Effect of Co doping on the conductive properties of ferromagnetic $Zn_xCo_{1-x}O$ films

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Abstract

The investigation of the electrical properties in Co-doped ZnO thin films provides two unexpected results: i) a decrease of the electrical conductivity and, ii) the contemporary occurrence of a reduction of conductivity and of an enhancement of ferromagnetic order. The former result is surprising since Zn atoms are replaced with *iso-valent* Co atoms. The latter finding questions previously suggested beneficial effects of *n*-type doping on the ZnO:Co magnetic behavior. While morphological and structural characterizations permit to exclude an influence of morphology and of the presence of Co metal or Co-oxides phases on present experimental findings, with the aid of first-principles electronic structure calculations, we propose a qualitative picture which can explain in a coherent way both the changes of conductivity and ferromagnetic behavior ensuing the Co doping and the mentioned, beneficial effects of *n*-type doping.

1. INTRODUCTION

In recent years, attention has been paid to the role of charge carriers in the room temperature ferromagnetism (FM) observed in transition metal (TM) doped ZnO.[1,2] Low carrier concentrations lead to an insulating regime where FM is due to the magnetic polarons and the conduction occurs in the variable hopping range regime, whereas high carrier concentrations provided by Al doping lead to a dilute magnetic semiconductor behavior.[3] The role of carriers and the intrinsic nature of the FM have been also investigated by measuring the Hall resistivity as a function of the magnetic field. The detection of the small values of the anomalous Hall resistivity indicates that both heavy *n*-doped ZnO:Co co-doped by Al[4] or Ga[5] ions and semiconducting[6] ZnO:Co behave as genuine magnetic semiconductors. For instance, correlations have been reported between carriers and FM in Co-doped ZnO films additionally *n*-doped by Zn[7-9] or Al[3,4] ions. A significant role of *n* carriers was also suggested by the results of a recent paper,[10] where we investigated the ferromagnetic behavior of differently Co-doped ZnO films by combining magnetic, XANES (X-ray Absorption Near Edge Structure), and EXAFS (Extended X-Ray Absorption Fine Structure) measurements with first principles density functional theory (DFT) calculations. The main result of that study was that the occurrence of FM in ZnO:Co can be associated to the presence of complexes (Co-V_O hereafter) formed by oxygen vacancies (V_O) close to Zn-substitutional Co atoms. It was also proposed that the presence of shallow donors is a *mandatory* requirement to realize long-range ferromagnetic coupling of the Co atoms involved in the Co-V_O complexes.[10,11] Stimulated by all of these results, suggesting an important role of *n*-type free-carriers in ZnO:Co ferromagnetism, here we focus on possible changes of conductivity induced by Co doping as well as on their influence on the ferromagnetic behavior. In this respect, we have taken advantage of our previous work[10] and investigated the bulk electrical properties of a set of samples, all grown under the same experimental conditions: an undoped ZnO film and a group of three Co-doped ZnO samples, with different Co concentrations. The latter group is built up by two of the Co-

doped ZnO films characterized in the previous work and a novel one. All samples have been magnetically and structurally characterized in the same way: thus, we have here integrated our previous spectroscopy measurements with further XANES and EXAFS analysis of the new Co-doped sample, providing estimates of Co metal fractions and Co-V_O complexes concentrations. Resistivity and Hall effect measurements have been performed on the four samples. Moreover, our investigations have included micro-Raman characterizations and AFM (atomic force microscopy) measurements focused on the identification of, respectively, possible nanoclusters of Co oxides and morphological changes induced by Co doping, that could both affect the electrical properties. Present experimental results show that Co doping affects the electrical conductivity of ZnO films, a rather puzzling result**,** given the *iso-valent* character of the Co impurity (i.e., Co^{+2} substitutes Zn^{+2}). Even more surprising, at variance with the results mentioned above, the changes of conductivity do not apparently go along with an improvement of the ferromagnetic behavior, a *decrease* of conductivity co-occurring indeed with an *increase* of *magnetization*.

