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EMR Spectra Thin Films Doped with High Concentration of Co and Cr on Quartz and Sapphire Substrates

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We have studied magnetic properties of zinc-oxide composite doped with high concentration (up to 20%) of Co and Cr ions. The pulsed laser deposition method was used to obtain samples on quartz glass and sapphire substrates. Samples were annealed at 100–250 °C for ZnO on quartz substrate, and 300–700 °C on sapphire substrate. EMR measurements were carried out and temperature dependence of the EMR spectra was obtained. The angular dependence in two samples orientation, vertical and horizontal, were also obtained. Analysis of the temperature dependences of the integral intensity of EMR spectra was carried out using the Curie–Weiss law.

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1. Introduction

Diluted magnetic semiconductors (DMS) are alloys where a stoichiometric fraction of the constituent atoms has been replaced by magnetic transition metal atoms. Based on mean-field models it was shown that wide band gap diluted semiconductors could lead to room temperature ferromagnetism [1]. Due to its rare physical properties, such as energy gap of about 3.4 eV at room temperature and the exciton binding energy of about 60 meV, zinc oxide (chemical formula ZnO) is used for devices based on semiconductor structures [2, 3], such as varistors [4] or sensors [5]. In additional, relatively simple production technology of ZnO crystals gives us hope to lower cost of production equipment based on ZnO in comparison to the popular GaN. This, together with the properties such as transparency in visual region and piezoelectricity have generated huge interest on ZnO based DMS [6, 7]. DMS are of interest for study for their unique spintronics properties with possible technological applications [8–10], such as spin-spin exchange interaction between the localized magnetic moments and the band electrons [11]. Some subsequent theoretical using density functional theory (DFT) [12, 13] and experimental [14, 15] works show that n-type Co-doped ZnO also possesses room temperature ferromagnetism.

Using a modified Zener model, Dietl et al. predicted that ZnO based DMS could lead the transition temperature to much higher than the room temperature [16]. According to this theory, $p-d$ interactions are the reason for long-range magnetic coupling. However, the investigated magnetic ZnO samples are either n-type conducting or insulating. The observed weak ferromagnetism in implanted ZnO containing ferromagnetic nanocrystals and in PLD grown ZnO with diluted magnetic ions is due to ferromagnetic nanocrystals and the acceptor-like defects [17], respectively. For the diluted ZnO:Co and ZnO:Cr, it would be interesting to check if there is interaction between free electrons and d-electrons in Co and Cr ions, and if this $s-d$ interaction results in ferromagnetic coupling.

Some groups have reported ferromagnetism in ZnO doped with transition metal systems Curie temperatures T_C ranging from 30 to 550 K [15, 18–23], while others have found antiferromagnetic, spin glass, or paramagnetic behaviour [7, 24, 25].

The existence of ferromagnetic ordering in (Zn,Co)O, has been theoretically proposed to be attributed to the double exchange interaction [6] or the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction between Co ions [26]. Later calculation showed that the ground state of Co-doped ZnO is spin glass without doping due to the short range interactions between transition metal atoms [27].

We report here the magnetic properties of zinc-oxide composite (ZnO) doped with Co and Cr ions. Electron magnetic resonance (EMR) spectra have been measured and analyzed to extract information on the characteristics of the incorporation of the ions in the lattice.

2. Experiment

Hard solutions of $Zn_{1-x}Co_xO$ and $Zn_{1-x}Cr_xO$ were obtained by the method of solid state reactions, which is widely applied in ceramic technology. Materials of special cleanness were used as initial components for preparation of charge. The powders of connections $CoCO_3$ and $CrCO_3$ obtained by growing shallow to the size of particles 50–100 nm, and mixed up with powder ZnO and small amount of water in the jasper drums of planetary mill SAND-1-1. Time of mixing and grating was determined by the degree of homogenization and was set to 16 h.

The mixture was drained in temperature 120 ± 5 °C. After that the mixture was annealing in air at 700 ± 5 °C for 4 h. Press-purveyances by a diameter 11.5–15 mm thick formed 1–2.5 mm by applying pressure of 40–60 MPa on a hydraulic press PG-10 without the use

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of plastificators. Mixtures were annealed at temperatures near to 1000 °C. Hard solutions of $Zn_{1-x}Co_xO$ and $Zn_{1-x}Cr_xO$ with $x = 0.2$ and $x = 0.04$ were obtained in this way. Standards were annealed in the chamber stove of periodic action VTP-06M1 in air (the accuracy of temperature control was ±5 °C) during 3 h. Maximal temperature of annealing, which replies the isothermal area of curve of heating-cooling, was 1110 °C.

Technology of preparation of ceramic materials on the basis of ZnO, as remarked earlier, utilizes solid states reactions. The reactions $CoCO_3 + ZnO > Zn_{1-x}Co_xO$ and $CrCO_3 + ZnO > Zn_{1-x}Cr_xO$ yield powders of $Zn_{1-x}Co_xO$ and $Zn_{1-x}Cr_xO$.

