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ZnCoO Films Obtained at Low Temperature by Atomic Layer Deposition Using Organic Zinc and Cobalt Precursors

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In this paper we report on ZnCoO thin films grown by atomic layer deposition method in reactor F-120 Satellite. ZnCoO films were grown at low temperature (T_s = 160°C) with a new zinc precursor (dimethylzinc — DMZn) and with cobalt (II) acetyloacetonate ($Co(acac)_2$) as a cobalt precursor and deionized water as an oxygen precursor. In this paper we concentrate on the methods of homogenizing Co distribution in ZnCoO films.

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1. Introduction

ZnO doped with transition metal (Co, Mn, Cr, Ni) ions is one of the most promising materials for spintronics [1, 2]. Theoretical calculation has shown that ferromagnetic state is easily obtained in *n*-type ZnCoO at room temperature [2, 3]. It was reported that ferromagnetic phases were observed for content of Co in ZnCoO less than 10% [4]. However, the following experimental observations for ZnCoO confirmed and other rejected the presence of ferromagnetic ordering in such samples. The conflicting reports raise questions about the genuineness of the

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observed ferromagnetism in Co-doped ZnO. After gaining some experience with Mn-doped ZnO we decided to apply growth methods used there. In a series of papers [5, 6] we have shown that in-plane and depth homogeneous ZnMnO films can be obtained in the atomic layer deposition (ALD) processes performed at low temperature. Such films (for low Mn fractions) were paramagnetic.

This paper presents and discusses the results of structural, magnetic, and electrical measurements made on ZnCoO thin films obtained at low temperature (LT) growth conditions by the ALD method.

2. Growth method and experimental results

We used ALD method to deposite ZnCoO layers at LT. In ALD method we can use more reactive precursors than in chemical vapor deposition (CVD), because the precursors are sequentially introduced to the growth chamber, so they meet only at a surface of a grown film. This permitted us the use of fairly reactive organic precursors to grow ZnCoO thin films. In our experiments we applied as a zinc precursor dimethylzinc (DMZn), as a cobalt precursor cobalt(II) acetyloacetonate ($Co(acac)_2$) and deionized water as an oxygen precursor. Precursors' temperatures were the following: DMZn $-30°C$, $Co(acac)_2$ $150°C$, and water $30°C$. Substrate (sapphire, GaAs, Si, glass, ITO-glass) temperature was $160°C$ in all processes discussed in the present work.

Referring to our experience with Mn we tried to reach a better quality of ZnCoO films by adding a buffer layer of ZnO. Thus, the obtained by us samples of ZnCoO can be divided into two groups. The first group (group I) are the samples with introduced buffer layer of ZnO, and the second group (group II) are the samples without such buffer layer. The second group of the samples was grown with different Zn-to-Co ratios of ALD cycles, which was aimed to obtain homogeneous ZnCoO layers. The parameters of the growth for both groups are given in Table. All samples discussed in the present work were grown on a silicon substrate.

TABLE

Growth conditions of ZnCoO thin films.

Group number	Zn precursor		O precursor		Co precursor		O precursor	
	application time [s]	purging time [s]	application time [s]	purging time [s]	application time [s]	purging time [s]	application time [s]	purging time [s]
I	1.1	1.1	2.75	4.4	3.3	1.65	1.65	2.75
I	1.1	1.1	2.75	4.4	1.1	1.65	1.65	2.75
II	1.1	1.1	2.75	4.4	1.1	1.65	1.65	2.75
II*	1.1	1.1	2.75	4.4	1.1	1.65	1.65	2.75
II	1.1	1.1	2.75	4.4	3.3	1.65	1.65	2.75
II	1.1	1.1	2.75	4.4	0.55	1.65	1.65	2.75
II	1.1	1.1	2.75	4.4	7.7	1.65	1.65	2.75

*different Zn-to-Co ratios of ALD cycles

Atomic force microscopy (AFM) investigations (see example of the AFM in Fig. 1a — for the group I and b — for the group II) indicate that roughness of layers increases with the thickness of ZnCoO samples. Such clear correlation was not observed by us in the case of ZnMnO films.