To the best of the authors' knowledge similar results have not been reported before. There are very few studies where both conductivity and magnetization have been investigated versus cobalt content.[12-14] These studies show a general agreement about the decrease in carrier concentration (or increase in resistivity) with Co doping, whereas they disagree about the magnetic properties. In fact, thin films[12,13] show absence of correlations between magnetization and Co content whereas nanocrystals show an increase of the magnetization with Co doping.[14] These studies do not fully agree, therefore, with our findings. However, it should be taken into account that, in the literature, they can be easily found studies where the FM increases for increasing Co concentrations as in the present case,[14-19] while, rarly, studies reporting absence of correlations.[12,13] Other studies address only the relationships between magnetization and carrier concentration.[3-9]

In order to clarify the causes of the observed changes in conductivity and their apparent inconsistencies with the occurrence of FM, we have performed also spin-polarized DFT

calculations of the band dispersion of neutral and negatively charged Co-V_O complexes. Founding on these results, we propose a theoretical picture which, although partially speculative, provides a coherent explanation of both the present experimental findings and the reported improvements of FM induced by *n*-doping of ZnO:Co samples. In the proposed model, the Co-V_O complexes play a double role by contributing both to the occurrence of ferromagnetism and to the decrease of electron conductivity.

2. EXPERIMENTAL AND THEORETICAL METHODS

The set of samples here investigated includes three ZnO:Co films, i.e., C_0, C_2, C_3, and C_4, deposited by pulsed laser deposition in O_2 atmosphere, starting from targets $Zn_{1-x}Co_xO$ with nominal content x of 0.00, 0.02, 0.03, and 0.04, respectively. In the case of the C_2 and C_4 samples, the results of the structural and magnetic characterizations as well as the estimates of the concentrations of Co-V_O complexes and of the fractions of metallic Co, as given by XANES and EXAFS experiments, have been reported in a previous paper.[10] There, we mainly focused on the structural difference between these two samples, grown in oxygen atmosphere, and a $C_{6,Ar}$ sample grown in Ar atmosphere. Here, in order to compare samples grown under the same conditions, we have disregarded the $C_{6,Ar}$ sample and included in our investigation two films, C_0 and C_3, grown in O_2 under the same experimental conditions of C_2 and C_4. In the case of the C_3 sample, the concentrations of Co-V_O complexes and of the fractions of metallic Co have been then estimated by XANES and EXAFS measurements (see Ref. 10 for details on the experiments). The thickness of the C_2 and C_4 samples has been measured by an Alpha-step profilometer. Details are given in Ref. 10. Similar measurements have been performed for the C_0 and C_3 samples which have a thickness of 500 and 900 nm, respectively. These four samples have been then characterized by performing electrical, AFM and micro-Raman measurements.

Carrier concentration has been estimated by measuring the Hall voltage and the mobility in the Van der Paw configuration by a Bio-Rad HL5900 Hall profiler. The electron concentration has

been calculated by taking into account the values of surface carrier density and thickness obtained from Hall voltage and Alpha-step profilometer measurements, respectively. Hall voltage has been measured by taking the average value of the differences between the values taken at positive and negative magnetic field. Resistivity has been also measured with a collinear four-point probe. Morphology has been investigated by employing a commercial AFM (NTMDT NTEGRA) operating in tapping mode with silicon cantilever typical resonant frequency 150kHz, whereas Raman spectra have been measured using a confocal Horiba XploRA Raman microscope system with a 100x objective at ⎣=532 nm.

Ab initio spin-polarized DFT calculations have been performed within the projector augmented wave (PAW) method[20,21] implemented in VASP (Vienna Ab initio simulation package).[22] The PBE (Perdew-Burke-Ernzerhof) approximation for the exchange-correlation functional has been corrected by Hubbard-U terms, in the Dudarev's rotationally invariant approach,[23] with U-values of $U_{zn\text{-}d}$=7.5 eV and $U_{co\text{-}d}$=2.8 eV. Defect configurations have been calculated in a ZnO wurtzite supercell with 72 atoms, a 4x4x2 Monkhorst-Pack k-points grid and a plane-wave cut-off of 400 eV. PAW potentials include Zn *d*-orbitals in the valence. From the formation energy difference between neutral, q=0, and q=-1 charged defect, we have calculated the transition energy level ∑(0/-) of the Co-V_O complex,[24] i.e., the Fermi-level position at which the lowest-energy charge state changes from neutral to -1, and compared it to the ZnO energy gap obtained from total energy differences.