Samples of zinc-oxide doped with cobalt and chromium from solutions above, were obtained by Pulsed Laser Deposition (PLD) method. The substrate temperature was 25 °C for quartz, and 200 °C for sapphire. Beam parameters: 0.2 mm, 0.5 J in 10 ns pulse, Gaussian distribution, repetition frequency 0.3 Hz. Time of layer growth was about 30 minutes. The layer thickness is from 300 to 500 nm. Samples were annealed in air. Compared to our previous work [28] with ZnO, samples with cobalt were received in different substrate temperature and with different thickness. EMR measurements were performed in the X-band on Bruker multifrequency and multiresonance FT-EPR ELEXSYS E580 spectrometer. The temperature of the samples was controlled in the range of 95–300 K using the Bruker liquid N gas flow cryostat with 41131 VT digital controller, and in the range of 4–300 K using the Oxford Instruments ESR 900 liquid He gas flow cryostat with MercuryITC digital controller.

3. Results and discussion

EMR spectra comparison for the annealed and non annealed sample of ZnO:Co and ZnO:Cr are similar and were analyzed. Samples on sapphire substrate in contrast to quartz have additional narrow line shown in Fig. 1. This line is coming from chrome inside substrate. We are interested more in magnetic properties of ZnO layer instead of substrate, that is why further in the work we focused on broad line around 350 mT. In the spectrum low-field strongly asymmetric line can be observed whose analysis will be made in a separated work. Anisotropy of EMR spectra of ZnO:Cr layer on sapphire substrate is shown in Figs. 2 and 3.

Effective spectroscopic g-factor and the peak-to-peak line width (H_{pp}) of the wide resonance line near 350 mT were determined. Based on those parameters the Curie–Weiss temperature was determinate. In addition, temperature dependence of intensity and peak-to-peak line width are shown in Fig. 4. Since the broad EMR line is asymmetric, the accuracy of parameters measured directly from the experimental spectrum is rather limited. Therefore, additionally the experimental line was fitted using the Lorentzian type curve, since such curves describe satisfactorily experimental EMR lines of DMS with manganese in high temperature range (see [6] and references therein). In this way we determined parameters for

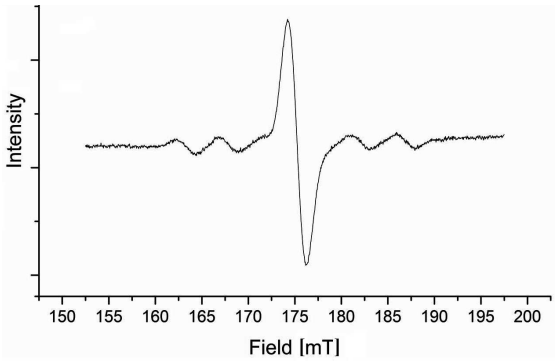

Fig. 1. EMR spectra of narrow Cr line from sapphire, ZnO:Cr annealed at 300 °C measured at temperature of 93 K.

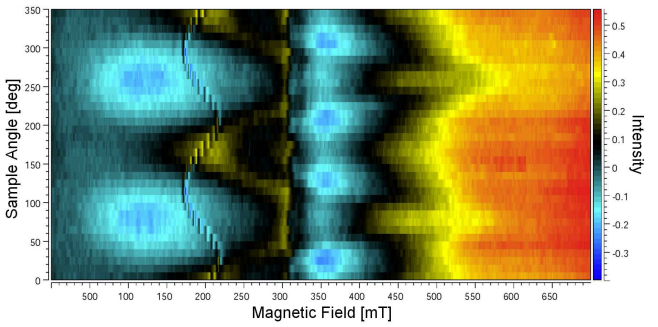

Fig. 2. Angular dependence of vertical orientation for ZnO:Cr sapphire sample annealed at 700 K.

EMR lines such as the peak-to-peak line width (H_{pp}), the intensity (I) as well as the resonance field (H_r). Based on these data we obtained the temperature dependences of gyromagnetic factor $g(T)$ and integral intensity. At fitting the Lorentz type curve the lower field part of EMR line was included because of its regular nature.

We used the Curie–Weiss law to analyze the temperature dependences of the integral intensity, which is directly proportional to the magnetic susceptibility χ. A linear increase of $\chi^{-1}(T)$ at higher temperatures can be fitted to the Curie–Weiss law [29, 30]:

$$(\chi(T) - \chi_0)^{-1} = (T - \theta_{\mathrm{CW}})/C, \qquad (1)$$

where C is the Curie constant, θ_{CW} is the paramagnetic

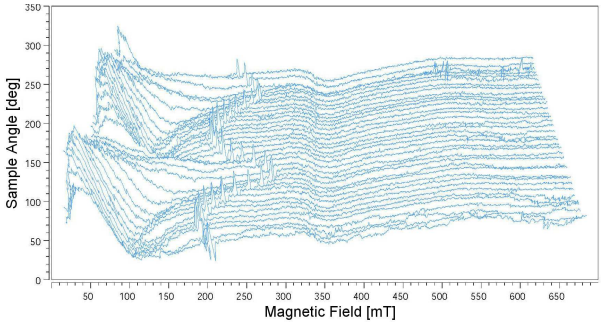

Fig. 3. Angular dependence of horizontal orientation for ZnO:Cr sapphire sample annealed at 500 K.

