Room temperature ferromagnetic (Zn,Co)O epitaxial films obtained by low-temperature MOCVD process

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Abstract

High quality epitaxial films of $Zn_{1-x}Co_xO$ solid solutions were obtained by low temperature MOCVD process using water vapor up to x 0.33. Depositions were carried out at 300 °C on r sapphire substrates. Films structure and composition were investigated by XRD, XPS and EDX measurements. Magnetic properties were examined using SQUID and Kerr effect measurements. All samples showed ferromagnetic behavior at room temperature. NEXAFS and PES were employed to investigate electronic structure of the films.

1. Introduction

Materials based on transition metals (TM) doped ZnO thin films belong to the so-called *diluted magnetic semiconductors* (*DMS*), which are promising materials for modern spintronics devices [1,2]. Such devices might have wide applications in a new generation of information storage and recording, as they can manipulate both spin and charge degrees of freedom, but the use of DMS is strongly limited by their low Curie temperatures (T_C). Starting with theoretical works of Dietl at al. [3], several groups have tried to obtain ferromagnetic (FM) TM-doped ZnO films with T_C close to room temperature. Cobalt is one of the promising dopants for high-T_C DMS, but reports concerning magnetic properties of Co-doped ZnO are still very contradictory. For instance, FM with T_C of about room temperature (RTFM) was reported in $Zn_{1-x}Co_xO$ thin films obtained by PLD technique [4–6], sol–gel synthesis [7], reactive magnetron

co-sputtering [8] and laser molecular-beam epitaxy [9]. Co^{2+} ions are suggested to be responsible for RTFM in these samples. On the contrary, other thin films obtained by molecular-beam epitaxy [10] as well as bulk $Zn_{1-x}Co_xO$ samples prepared by thermal decomposition of oxalate [11,12] and acetate [13] precursors show no ferromagnetism. Some recent papers [14,15] implied that the ferromagnetism observed in samples with rather high Co concentration could be rated as an extrinsic nature phenomenon resulted from separation of the metal cobalt phase.

Besides the demand of high T_C of spintronics materials, integration of spintronics with semiconductors technology requires low-temperature deposition process for ZnO-based films. The majority of MOCVD processes of thin oxide films (zinc oxide as well) is performed at high temperatures – 500 °C and above – with the use of O_2 as an oxidizing agent [16]. Several approaches have been developed to decrease the deposition temperature. One of them consists in the use of water as a reacting agent. Water-assisted MOCVD of oxides from metal β-diketonates has been demonstrated previously for Al_2O_3 [17], ZrO_2 [18] and PbO [19] growth. It has been observed that addition of water leads to remarkable increase of deposition rate and a high films epitaxial

Fig. 1. Scheme of the deposition setup.

Fig. 2. XPS spectrum of the $Zn_{1-x}Co_xO$ films with different Co content: a) x 0.12, b) x 0.20, c) x 0.33, d) x 0.50.
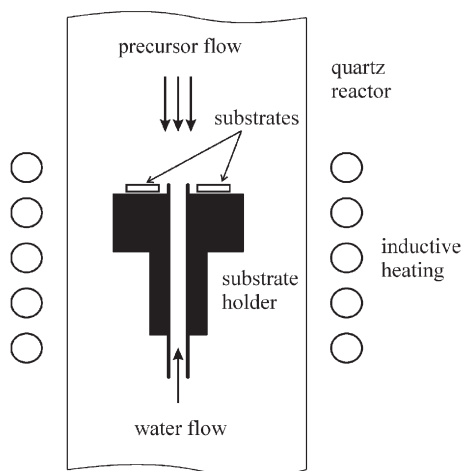
quality at comparatively low deposition temperatures (below 400 °C) [18].

The aim of our work was to perform a study of MOCVD using water vapor in relation to deposition of Co-doped zinc oxide thin films. The main intentions were to study the effect of water vapor on MOCVD at low temperature and to check the possibility of ferromagnetic Co-doped ZnO films epitaxial growth under these conditions.