3. RESULTS AND DISCUSSION

XRD (X-ray diffraction) patterns of the C_2 and C_4 samples only exhibited peaks corresponding to the epilayer and to the substrate.[10] Similar features are present in the patterns of C_0 and C_3 samples, not shown here. In view of an electrical characterization, morphological effects have to be taken into account. For instance, in polycrystalline ZnO, the effective mobility can be limited by the grain size in addition to the carrier concentration.[25] Such an effect on the conductive properties can be ruled out here since the C_0, C_2, C_3, and C_4 samples

do not show differences in the grain size, see Fig. 1. According to that figure, the morphology consists on a distribution of grains whose average size is 191(±66) nm, 171(±44) nm, 165(±33), and 180(±54) nm for C_0, C_2, C_3, and C_4, respectively, thus indicating no significant change in grain size with dopant percentage. For the same four samples, roughness values (root mean squares) are 13.8 nm, 29.5 nm, 36 nm, and 14.6 nm, respectively.

It is also important to investigate whether the host ZnO lattice contains nanoclusters of metallic Co or Co oxides that could affect the electrical properties and be under the detection limit of the XRD. The Co metal fraction is negligible in the C_2 sample and small in the C_3 and C_4 samples, see the results reported in Table I.

	C_0	C_2	C_3	C_4
M_s (emu/cm^3) (mean error ±0.45)	0.0	0.80	2.22	5.08
M_s (μ_B/cm^3) (mean error ±0.45 x10^{20})	0.0	0.86x10^{20}	2.40x10^{20}	5.48x10^{20}
Co-V_O (% of Zn ions) (mean error ±0.2)	*n.d.*	0.0	0.6	1.2
Co-V_O (cm^{-3}) mean error ±0.9 x10^{20}	*n.d.*	0.0	2.0x10^{20}	4.0x10^{20}
Co metal (% of Co ions) (mean error ±2)	*n.d.*	0.1	2.1	3.7
carrier concentration (cm^{-3}) mean error ±10^{17}	9.5x10^{18}	7.5x10^{18}	2.5x10^{18}	3.5x10^{18}

Tab.1 Experimental values of some magnetic, structural and electrical parameters for C_0, C_2, C_3, and C_4 films. Values of the magnetization M_s and estimates of the Co metal and Co-V_O complex concentrations for the C_2 and C_4 films are taken from Ref. 10.

The possible presence of Co-rich oxide phases (CoO, Co_3O_4 or $ZnCo_2O_4$) has been investigated here by Raman spectroscopy, which is highly sensitive to the position of the dopant ions in the

host ZnO lattice as well as to the presence of possible non-metallic precipitates and structural defects. The spectra of the investigated samples, shown in Fig. 2, only exhibit peaks corresponding to the fundamental modes of the ZnO, in addition to those arising from the sapphire substrate.[26] In detail, the peaks at 99 and 437 cm-1 correspond to E_2 (low) and E_2 (high) modes of ZnO, respectively. The other active modes predicted by the group theory for ZnO are at 381 (A_1(TO)), 407 (E_1(TO)), 574 (A_1(LO)) and 583 cm^{-1} (E_1(LO)), partially overlapped with the sapphire vibrations. We observe also peaks due to multi-photon processes, E_2 (low)-E_2 (high) at ~330 cm^{-1}, and disorder-actived additional modes (AM) at 255 cm^{-1} ((B_1 (low)), 470 cm^{-1}, and 550 cm^{-1} (B_1 (high)).[27-30] In conclusion, micro-Raman results permit to rule out the presence of Co oxides.

Then, in order to clarify the relationships between the occurrence of free carriers and the ferromagnetic behavior, we have estimated the resistivity and the carrier concentration in the bulk of the Co-doped ZnO films and of the undoped C_0 sample through Hall effect and resistivity measurements see Fig. 3 and Table I. All samples are unintentionally *n*-type; however, the carrier concentration decreases from the values of $9.5x10^{18}$ and 7.5 $x10^{18}$ cm^{-3} for the C_0 and C_2 films to the values of $2.5x10^{18}$ and $3.5x10^{18}$ cm^{-3} for the C_3 and C_4 samples, respectively. Accordingly, the resistivity of C_4 and C_3, 0.116 and 0.146 Ω cm, respectively, is higher than that of C_0 and C_2 of ~0.05 Ω cm. Instead, the mobility values are almost unchanged, around 16 cm^2 V^{-1} s^{-1}.

