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# Optical and magnetic properties of ZnCoO layers

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ABSTRACT

Optical and magneto-optical properties of ZnCoO films grown at low temperature by Atomic Layer Deposition are discussed. Strong wide band absorption, with onset at about 2.4 eV, is observed in ZnCoO in addition to Co-related intra-shell transitions. This absorption band is related to Co 2+ to 3+ photo-ionization transition. A strong photoluminescence (PL) quenching is observed, which we relate to Co recharging in ZnO lattice. Mechanisms of PL quenching are discussed.



## 1. Introduction

Wide band gap II–TM–VI and III–TM–V alloys (TM stands for a transition metal) are intensively studied for possible spintronic applications (see e.g. [1–4]). For some of them a room temperature ferromagnetism (RT FM) was theoretically predicted [2–4], which, if achieved, will result in several applications of these materials.

Whereas carrier mediated magnetic properties of GaMnAs are relatively well controlled, the present situation for ZnMnO and ZnCoO remains very unclear. RT FM was theoretically predicted in heavily p-type ZnMnO [2] and n-type ZnCoO alloys [3,4] and then observed experimentally. However, the origin of the observed magnetic ordering remains not clear (see e.g. [5] and references given there). It is more likely that RT FM of ZnCoO (also ZnMnO and GaFeN [6]) is due to inclusions of foreign phases and metal accumulations, rather than to "volume properties" of these two alloys (see e.g. [5] and references given there). We observed that samples with the uniform TM distribution show a paramagnetic response. Such samples were grown by us at a low temperature using Atomic Layer Deposition (ALD) [7,8]. They are used in the present study.

In the present work we investigate relation between optical and magnetic properties of ZnCoO layers grown at low temperature by the ALD. Some test measurements are also performed on bulk ZnO sample doped with Co, with a low Co concentration in the range of $10^{18}$ cm$^{-3}$. First we verify if we can realize conditions required for the FM ordering, as assumed in the theory. Then, we describe relations between optical and magnetic properties of ZnCoO (and also ZnMnO). We demonstrate that Mn and Co introduction to ZnO samples results in several new properties, not observed e.g. in ZnMnS [9]. In particular, the introduction of Mn and Co ions efficiently quenches visible emission of ZnO.

PL quenching is more efficient in ZnCoO, which was not surprising, since Co is known as a killer center in wide band materials, e.g. in ZnS [10]. Surprisingly, Mn ions also act as emission deactivator in ZnO, which is not observed in ZnS and many other II–VI compounds. This unexpected effect (in ZnS Mn is emission activator [9]) we utilize in practice to get information on samples uniformity. Efficient emission quenching in TM rich regions of a sample allows evaluation of uniformity of Co distribution in the samples studied. This information we obtain from maps of in-plane variations of the CL intensity, as already demonstrated for ZnMnO [11,12]. TM rich regions are observed as dark regions in the CL intensity maps.

In-depth and in-plane CL mapping performed by us evidence uniform Co distribution in the samples grown at low temperature by the ALD and nonuniform in the one grown at higher temperature, or annealed after the growth. Such experiments together with SIMS, XPS and magnetic investigations allowed us to find growth conditions to get ZnCoO layers with uniform Co distribution, as already discussed in Refs. [7,8,13] for ZnMnO layers. Uniform layers show a paramagnetic response at room temperature. A ferromagnetic one was detected in nonuniform films (grown at higher temperature) and was related to the presence of foreign phases and (dominant contribution) metal accumulations [5].

Despite the fact that a volume related ferromagnetism is not observed by us, the samples studied show some attractive magneto-optical properties, which we will relate to the observed non-uniformity in TM distribution and large carrier capture rates by Co (and Mn) ions in ZnO, as discussed below.

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## 2. Experimental

Optical and magneto-optical investigations were performed on ZnCoO layers grown at relatively low temperature (LT, between 160 °C and 200 °C) by the Atomic Layer Deposition (ALD). Some test measurements were done on a bulk ZnO doped with Co, with Co concentration in the range of $10^{18}$ $cm^{-3}$. In the ALD process we used metalorganic zinc and manganese precursors – diethylzinc (DEZn) as zinc precursor and cobalt(II) acetyloacetonate – ($Co(acac)_2$) as cobalt precursor. As an oxygen precursor we used deionized water. We used 8:1 ratio of Zn–O to Co–O ALD pulses and low temperature of a growth (160 °C), which we proved to be crucial to get uniform TM distribution in our alloys [5,7,8,13]. The so-obtained films were polycrystalline and contained about 1% of Co, uniformly distributed in plane and depth. Different substrates were used depending on experiment requirements – Si for magnetic investigations, (0 0 0 1) sapphire or quartz for optical transmission investigations, glass for electrical measurements.

Most of investigations were performed on ZnCoO samples with relatively low Co fractions (about 1%). The larger Co fractions (about 7–8%) were observed by us for thin films grown with 2:1 ratio of Zn–O to Co–O ALD cycles at slightly increased temperature (about 200 °C), for which we observed a FM response, as reported in [5]. FM response was related to Co metal accumulation at the Si/ZnCoO interface [5]. For thicker samples grown at a lower temperature and with a lower Co fraction we observed a paramagnetic response at room temperature and Co metal inclusions were absent or very rare [5]. EXAFS investigations (A. Wolska, unpublished results) confirm that Co enters substitutional positions ($Co_{Zn}^{2+}$) in these ALD-grown ZnO samples. Some traces of metal inclusions were detected in XPS investigations of nonuniform samples (the one grown with 2:1 ratio of the ALD cycles and at 200 °C) [5]. We also searched for inclusions of various oxides (Co oxides), as seen for us for studied in parallel ZnMnO films ($Mn_xO_y$), but their concentration (if they are present) must be very low. This is quite different situation to the one seen by us for ZnMnO. Co–OH formation was only detected in the XPS study.