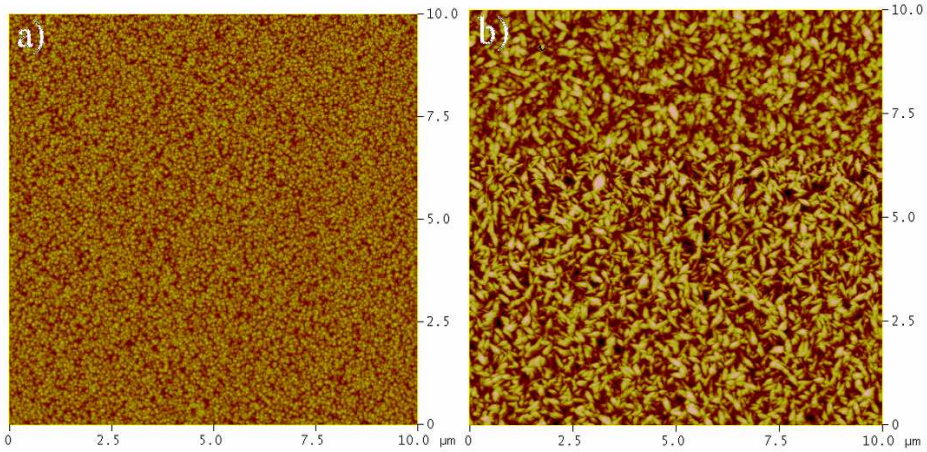

Fig. 1. AFM image of ZnCoO film for: (a) group I, (b) group II.

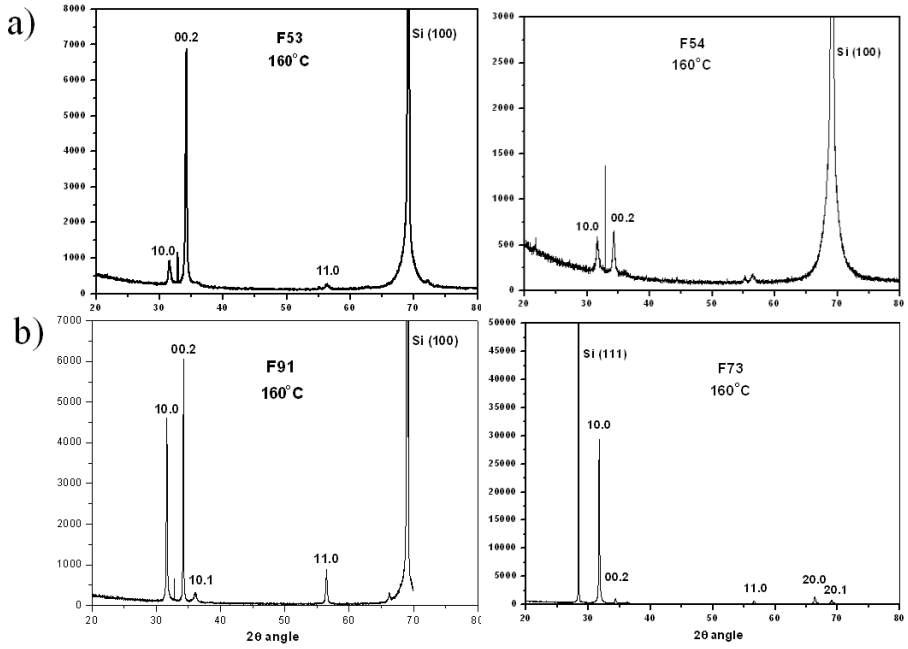

Fig. 2. XRD spectra for: (a) group I, (b) group II.

Structural properties of ZnCoO films were evaluated with the X-ray diffraction (XRD) method. The XRD measurements show a polycrystalline nature of ZnCoO layers. In all the cases we observed the diffraction maxima related to (10.0), (00.2) and (11.0) crystallographic orientations. Moreover, the XRD spectra indicate a change of a preferential growth orientation (00.2) for samples of the group I (Fig. 2a). XRD spectra for samples ZnCoO of the group II are shown in Fig. 2b.