The carrier concentrations and resistivity values of the C_3 and C_4 films deserve some careful considerations. Despite a larger Co concentration, the C_4 sample shows indeed a small increase of the carrier concentration (a small decrease of resistivity) with respect to the C_3 one, in partial disagreement with the overall trend shown by the four samples. In this regard, let us note that, in these two samples, the effective carrier concentration could be strongly affected by the presence of Co metal (see Table 1). In principle, indeed, since metals have free carrier concentrations of ~10^{23} cm^{-3} the amount of Co metal phase could account for $0.6x10^{20}$ cm^{-3} in C_3 and $1.5x10^{20}$ cm^{-3} in C_4. Roughly, a Co-metal contribution to the conductivity in C_4 is

thefore about three times the one occurring in C_3, thus suggesting that the different Co metal amount may be responsible of the observed deviation from the general trend. More accurately, it has to be taken into account that only a fraction of carriers provided by the metal phase could contribute to the macroscopic transport properties of ZnO:Co, due to the Schottky barriers which may form between Co metal clusters and the host ZnO:Co semiconductor.[31] Accurate estimates of the contributions of Co metal clusters to the measured carrier concentrations would require delicate experimental investigations which are beyond the scope of the present work. Notwithstanding, let us introduce some speculative considerations which may account for the results found in the cases of the C_3 and C_4 samples. By taking into account the fractions of Co metal of C_3 and C_4 and assuming a small Schottky barrier height (~0.1 eV), we estimate carrier concentrations of 1.3×10^{18} cm^{-3} for the C_3 and 3.0×10^{18} cm^{-3} for the C_4 samples, which may be injected from the Co metal phase into the ZnO:Co through the metal-semiconductor junction. This barrier height is quite reasonable if one takes into account the effect of Co doping on the ZnO Fermi level.[32,33] With this assumption, the free carriers due only to the semiconducting ZnO:Co are 1.2×10^{18}cm^{-3} in C_3 and 0.5×10^{18}cm^{-3} in C_4, in agreement with the observed trend.

Let us now consider these results together with the magnetic parameters and the concentration of Co-V_O complexes taken from Ref. 10 and reported in Table I. We first recall that a clear evidence of FM associated to the presence of Co-V_O complexes was given in our previous work,[10] as mentioned above. In the present case, no FM behavior has been observed for the C_0 sample (magnetic characterization not reported here). In the C_2 sample, which exhibits a low magnetization value (0.8 emu/cm^3), the occurrence of some Co-V_O complexes can be reasonably assumed, although with a concentration lower than the detection limit, 0.2% of total Zn ions, which corresponds to an upper bound of 0.9×10^{20} cm^{-3}, as indicated in Table 1. In C_3, we measured larger values of both M_s and CoV_O concentration than the C_2 sample, i.e., 2.22 emu/cm^3 and 0.6% of total Zn ions, respectively. In turn, the C_4 sample shows larger values of magnetization and concentration of Co-V_O complexes (5.08 emu/cm^3 and 1.2% of total Zn ions,

respectively), than the C_3 sample. Let us note that within the model proposed in Refs.[10,11], the values of M_s in μ_B per unit volume for the three Co-doped samples favorably compare with the estimated concentration of Co-V_O complexes per unit volume, see Table I, when one takes into account that only ferromagnetically coupled Co-V_O complexes contribute to the total magnetic moment,[10,11] with a magnetic moment of ~2 μ_B per Co-V_O.[34] Present results confirm therefore the existence of a direct relationship between magnetic moment and concentration of Co-V_O complexes. Moreover these results and those regarding the *n*-carrier concentrations, given in the same Table, show the occurrence of two rather unexpected phenomena: i) the carrier concentration decreases with Co doping despite of the iso-valent Co/Zn substitution and, ii) an increase of the FM and of the amount of Co-V_O complexes is accompanied by an opposite trend of carrier concentration. Co doping could reduce the concentration of the unintentional shallow donor defects (e.g., Zn interstitials) responsible of the intrinsic *n*-type conductivity observed in the undoped ZnO film, thus accounting for the former result. However, the observed increase of FM would suggest an opposite effect of Co-doping, that is, an increase of shallow donor defects, in agreement with the observed, beneficial effects of *n*-type doping on FM.[3-5,7-9] The lacking of measurements of the concentration of unintentional donors in the present ZnO:Co films prevents to confirm a decrease of the shallow donors caused by the Co-doping, as well as a quantitative analysis of the present experimental findings. However, it has to be noted that even an affirmative result of such measurements could not explain the increase of FM accompanying the decrease of *n* carriers. In respect to these contradictory findings, based on theoretical results, we propose an explanation of the observed phenomena which may provide a coherent picture of both the observed changes of conductivity and ferromagnetism induced by Co-doping and the mentioned, positive effects of *n*-type doping on the ZnO:Co ferromagnetic behavior.