2. Experimental

The laboratory-type MOCVD apparatus of the cold-wall type has been used (Fig. 1). Heated water vapor was added to the precursor gas directly above the substrate surface. The water consumption has been controlled by weighing of the vessel with water before and after the deposition. The temperature of process was controlled by thermocouple placed inside the substrate holder. Silver paste was used to attach the $r-Al_2O_3$ substrates to the holder. Precursors, Zn acetylacetonate and Co bis(2,2,6,6-tetramethylheptanedionate ($Zn(acac)_2$ and $Co(thd)_2$), have been evaporated in powder flash-evaporation system described elsewhere [20] at 265 °C. Substrate temperature was fixed at 300 °C. Argon was used as a carrier gas (50 l/h); no oxygen was added to the gas mixture. Total pressure of the process was 10 mbar. The growth time was 35–40 min. The samples have been characterized with the use of XRD analysis (SIEMENS D5000 diffractometer), SEM with EDX (CamScan electron microscope equipped with EDAX9800 unit), SQUID measurements (MPMS XL5, Quantum Design) and magnetooptical measurements in the geometry of the transversal Kerr 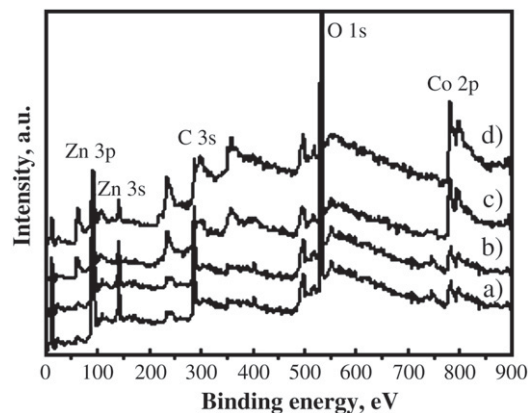effect using automatic MO spectrometer. XPS, NEXAFS and PES were performed using synchrotron radiation (RGBL-PGM beamline at the BESSY II storage ring, Berlin).

3. Results and discussion

The results of quantitative EDX analysis of the samples as well as film thicknesses are given in Table 1. The film thickness has been determined using SEM images of films cross-sections. It can be seen that at the substrate temperature as low as 300 °C the growth rate averages 200–600 nm/h, which exceeds conventional growth rates in MOCVD process using β-diketonates. XPS spectrum of $Zn_{1-x}Co_xO$ films for different x values after 30 min of Ar^+ sputtering at 0.9 keV is given at Fig. 2. One can see that intensities of Co 2p peaks correlate with the Co content in the samples measured by EDX.

XRD analysis shows epitaxial growth of wurtzite-type $Zn_{1-x}Co_xO$ phase on r-sapphire (Fig. 3, space group $P6_3mc$). The following epitaxial relations were found:

$(1\bar{2}10)ZnO||(1\bar{1}02)Al_2O_3$ (out of plane)

$[1-100]ZnO||[-1-120]Al_2O_3$ (out of plane).
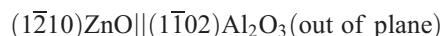
In the whole range of Co concentrations ($x \leq 0.33$) no secondary phases were observed. Fig. 4 presents a Vegard's law behavior of the (1210) interplane distance with increasing of Co content in the films. Only a slight increase of 0.2% is observed in the whole concentration range, in accordance with observations made for (Zn,Co)O films on c-sapphire [21] and bulk ZnO–CoO solid solutions [22]. It is not surprising, because the difference between Co^{2+} and Zn^{2+} ionic radii in tetrahedral coordination is also small (0.72 Å and 0.74 Å, correspondingly) [23]. The increase of cell dimensions is possibly due to Co^{2+} ions in octahedral coordination. Indeed, coordination number (CN) 6 is more suitable for Co^{2+} than CN 4, while Co^{2+} radius in octahedral coordination (1.04 Å) exceeds significantly Zn^{2+} radius in tetrahedral coordination (0.74 Å).

