ELECTRONIC STATE OF COBALT IN ZnO:Co FILMS

G. LASHKAREV, V. KARPYNA, V. DOBROWOLSKI, V. LAZORENKO, V. BATURIN[1], A. KARPENKO[1], R. SZYMCZAK[2], M. BARAN[2], W. PACUSKI[3]

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Institute for Problems of Materials Science, Nat. Acad. Sci. of Ukraine
(3, Krzhyzhanovskyi Str., Kyiv 03142, Ukraine; e-mail: gvl35@ipms.kiev.ua),

[1]**Institute of Applied Physics, Nat. Acad. Sci. of Ukraine**
(58, Petropavlivska Str., Sumy 40034, Ukraine),

[2]**Institute of Physics, Polish Academy of Sciences**
(32/46, al. Lotników, Warsaw, Poland)

[3]**Institute of Experimental Physics, Warsaw University**
(69, ul. Hoża, Warsaw, Poland)

The results of researches of the electron state of cobalt in thin zinc oxide films deposited by the method of radio-frequency magnetron sputtering have been reported. X-ray absorption spectroscopy was used to study the K-absorption spectra of cobalt in ZnO:Co. The temperature dependence of the magnetic moment of the films within the temperature interval 4.2—300 K has been measured.

1. Introduction

Diluted magnetic semiconductors (DMSs) have attracted considerable interest, because they possess magnetically sensitive transport and optical properties. This circumstance opens the way to the creation of new devices of spin electronics. In the cation sublattice of a DMS, some part of diamagnetic cations is replaced by paramagnetic ions of a transition metal. The exchange interaction between the localized magnetic moments of the d-shells of these ions and free current carriers, excitons, as well as between one another, results in that a material acquires such nontrivial properties as the huge splitting of exciton levels in a magnetic field, the huge Faraday effect, ferromagnetic ordering, large magnetoresistance, the anomalous Hall effect, and others.

The most prominent representative of ferromagnetic DMSs is (Ga,Mn)As. However, its Curie point T_c does not exceed 175 K [1]. For practical applications, materials with a high Curie point that exceeds room temperature are needed. One of the perspective DMS materials is zinc oxide doped with transition $3d$-metals. The theoretical works of Dietl [2] and Sato [3] predict ferromagnetism with the Curie point above room temperature in such a material. Mn and Co are considered as the most suitable ions for replacing Zn in the ZnO lattice, because they possess a high solubility in ZnO (up to 35%). It is quite probable that high spin states Mn^{2+} (d^5) and Co^{2+} (d^7) are realized. Moreover, ZnO is transparent in the visible range of the spectrum and can be doped with impurities of group III (Al, Ga, and In) to provide high concentrations of electrons (of the order of 10^{21} cm^{-3}).

The indicated features of zinc oxide draw attention of many researchers to this semiconductor. There are works dealing with obtaining ferromagnetic zinc oxide by its doping with various transition metals, including manganese and cobalt. Such works are few in number, and they have inconsistent character. For example, in work [4], its authors inform on ferromagnetism in Co-doped ZnO films at room temperature. However, their results were poorly reproduced, less than 10% of them. Moreover, ferromagnetism was observed only in films with the concentration of carriers not lower than 10^{20} cm^{-3}. Other authors [5] inform on ferromagnetism in ZnO:Co films without additional doping at 350 K. In work [6], the increase of the electron concentration in a ZnO film codoped with manganese and tin has been demonstrated to result in a reduction of magnetization. However, a number of authors [7, 8] emphasize the absence of ferromagnetism in ZnO at its doping with transition metals, although the films have been fabricated by the method of molecular-beam epitaxy, which is one of the most modern technologies. If the formation of cobalt precipitates (clusters) is excluded from consideration, one may suggest that the observable ferromagnetism is caused by a special state of cobalt in the lattice. We believe that the valence of cobalt does not play a minor role in the establishment of high-temperature ferromagnetism.