First, let us note that the decrease of carrier concentration observed at high doping level cannot be attributed to the Co/Zn substitution. In fact, a Co^{2+} impurity at the Zn site adds occupied electronic levels of minority spin just below the Fermi energy, EF, and unoccupied levels ≈2

eV above the conduction band minimum (CBM), that can be hardly populated by electrons introduced by shallow donors.[10] Similarly, oxygen vacancies induce doubly occupied levels just above the top of the valence band with unoccupied levels located at more than 1 eV above the CBM. On the other hand, upon formation of Co-V_O complexes, hybridization occurs between Co-*d* and V_O-induced states, with empty electronic levels close to the CBM giving rise to an impurity band, see Figure 4(a). In presence of unintentional shallow donors, this impurity band might be populated from free-electron-like CB electrons, thus at the expenses of the bulk electrical conductivity of ZnO:Co. Moreover, when filled by electrons, this spin-polarized Co-Vo band, thanks to its partial mixing with the CB, could account for long-range ferromagnetic coupling of Co dopants.[10,11] In order to verify these hypothesis, we have calculated the band structures of neutral and negatively charged Co-V_O complexes in the 72-atoms ZnO supercell (see Figs. 4 a) and b), respectively), and their corresponding $\sum(0/-)$ transition energy level.[24] Spin-polarized band structures are reported in Fig.4 (black and red lines for majority and minority spin, respectively) along the H-$\wp$-M high-symmetry direction in the wurtzite reciprocal Brillouin zone; circles indicate Co-*d* contribution to the electronic levels, as circles radii are proportional to the integral of the corresponding charge densities projected on atom-centered orbitals. Fig. 4 a) shows that empty minority-spin levels induced by neutral Co-V_O are resonant in CB, about 0.5 eV higher than CBM: a flat dispersion along the H-$\wp$-M direction indicates scarce interaction between Co-V_O's. Adding one electron in the 72-atoms supercell containing a Co-V_O complex approximately corresponds to a doping level of (2×10^{20} cm^{-3}): a spin-minority Co-V_O level gets filled. Its energy position (see Fig.4b)) is below the CBM, with a k-space dispersion showing a slight curvature around $\wp$. These results confirm that the Co-V_O level can subtract electrons from the CBM remaining, when occupied, partially mixed with the CB states, an important feature to realize long-range magnetic coupling of Co dopants. Calculating the transition energy level to estimate the position of the defect-induced state with respect to ZnO band-edges, we obtain $\sum(0/-) = 2.5$ eV for Co-V_O, together with a corresponding value of 2.8 eV for the ZnO energy gap obtained from total energy differences.

Although still partially affected by errors due to the PBE approximation of the exchange-correlation (partially amended by the Hubbard-U corrections), these results consistently support that the occupied Co-V_O level descends in the energy gap remaining close to the CBM. Based on these results, we suggest a qualitative picture which can explain the experimental findings. In native *n*-type ZnO, unintentional shallow donors fill the bottom of the CB, accounting for the observed conductivity. In Co-doped ZnO, empty electronic levels induced by Co-V_O complexes can subtract free carriers from the CB, thus giving reasons for the reduced carrier concentration seen by the Hall effect measurements. The energy dispersion E(**k**) of the *occupied* Co-V_O level suggests also a certain degree of mixing with the CB and, therefore, of coupling between complexes, which can favor FM coupling. These considerations can explain why in Co-doped ZnO the increase of ferromagnetism and of Co-V_O complexes concentration is accompanied by a decrease of carrier concentration. The same considerations also rationalize previous experimental findings indicating improved ZnO:Co magnetic properties induced by *n*-type doping.[3-5,7-9] Additional shallow donors would increase indeed the filling of the Co-V_O level and, therefore, the magnetic coupling of an increasing number of Co atoms. This picture provides a coherent explanation of the experiments, but needs a basic assumption: the introduction of Co atoms in ZnO increases the concentration of *n* carriers in the undoped sample of about an order of magnitude, that is, it induces the formation of defects like, e.g., Zn interstitials behaving as shallow donors (whose estimate is beyond the scope of the present work). Theoretical results suggest indeed a filling of the Co-V_O levels with about one electron for each complex, thus requiring *n*-carrier concentrations of the same order than those of the Co-V_O complexes. The filling process leaves about 10^{18}cm^{-3} free carriers in the CB, see Table I.