Co introduction to the films was confirmed with secondary ion mass spectroscopy (SIMS), electron probe micro-analysis (EPMA) and superconducting quantum interference device (SQUID). SIMS investigations showed high homogeneity of the obtained ZnCoO layers. We tested several sequences of elementary ALD cycles and times of pulses of cobalt precursor to optimize in-depth homogeneity of Co distribution. We observed the best results for a 1.1 s time of cobalt precursor pulse and sequences of eighty layers of ZnO and five layers of CoO (SIMS profile visible in Fig. 3a). We observed similar results for sequences of eighty layers of ZnO and ten layers of CoO (SIMS profile visible in Fig. 3b). Co fraction in both of these films was below 1% as concluded from the EPMA and SIMS measurements. This means that Co incorporation does not scale with Co-to-Zn ratio. We achieved the highest Co fraction in our films for process in which sequences ZnO to CoO were eight to one. For such samples Co fraction was about 3%. SIMS and SQUID measurements gave similar Co fractions.

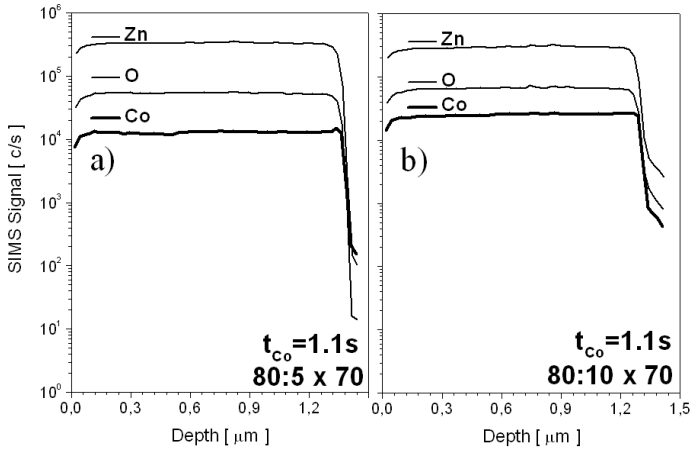

Fig. 3. SIMS profiles of Co depth distribution for ZnCoO layers ALD-grown on silicon with DMZn and $Co(acac)_2$ for time pulse Co 1.1 s using: (a) 80:5 ratio and (b) 80:10 ratio for the zinc to Co and for the sequences of the ALD pulses repeated 70 times.

We obtained information about magnetic properties of our films from magnetization investigations performed using a home made SQUID magnetometer. Films of ZnCoO with homogeneous Co distribution, with Co fraction below 5%

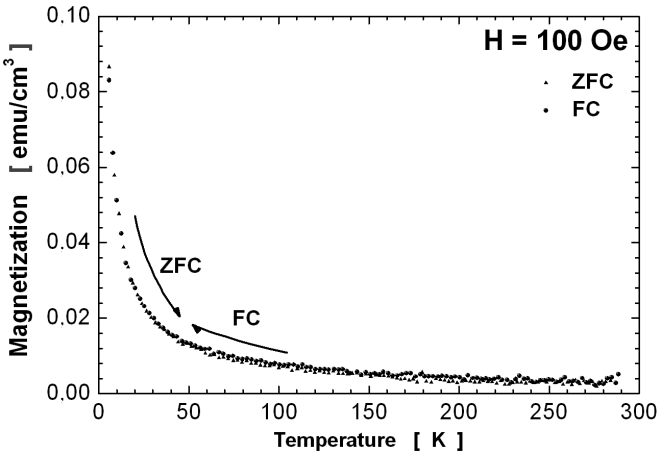

Fig. 4. Magnetization of the ZnCoO ALD film as a function of temperature T. The magnetization curves were collected under both the field cooling (FC) and the zero field cooling (ZFC) conditions. Curves of ZFC and FC overlap.

and grown at LT by ALD, show paramagnetic magnetic properties at room temperature. Figure 4 shows the temperature dependences of magnetization for such ZnCoO samples.

The electrical measurements (Hall measurements) conducted on the samples of ZnCoO layers show that the free carriers' concentration varied between 10^{19} cm^{-3} and 10^{17} cm^{-3} depending on the growth temperature, film thickness and Co fraction. The values of carriers' Hall mobility were usually about of 3 cm^2/(V s). Electrical measurements indicate preferential n-type conductivity of our films.

3. Conclusions

We have grown at low temperature ZnCoO films by ALD with organic cobalt and zinc precursors. The highest Co concentration achieved in the present work was below 5%. For such films we obtained in-plane and depth homogeneous ZnCoO films, which are paramagnetic for n-type films with free electron concentration up to 10^{19} cm^{-3}. We report also that Co doping does not affect free electron concentration in our films but reduces their mobility.

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