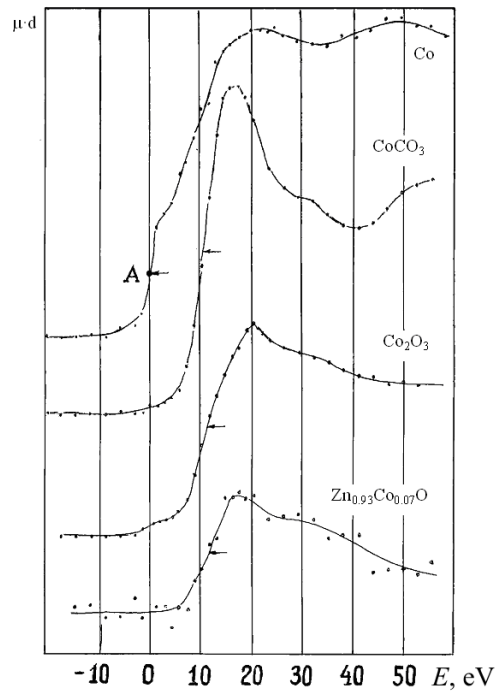

Fig. 1. Absorption spectra of Co ions in the thin $Zn_{0.93}Co_{0.07}O$ film and in the reference specimens Co, $CoCO_3$, and Co_2O_3

Since cobalt can possess various valences (Co^{2+} and Co^{3+}), it is of interest to find out, whether Co is a mere source of the localized magnetic moment (Co^{2+}), or it also supplies electrons to the conduction band (Co^{3+}). To find out the answer, we have studied the valence state of cobalt in zinc oxide films deposited by the method of magnetron sputtering. With this purpose in view, we considered a shift in the energy scale of the X-ray K-absorption edge of cobalt in the film under investigation with respect to the K-edge of metal cobalt and the K-edge of cobalt in its salts, where it exists in a di- or a trivalent state, and applied the Kunzl rule. [The mechanism, which explains the chemical shifts of various characteristics of X-ray spectra (the absorption edges, K_α-lines, etc.) occurring at the transition from elements to their compounds or alloys, interpreting thus the Kunzl rule, is based on the physical model of the external screening of internal electrons by peripheral ones, when the interatomic bond state varies [9].] The electron state of cobalt was studied also by measuring the magnetic moment of the film within the interval 2—300 K, as well as the absorption and luminescence spectra and conductivity at room temperature.

2. Experimental Part

Co-doped ZnO films were grown by radio-frequency magnetron sputtering. The target was fabricated by applying the cold pressing to a mixture of ZnO and CoO powders, followed by the subsequent sintering of the target at 900°C. The target was sputtered in the argon-oxygen environment. The total pressure in a chamber was 1 Pa, while the partial pressure of oxygen 0.2 Pa. Sapphire or glass served as the substrate. The temperature of the substrate was maintained in the range 100–300°C. For X-ray researches, the films were also deposited onto a thin aluminum foil. The X-ray absorption spectroscopy (XAS) researches of the valence state of cobalt were carried out by measuring the shift of the position of the K-absorption edge of cobalt in the specimen concerned with respect to those in metal cobalt and reference specimens. The K-absorption spectra were studied with an X-ray absorption spectrometer of original design. A quartz crystal with a reflecting plane $(1\bar{3}40)$ in the first order of reflection was used in the spectrometer as a crystal-analyzer. X-ray radiation was emitted by a sealed X-ray tube of the BSV type with a tungsten anode. X-ray quanta were registered by a scintillation detector. The registration of all absorption spectra was carried out precisely, point by point. Specimens made of metallic cobalt, as well as of its compounds $CoCO_3$, $CoCl_2$, and Co_2O_3, were used as the reference ones. The position of the K-edge in the energy scale was determined by the position of the inflection point of the first jump in the absorption spectrum. The charge state of Co ions and, hence, their valence were determined by the shift of the cobalt K-absorption edge in the examined films with respect to its position in the metal and the reference compounds. The coordinate of the inflection point of the first jump of the K-absorption edge of metallic cobalt was adopted as the zero reference point.

The magnetic moments of the films were measured within the temperature range 4.2—300 K, making use of a superconducting quantum interferometer. The electroconductivity at room temperature was measured by the standard method.

3. Results and Discussion

The K-absorption spectra measured in the investigated specimen $Zn_{0.93}Co_{0.07}O$ (the composition content was found by the method of X-ray fluorescent analysis) and in the reference ones are depicted in Fig. 1. The analysis of these spectra brings about the following conclusions.