4. CONCLUSIONS

We have investigated the effects of Co doping on the electrical properties of ZnO films. Surprisingly, Hall effect measurements revealed a decrease of the conductivity that takes place

as Co content increases, despite of the iso-valent character of Co substitution for Zn. Moreover, such a decrease is accompanied by an improvement of the ferromagnetic behavior, which apparently contrasts with the previously reported beneficial effects of *n*-type doping on the ZnO:Co ferromagnetic behavior. Present Raman and AFM measurements permit to rule out possible effects of oxides nanoclusters and of differences in the sample morphology on the conductivity decrease. Even Co metal phases do not significantly affect the general trend shown by the changes of conductivity. Based on theoretical results, we propose a qualitative explanation of the above findings, which involves the formation of Co-V_O complexes and assumes an increase of the shallow donor contents induced by the Co doping. While the introduction of Co atoms indirectly increases the number of electrons in the conduction band, the occurrence of Co-V_O complexes modifies the electronic structure of Co-doped ZnO films by adding empty levels forming an impurity band near the conduction band minimum. Such levels can spill out electrons from the bottom of the conduction band, thus accounting for an overall decrease of the carrier concentration, which follows the Co doping. The same phenomenon can account for the improvement of ferromagnetism induced by increasing Co contents. In fact, the Co-V_O impurity band is partially mixed with the conduction band and, when filled by electrons, can account for the magnetic coupling of Co impurities. The proposed picture also explains the improvement of ferromagnetism induced by additional shallow donors: an enhanced filling of the impurity band increases indeed the number of Co atoms magnetically coupled. Thus, although based on qualitative considerations, the present theoretical picture permits to explain in a coherent way the coexistence of reduced conductivity and of an increased ferromagnetic coupling in ZnO films ensuing an increasing Co doping as well as the previously reported improvement of ferromagnetism induced by *n*-type doping of Co-doped ZnO.[3-5,7-9]

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31 A. Kumar, T.S. Herng, K. Zeng, J. Ding, ACS *Appl. Mater Interfaces* 2012, **4**, 5276.32 By following the approach used in Ref. 19, we consider that Co doping causes a significant increase in the ZnO work function. In fact its value moves from ~4.5 eV (ZnO) to 5.13 eV ($Zn_{0.91}Co_{0.09}O$) and 5.37 eV (ZnO:Co:Cu), thus allowing even transitions in contact nature from Schottky to ohmic at high Co/Cu content in ZnO:CoCu/Pt.[19] Based on these results we consistently assume for the C_3 and C_4 samples a work function value of ~4.8-4.9 eV which is quite close to the work function value of Co metal, in the ZnO lower than the pure value of 5.0 eV. The assumption of the barrier heigth of ~0.1 eV is also consistent with the lower values of barriers measured for some metals in contact with ZnO lower than those expected.[33]33 L. J. Brillson, Y. Lu, *J. Appl. Phys.* 2011, **109**, 121301.34 The theoretical magnetic moment associated to the charged $(Co\text{-}V_O)^{-1}$ complex is $\mu=2\mu_B$ (to be compared to $\mu=3\mu_B$ for both substitutional Co^{2+} atom and neutral $Co\text{-}V_O$).