Magnetic properties of the $Zn_{1-x}Co_xO$ films were characterized by a SQUID magnetometer from 0 up to 5 T at 5 K and 300 K. All samples show ferromagnetic behavior with T_C about

Table 1
Film thickness, growth rate and Co content in the $Zn_{1-x}Co_xO$ films

Film thickness, nm	400	200	140	150	150	132
Growth rate, nm/h	630	315	210	243	200	158
Co content (x), at.% (measured with EDX)	0.12	0.17	0.20	0.27	0.33	0.50
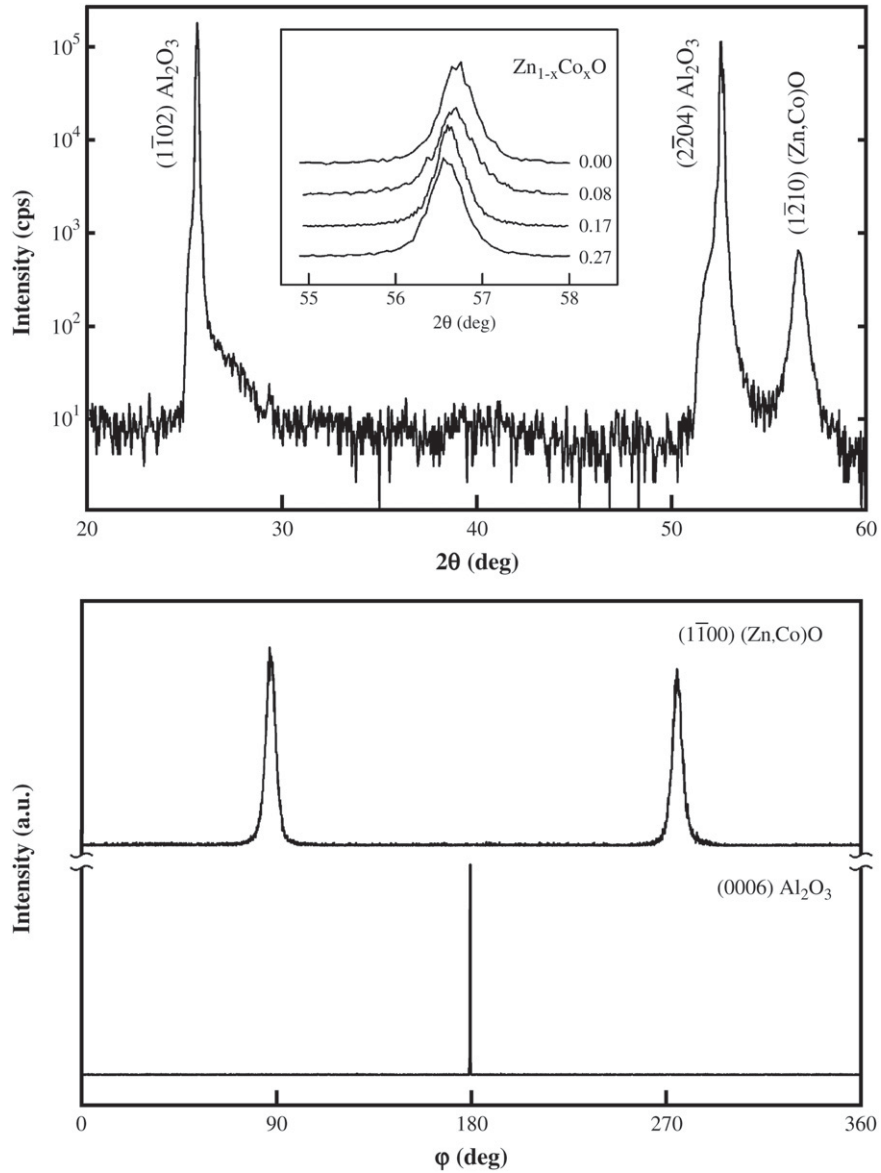
Fig. 3. XRD study of the Zn$_{1-x}$Co$_x$O film with x 0.27 (theta 2theta and phi-scans). Inset: the enlarged view of Zn$_{1-x}$Co$_x$O peak for various x values.
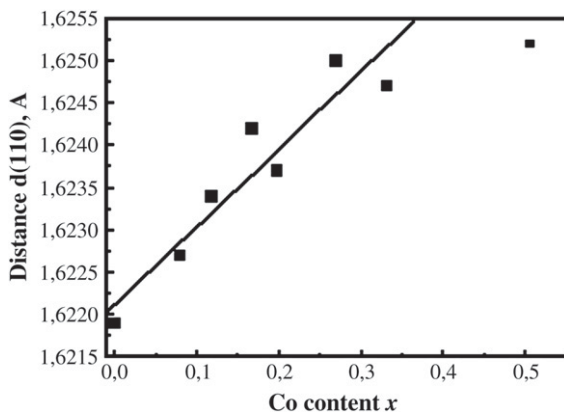