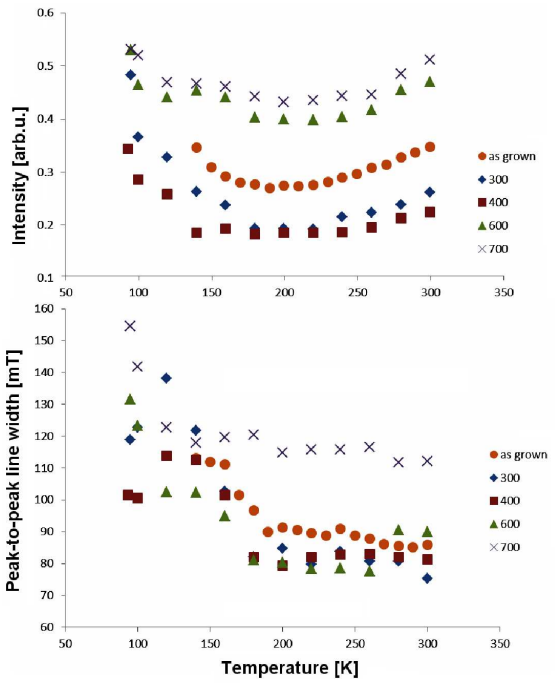

Fig. 4. Temperature dependence of intensity (top) and peak-to-peak line width (bottom) of ZnO:Co samples on quartz substrate.

TABLE I
Curie–Weiss temperature of all samples.

	Temperature [K]	θ_{CW}
Samples on quartz substrate		
ZnO:Cr annealed	136.2	3.33×10^5
ZnO:Cr	138.3	2.00×10^5
ZnO:Co	165.5	1.00×10^5
ZnO:Co annealed	150.8	1.43×10^5
Samples on sapphire substrate		
ZnO:Cr as grown	94.5	2.16×10^5
ZnO:Cr 300 K annealed	109.6	1.02×10^5
ZnO:Cr 400 K annealed	86.9	1.24×10^5
ZnO:Cr 600 K annealed	50.3	3.78×10^5
ZnO:Cr 700 K annealed	44.0	5.93×10^5

Curie temperature, and χ_0 is a temperature independent term to account for the diamagnetic host and any Pauli paramagnetism contribution. Fitting yields the following values shown in Table I.

4. Conclusions

For annealed and non annealed layers on quartz substrate observed characteristic Curie–Weiss temperature around 200 K in which all EMR line parameters such as: peak-to-peak line width (H_{pp}), the intensity I as well as the gyromagnetic factor $g(T)$ are changed. For samples on sapphire substrate the Curie–Weiss temperature decreases with increase of the annealing temperature, which is shown in Fig. 5.

In summary, we have reported the X-band EMR studies of ZnO:Co and ZnO:Cr. We have determined from the

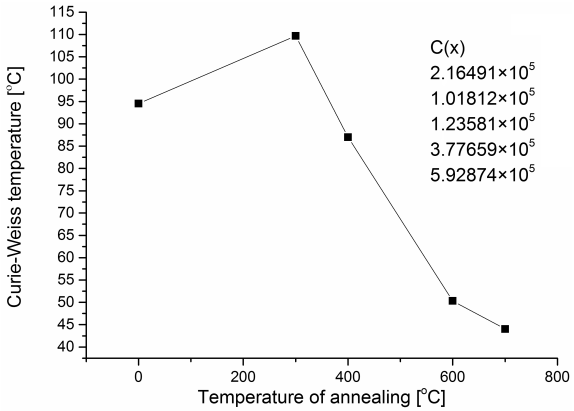

Fig. 5. Curie–Weiss temperature dependence of the temperature of annealing for ZnO:Cr samples on sapphire substrate.

EMR lines the parameters: the peak-to-peak line width H_{pp}, the intensity I as well as the resonance field H_r. The results of temperature dependence of EMR spectra for the samples and linear extrapolations to the Curie–Weiss law indicate the ferromagnetic interaction between Co and Cr ions characterized by the Curie temperatures from 44.0 K to 109.6 K and from 136.2 K to 165.5 K, respectively.

In this study the magnetic properties of Cr and Co with a high concentration up to 20% were analyzed. The line in a broad asymmetric Dyson shape was observed, consisting of two different lines staggered. We have determined from the EMR lines the parameters: the peak-to-peak line width H_{pp}, the intensity I as well as the resonance field H_r. The results of temperature dependence of EMR spectra for the samples and linear extrapolations to the Curie–Weiss law indicate the ferromagnetic interaction between Co and Cr ions.

With increase of the annealing temperature we observe stronger paramagnetic properties as a result from weakening the exchange coupling between Cr and Co ions. A similar effect was observed at work [24] for ZnO:Co layers, with Co = 25%. The mechanism responsible for the observed ferromagnetism is still not clear, and the source of the ferromagnetism remains controversial.

By analyzing the EMR linewidth behavior, similar as in previous paper [30] for low concentration of ions, we claim that a combined effect of the exchange and dipolar broadening plays an important role in the mechanism of linewidth formation in those materials.

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