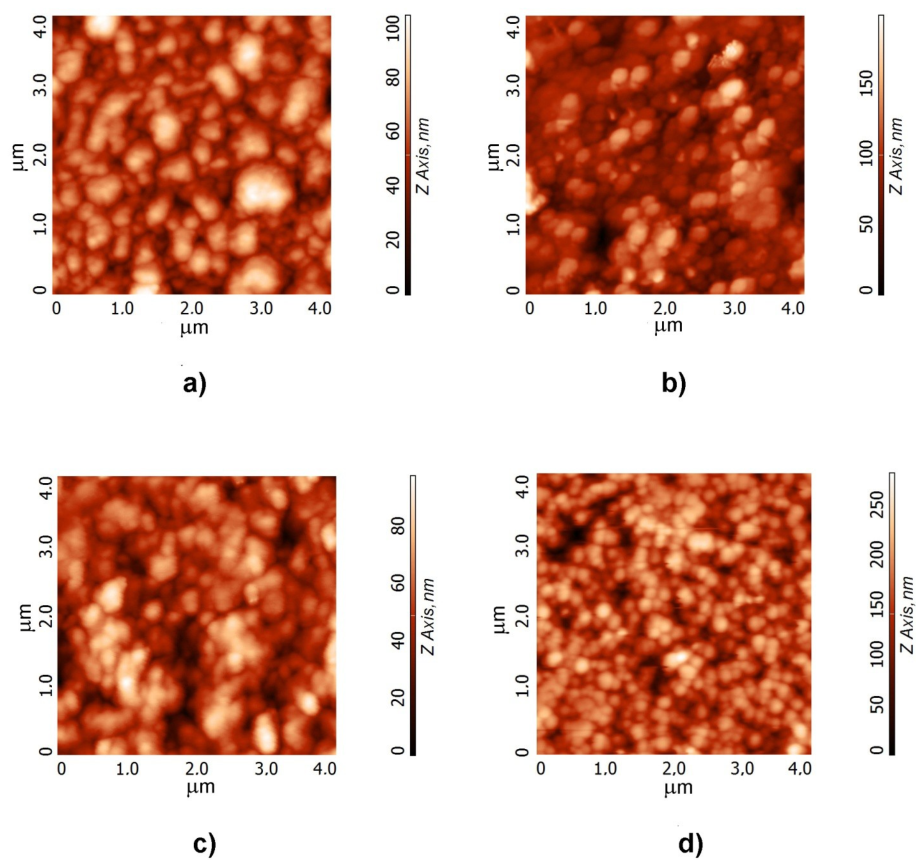

Figure 1. AFM morphologies corresponding to the C_0, C_2, C_3, and C_4 films are shown in a), b), d) and c), respectively. The vertical direction (out-of-film plane) is set as *Z* axis. Roughness values (root mean squares) are 13.8 nm, 29.5 nm, 36 nm, and 14.6 nm for a), b), d) and c), respectively.

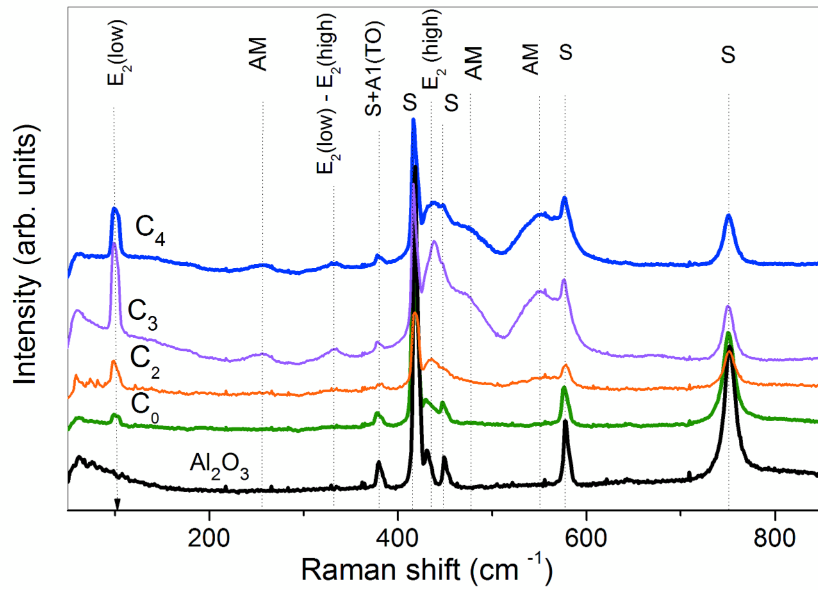

Figure 2. Micro-Raman spectra of C_0, C_2, C_3, and C_4 films showing the ZnO fundamental modes and some additional modes in the ZnO:Co films. S indicates the sapphire vibrations.