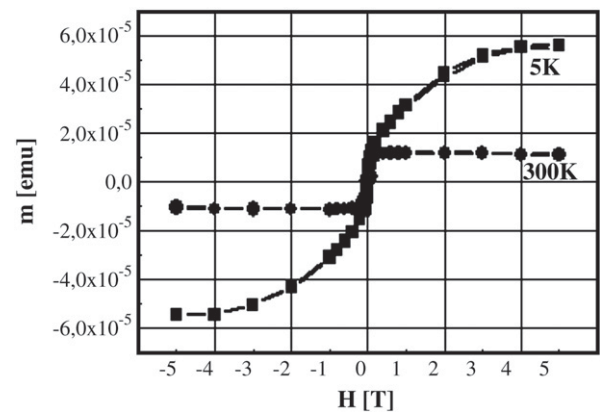Fig. 4. Variation of d (110) distance in Zn$_{1-x}$Co$_x$O samples as a function of Co content.

Fig. 5. M(H) of the Zn$_{1-x}$Co$_x$O film (x 0.2) recorded at 5 K and 300 K.
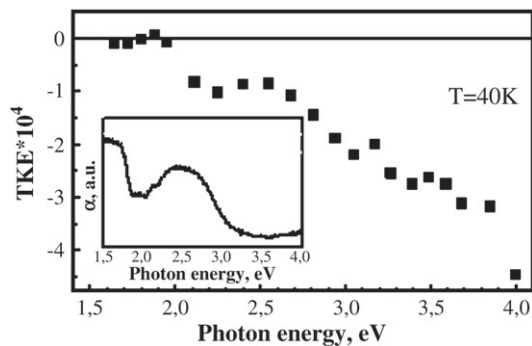
Fig. 6. Spectral dependency of the transversal Kerr effect and (inset) optical absorption spectrum for the $Zn_{0.88}Co_{0.12}O$ film.

Fig. 8. Valence band PES spectra of $Zn_{0.88}Co_{0.12}O$ film obtained at photon energies marked by numbers in the corresponding NEXAFS spectrum.

the room temperature. Fig. 5 presents typical magnetization curve for our samples ($Zn_{0.8}Co_{0.2}O$ composition, saturation magnetization $M_s \approx 4.7$ emu/mol at 300 K). M(H) loops for other samples look similar to the presented one with close values of M_s. Ferromagnetic behavior up to about 300 K is also confirmed by temperature dependence of transverse Kerr effect measurements (not shown here).