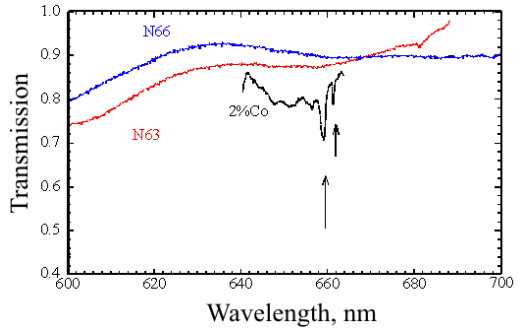

Fig. 2. Transmission spectra of the $Zn_{1-x}Co_xO$ films with $x = 0.036$ (N63) and 0.078 (N66), and a typical absorption spectrum of Co^{2+} in $Zn_{1-x}Co_xO$ ($x = 0.02$)

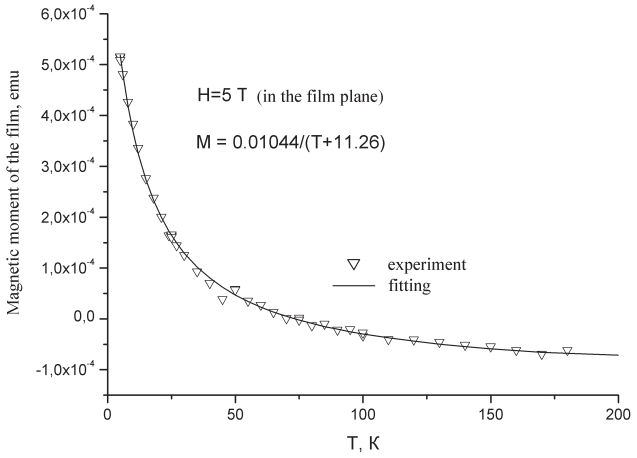

Fig. 3. Temperature dependence of the magnetic moment of the thin $Zn_{0.93}Co_{0.07}O$ film in a 5-T magnetic field

The edge of the K-absorption spectrum of Co in $CoCO_3$ is shifted in energy with respect to the relevant position for metallic Co by 10.6 eV and for Co in Co_2O_3 by 11.2 eV towards higher energy values. The shift of the K-absorption edge of the Co ion in $Zn_{0.93}Co_{0.07}O$ amounts to 11.8 eV. Therefore, one may draw conclusion that the charge state of Co ions in the specimen studied, $Zn_{0.93}Co_{0.07}O$, is close to the state, in which Co atoms are in the compound Co_2O_3, and, hence, the formal valence of cobalt ions in this specimen is +3.

We also studied the transmission (Fig. 2) and photoluminescence (PL) spectra of the deposited ZnO:Co films at a temperature of 1.7 K. They did not reveal the characteristic absorption lines of isolated Co^{2+} ions (pointed by arrows in Fig. 2) [10]. As a rule, these lines are observed in the transmission spectra of ZnCoO with the concentration of Co ions between 0.1 and 35 at.%. Therefore, the absence of these lines testifies to that either these are not isolated Co ions, or Co ions are not in the bivalent state. The cited optical data also indicate that Co in our specimens may be in another electron state.

In order to obtain the additional information concerning the electron state of cobalt ions, we have carried out researches of the temperature dependence of the magnetic moment M of the $Zn_{0.93}Co_{0.07}O$ film in a magnetic field of 5 T. Fitting the temperature dependence of the magnetic moment $M = \chi H$ to experimental data (Fig. 3) showed that the Curie–Weiss law $M = C/(T - \Theta)$, where the constant $\Theta = -11.4$ K, holds true. The negative sign of the latter evidences for the antiferromagnetic character of interaction between cobalt ions and, probably, for the temperature dependence of their magnetic moments. As the temperature increases, the paramagnetic susceptibility of ions decreases and, at $T = 75$ K, a transition into the diamagnetic region is observed.

At a temperature of 5 K, the measured magnetic moment amounts to 0.6×10^{-3} emu, which corresponds to the effective magnetic moment $p_{\text{eff}} \approx \mu_B$ per formula unit, where μ_B is the Bohr magneton, or, taking into account the cobalt content in the investigated ZnO film (6.8 at.%), $p_{\text{eff}} = 3.88\mu_B$ per cobalt ion. The amplitude of p_{eff} of a cobalt ion in the film, calculated from the coefficient C, turns out smaller than the theoretically calculated value $p_{\text{eff}} = 4.9\mu_B$ for a Co^{3+} ion. In some cases (for example, in salts $CoSO_4$, $CoCl_2$, and others), the value of p_{eff} calculated from experimental results exceeds the theoretical value of about $5\mu_B$ [11].