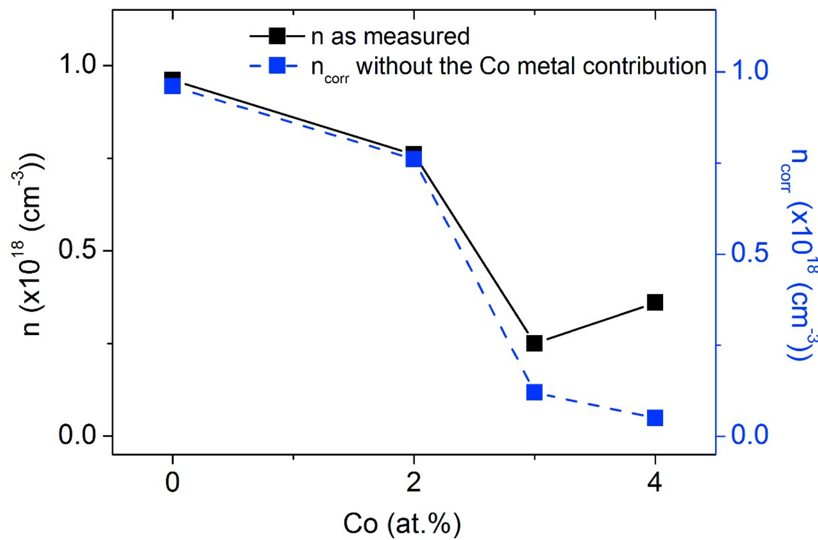

Figure 3. Plot of carrier concentration (n) versus Co concentration (percent of Zn atoms) for C_0, C_2, C_3, and C_4 films. The figure shows values of the carrier concentrations "as measured" (n) and without the Co metal contribution (n_{corr}).

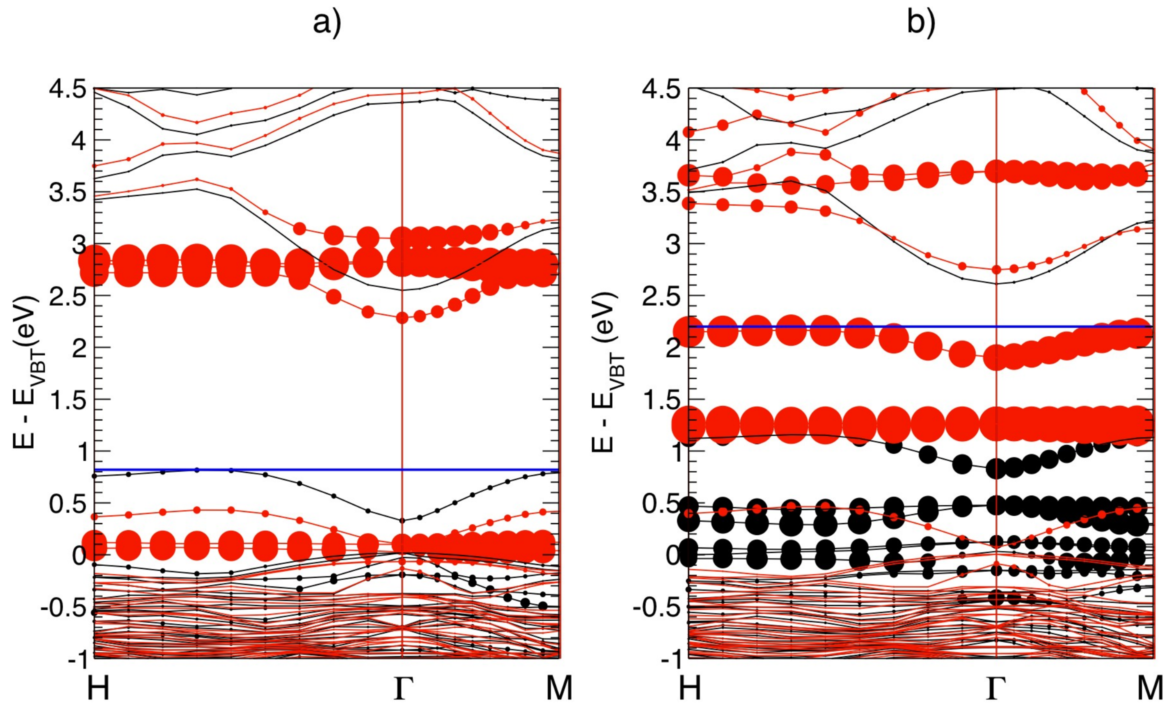

Figure 4. Spin-polarized electronic band structure along the H-Γ-M direction, for the neutral (a) and –1-charged (b) Co-V_O complex in ZnO. Black and red lines correspond to spin-up and spin-down states, respectively. Circles indicate Co-d contribution to the electronic levels, as circles radii are proportional to the integral of the corresponding charge densities projected on atom-centered orbitals. The horizontal blue line marks the position of the last occupied eigenvalue (Fermi energy). In a), empty levels induced by neutral Co-V_O are resonant in CB, about 0.5 eV higher than CBM. The zero of the energy scale is the valence band top (E_{VBT}).