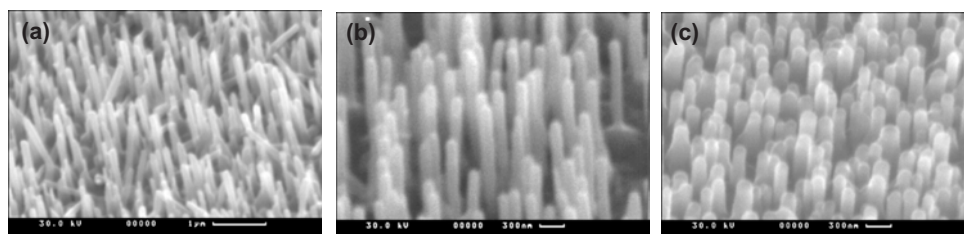


Fig. 1. Typical SEM images of ZnO:5 at. % Co (a); ZnO:3 at. % Mn (b), and (c) ZnO:10 at. % Mn. All pictures were taken under a 45° viewing angle.

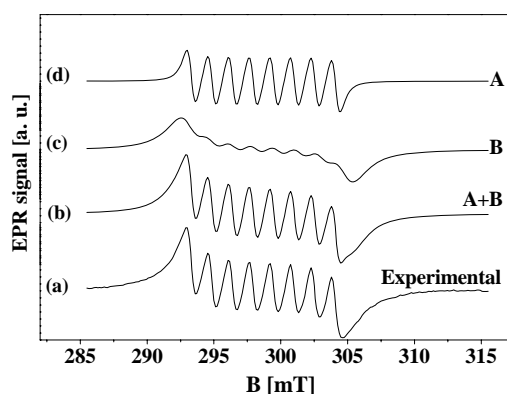


Fig. 2. (a) Experimental EPR spectrum of Co^{2+} in ZnO nanowires (nominal content of 5 at. %), measured in the X-band at 4.2 K for $B \parallel c$. (b) Result of the fitting of the experimental spectrum by the sum of components A and B shown in (d) and (c), respectively.

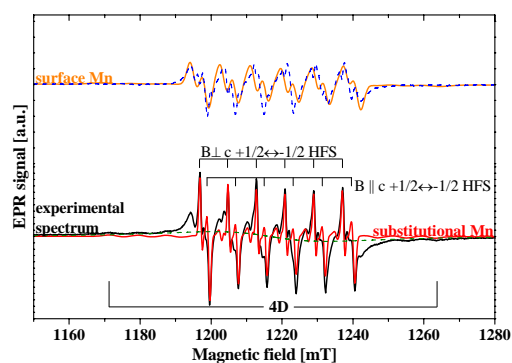


Fig. 3. Simulation of the EPR spectrum for 5 and 10 at.% Mn-doped ZnO colloidal QDs, measured in the Q-band at 60 K. In the bottom part of the plot we present the simulation of the substitutional Mn together with the experimental spectrum. There also is a broad Lorentzian component represented by a dashed line. The dashed line in the upper part of the plot is the difference between the experimental spectrum and the substitutional Mn simulation plus the broad Lorentzian component. The overlapping solid line is the simulation of the surface Mn spectrum.

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