The observed value $p_{\text{eff}} = 3.88\mu_B$ can be explained by the formation of Co^{3+}–Co^{3+} pairs coupled by the antiferromagnetic interaction (their spins are mutually compensated, i.e. for every pair, $p_{\text{eff}} = 0$) in $Zn_{1-x}Co_xO$. Really, the non-magnetic states of the isolated pairs of Mn^{2+} magnetic ions coupled by the antiferromagnetic exchange interaction are known to exist in semiconductors of the $A^{II}B^{VI}$ type [12]. Therefore, it is natural to assume that the pairs of Co^{3+} ions with the zero magnetic moment, which are coupled by the exchange interaction, should exist in Co-doped ZnO as well. Therefore, 40% of the inserted cobalt are in the form of non-magnetic pairs Co^{3+}–Co^{3+}.

The measurements of the conductivity of ZnO and ZnO:Co films showed that the insertion of cobalt does not change the film electroconductivity, which testifies to a substantial ionization energy of the Co donor state.

4. Conclusion

Making use the method of X-ray absorption spectroscopy, the absorption spectra of Co in ZnO:Co films have been studied. The comparison of the obtained K-spectra with the absorption spectra of Co in a metallic cobalt and its compounds allows us to conclude that the charge state of Co in $Zn_{1-x}Co_xO$ films is practically the same as in the reference specimen Co_2O_3. Thus, the formal valence of Co ions in $Zn_{1-x}Co_xO$ (with $x < 0.08$) is equal to +3. The lines corresponding to the absorption by Co^{2+} ions were not found in the transmission and PL spectra of ZnO:Co films, which may also confirm the viewpoint about another electron state of Co ions. The temperature dependence of the magnetic moment of the film within the interval 4.2–180 K obeys the Curie—Weiss law. The effective magnetic moment of a cobalt ion $p_{\text{eff}} = 3.88\mu_B$ is smaller than the theoretically predicted value $p_{\text{eff}} = 4.9\mu_B$ for a Co^{3+} ion. The assumption has been made that, in $Zn_{1-x}Co_xO$, cobalt forms antiferromagnetic pairs Co^{3+}—Co^{3+} which do not contribute to the magnetic moment of the film. We think that the absence of ferromagnetism is caused by a low content of Co in the films, and, probably, by the insufficient concentration of charge carriers.

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ЕЛЕКТРОННИЙ СТАН КОБАЛЬТУ В ПЛІВКАХ ZnO:Co

Г. В. Лашкарьов, В. А. Карпина, В. Д. Добровольский, В. Й. Лазоренко, В. А. Батурін, А.Ю. Карпенко, Р. Шимчак, М. Баран, В. Пакузкі

Р е з ю м е

Методом рентгенівської абсорбційної спектроскопії досліджено спектри поглинання Co в плівках ZnO:Co. Порівняння одержаних K-спектрів зі спектрами поглинання Co в металі та його сполуках дозволяє зробити висновок, що зарядовий стан іонів Co в плівках $Zn_{1-x}Co_xO$ майже такий, як і в еталонній сполуці Co_2O_3. Таким чином, формальна валентність іона кобальту в $Zn_{1-x}Co_xO$ (x<0,08) дорівнює +3. На спектрах пропускання та фотолюмінесценції плівок ZnO:Co не було знайдено ліній, які відповідають поглинанню іонів Co^{2+}, що також, можливо, підтверджує висновок про інший електронний стан. Температурна залежність магнітного момента плівки в інтервалі температур 4,2—180 K відповідає закону Кюрі—Вейсса. Ефективний магнітний момент іона кобальту $p_{\text{eff}} = 3{,}88\ \mu_B$ менший ніж теоретично розрахований $p_{\text{eff}} = 4{,}9\ \mu_B$ для іона Co^{3+}. Зроблено припущення, що в $Zn_{1-x}Co_xO$ кобальт частково формує антиферомагнітні пари Co^{3+}—Co^{3+}, які не дають внеску в магнітний момент плівки. Ми вважаємо, що відсутність феромагнетизму зумовлена малим вмістом Co в плівках, а, можливо, й недостатньою концентрацією носіїв заряду.