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Microwave Techniques Investigations of ZnCoO Films Grown by Atomic Layer Deposition

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Electrical and magnetic properties of ZnCoO thin films grown on silicon substrates by atomic layer deposition method are investigated. The films were grown using reactive organic precursors of zinc and cobalt. The use of these precursors allowed us the significant reduction of a growth temperature to 200 °C and below, which proved to be very important for the growth of uniform films of ZnCoO. We have measured the microwave AC conductivity and EPR for two types of ZnCoO samples, with different Co fractions.

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1. Introduction

Dilute magnetic semiconductors (DMS) based on ZnO have attracted special attention because of their attractive properties and a wide range of applications. First theoretical papers, but then experimental have shown that ZnO-based DMS samples can be ferromagnetic (FM) at room temperature (RT), when doped with Mn or Co [1–3]. At present, a large number of papers reports ferromagnetic ordering at RT in ZnCoO. However, the origin of the FM response in ZnCoO is not clear [4]. FM response was related to defects in ZnO host [5], formation of foreign phases (e.g. Co_xO_y) [6], Co–metal accumulations [7] (Co clustering [8]), or due to uncompensated spins at surfaces of Co-rich ZnCoO regions [9], which may be of nm sizes (see [9, 10]) and thus are difficult to detect. Our earlier magnetic investigations indicate that RT FM response is observed in films with non-uniform Co distribution [7] and is due to Co metal accumulations at the ZnCoO/Si interface.

The objective of the present investigations is to analyze the results of magnetic and electrical measurements of the ZnCoO thin films obtained at low growth temperature by the atomic layer deposition (ALD) method. We employ two microwave techniques — microwave AC conductivity and electron paramagnetic resonance (EPR) for these studies.

2. Experimental

All discussed ZnCoO samples were grown between 160 °C and 200 °C by the ALD technique using the F-120 Microchemistry reactor and double exchange reactions [11]. In our experiments we applied diethylzinc (DEZn) or dimethylzinc (DMZn) as a zinc precursor, cobalt(II) acetylacetonate ($Co(acac)_2$) as a cobalt precursor and deionized water as an oxygen precursor. These highly reactive precursors are sequentially introduced to the growth chamber, so they meet only at a surface of a grown film. Investigations were performed for the two types of ZnCoO films, with different Co fractions. Samples of the first type have lower Co concentration $\leq 5\%$ and were more uniform, due to lower growth temperature (160 °C). Samples of the second type were grown at 200 °C, were less uniform and had larger Co concentration $> 5\%$.

The EPR measurements of ZnCoO films were performed using a Bruker ESP 300 spectrometer operating in X-band, with a microwave frequency of 9.5 GHz. The EPR signals were collected at temperature between 2.4 K and 300 K. The angular dependence of EPR signals was measured rotating samples from the out-of-plane to the in-plane magnetic field configuration. Microwave AC conductivity was measured using a home-built system monitoring changes of a cavity resonance frequency and its quality factor.

3. Results

Magnetic resonance (MR) investigations of ZnCoO thin films reported in the literature show different types

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of MR signals. For samples with a low Co fraction EPR signals of isolated Co^{2+} ions and Co–Co pairs were detected, showing characteristic hyperfine structure of Co [12]. Jedrecy et al. [13] reported (for ZnCoO layers with 10% Co concentration) that Co^{2+} ions substitute Zn^{2+}. They observed broadened and anisotropic paramagnetic signal related to substituting Co^{2+} ions. Hyperfine structure was not resolved. They also reported that free-carriers concentration is low in their films.

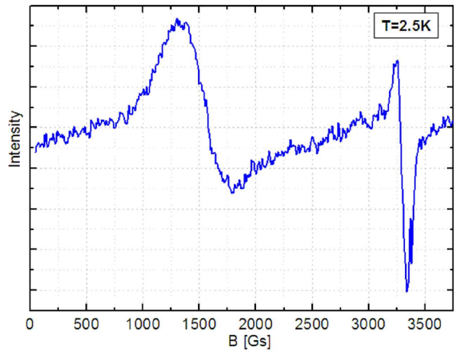

Fig. 1. EPR spectrum for the ⊥ orientation of the magnetic field relative to the crystal *c* axis. EPR was measured for ZnCoO of the first type with 5% Co concentration.

The same situation can be observed for samples of the first type with 5% Co concentration and lower. The EPR signal of Co^{2+} ions detected in such samples is shown in Fig. 1. The signal is broad, hyperfine structure of Co is not resolved and is anisotropic.

Bardeleben et al. [14] observed another MR signal in ferromagnetic ZnCoO samples with 30% Co concentration. The authors suggested that this signal comes from the metallic Co clusters with typical size of ≈ 5 nm.

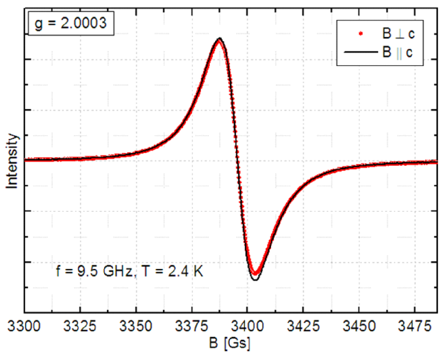

Fig. 2. EPR spectra collected for two orientations of the magnetic field relative to the crystal *c* axis (sample of the second type with Co concentration higher than 5%).

In our samples we do not observe such signal. Instead a new type of the MR resonance is detected. Samples of the second type (the one less uniform) show a strong isotropic signal (see Fig. 2) with a fairly low paramagnetic Curie temperature of about 10 K (see Fig. 3). For these samples X-ray photoelectron spectroscopy (XPS) investigations (not discussed here) show the presence of small inclusions of Co metal and various Co-oxides [7].

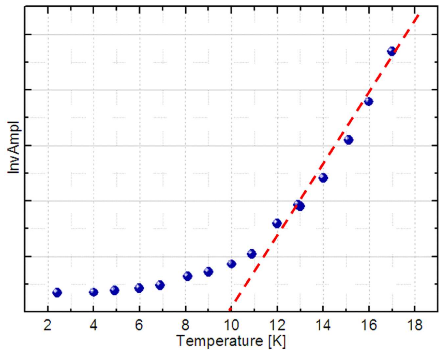

Fig. 3. Temperature dependence of width of EPR signal for sample of the second type.

Occurrence of positive Curie temperature for the second type EPR signal and its isotropy suggest that this signal is related to some spherical inclusions of foreign phases (likely Co oxides) rather than metallic ones, since much higher Curie temperature was expected in the latter case. The most surprising result is that Co^{2+} related paramagnetic EPR signal is ALD layer not observed.

Measurements of microwave AC conductivity allow us to investigate electrical uniformity of Co-distribution in ZnCoO films. This method is highly sensitive to detection of small metal inclusions with a high conductivity [7]. Moreover, this is a contactless method. Thus, we avoid problems with contact stability and measurements of highly resistive samples.

Whereas the DC conductivity of our ZnCoO films varies a little among all studied samples, the AC one increases considerably for the layers with a substantial non-uniform Co-distribution. We observe a strong correlation between Co concentration and AC conductivity.

The larger AC conductivity was observed for thinner samples and these of the second type, strongly indicating an important, if not a dominant, role of metallic inclusions in the observed discrepancy between DC and AC measurements.

4. Conclusions

The present investigations indicate a direct link between uniformity of the samples studied and their electrical and magnetic properties. In non-uniform samples we observe large deviations between DC and AC conductivity and the appearance of a new MR signal.

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