Thickness of our samples was between 0.2 and 2 μm, which turned out to be crucial parameter for understanding magnetic properties of investigated samples. We observed a clear correlation between layer thickness and FM response for nonuniform ZnCoO layers [5]. Further details on growth conditions can be found in [5,7,8,13].

Investigations of RT transmission and photoluminescence (PL) spectra were performed using the Solar Spectrofluorimetr CM 2203 with two double monochromators, the Xe lamp as excitation source and the Hamamatsu photomultiplier (PMT). LT magneto-PL investigations were performed using a Spectromag 6000 split coil superconductive magnet of Oxford Instruments, He–Cd laser PLASMA model HCCL-15UM, a double monochromator equipped with Hamamatsu S7035 CCD camera and Hamamatsu photon counting system with R2531 PMT and FAST ComTec 7887 card. CL and SEM measurements were performed using Scanning Electron Microscope Hitachi SU-70 equipped with a GATAN MonoCL System.

RT Hall effect measurements were performed using the RH2035 PhysTech GmbH system equipped with a $B = 0.426$ T permanent magnet. Electrical measurements were done in the van der Pauw geometry using e-beam evaporated Ti/Au as an Ohmic contact to ZnO.

## 3. Experimental results and their discussion

In absorption/transmission study of ZnCoO we observed the appearance of two types of Co-related absorption bands (see Figs. 1 and 2). In addition to a characteristic $Co^{2+}$ intra-shell transitions, being due to the $Co^{2+}$ intra-shell $^4A_2(^4F) \rightarrow {}^2A_1(^2G)$, $^4A_2(^4F) \rightarrow {}^2A_1(^4P)$ and $^4A_2(^4F) \rightarrow {}^2A_1(^2G)$ transitions, also reported by Koidl [14], Jin et al. [15], Dinia et al. [16], Liu et al. [17], and Ramachandran et al. [18], a broad absorption band is detected below the band-to-band transition. This is a similar situation as for ZnMnO, where we observed a broad band absorption below the onset of the band-to-band transitions, which was first reported by Fukumura et al. [19] and related to charge transfer transitions [19,20], smeared out the $Mn^{2+}$ intra-shell transitions [21], or to Mn 2+ to 3+ photoionization, as we discussed in details in our recent publication [22]. Transmission spectrum for the studied ALD-grown samples is shown in Fig. 2. The appearance of Co related charge transfer band is seen as in the bulk sample (see Fig. 1). For thin layers we also observed interference fringes superimposed on transmission spectra, as seen in Fig. 2. There the broad absorption band is so strong that it may result in an incorrect conclusion that the fundamental absorption (band-to-band) is reduced by Co introduction.

For ZnCoO a band overlapping the band-to-band transition was reported earlier by [23–29]. The origin of the latter absorption is still disputed. It was related to Co charge transfer transition [26,27,29], but also to excitation of surface plasmons resonances in nanometer size metallic Co inclusions [30]. The first interpretation was supported by the results of photoconductivity measurements [23–25].

The present study supports this identity of the absorption spectrum. We observe that PL excitation (PLE) within this absorption band results in recombination via $Co^{2+}$ intra-shell 3d states. This is not observed after the host excitation. Such property of the PLE spectrum is expected if the photogenerated free carriers recombine via a ladder of Co 2+ intra-shell states (electrons are retrapped by Co 3+ via excited Co 2+ states).

Origin of proposed charge transfer transitions was discussed by Liu et al. [26]. The authors proposed competition of two types of photoionization processes – Co 2+ to 3+ (at a lower energy) and 2+ to 1+ (close to the band-to-band transition), the latter overlapping with a process of photogeneration of Co localized excitons.

If the model proposed by Liu et al. is correct, films containing Cobalt should be resistive and high n-type conductivity could not be achieved in ZnCoO, i.e., the condition required for achieving a carrier related ferromagnetic coupling [3,4] could not be realized. $Co^{1+}$ level localized at about 0.28 eV [27] below ZnO conduction band edge should compensate shallow donors of ZnO. However,

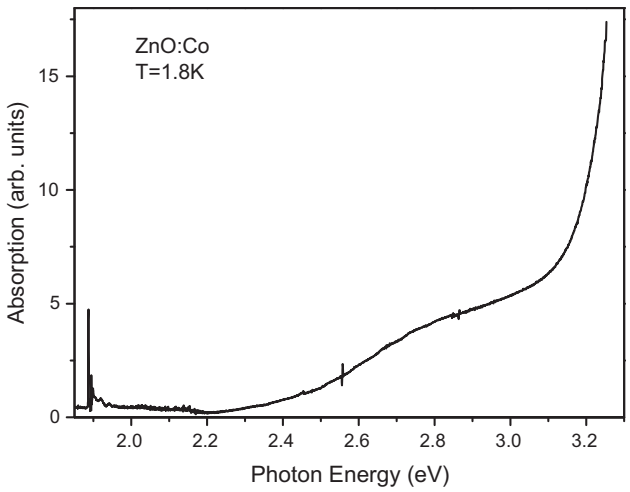


**Fig. 1.** Absorption spectrum of the reference bulk ZnO:Co sample measured at 2 K temperature.