In order to investigate the origin of magnetism in $Zn_{1-x}Co_xO$, spectral dependency of transverse Kerr effect was examined. From the similarity of transverse Kerr effect spectrum with the UV–Vis optical absorption spectrum (Fig. 6) we can conclude that Co^{2+} ions rather than Co precipitates are responsible for ferromagnetism in the films. This conclusion is in agreement with some other published results [4,8,9] concerning magnetism in thin films of $Zn_{1-x}Co_xO$ solid solutions.

The electronic structures of $Zn_{1-x}Co_xO$ samples were investigated by employing near-edge X-ray absorption spectroscopy (NEXAFS) and photoemission spectroscopy (PES). Fig. 7 presents Co $L_{2,3}$ NEXAFS spectra of $Zn_{1-x}Co_xO$ samples. For all compositions investigated Co $L_{2,3}$ edge XAS spectra look similar to that of CoO and are quite different from those of Co metal as well as of Co^{3+} indicating that Co ions in all samples are presented in bivalent Co^{2+} state [24]. Fig. 8 shows representative valence-band PES spectrum of $Zn_{0.8}Co_{0.2}O$ as a function of photon energy including the Co 2p−3d core-excitation region (765 eV $\leq$

$h_v \leq 785$ eV). The valence band spectrum of $Zn_{0.8}Co_{0.2}O$ corresponds to the literature data [24,25] and is similar to that of ZnO showing a sharp peak at about 11 eV of the binding energy (BE). This peak corresponds to Zn 3d states, while a broad band between 3 and 7 eV of BE corresponds to O 2p state. The emission near EF is negligible, that suggest the insulating nature of the films. Co 3d partial density of states (PDOS) can be obtained by subtracting the *off*-resonance spectrum from the *on*-resonance one. Fig. 9 represents 2$p_{3/2}$−3d off-resonance ($h_v \approx 770$ eV) and on-resonance ($h_v \approx 774$ eV) valence band photoemission spectra of $Zn_{0.8}Co_{0.2}O$ which are scaled to each other at ≈ 7.5 eV BE. The corresponding difference spectrum with a sharp peak at about 3.5 eV of BE is inset. This result shows that the Co 3d states are located near the top of the O 2p valence band.

In conclusion, we have successfully grown high quality epitaxial films of $Zn_{1-x}Co_xO$ solid solutions with doping up to $x = 0.33$ by low-temperature MOCVD technique using $Zn(acac)_2$ and $Co(thd)_2$ as precursors and water vapor as the reacting agent. Epitaxial growth of high-quality films on r-sapphire substrates was achieved at substrate temperature as low as 300 °C. It was shown that the use of water vapor results in high deposition rate
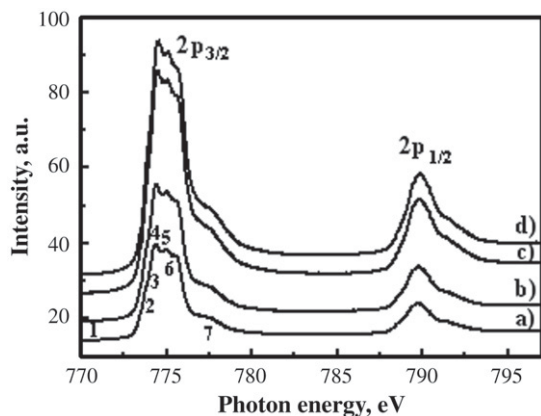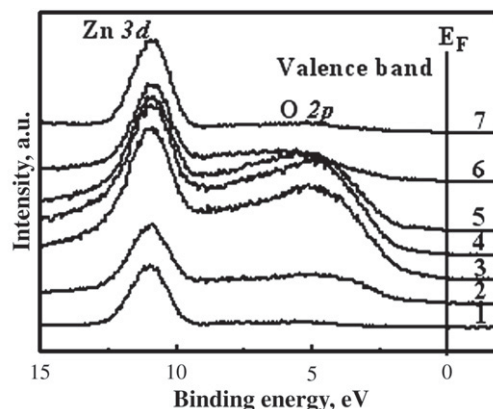

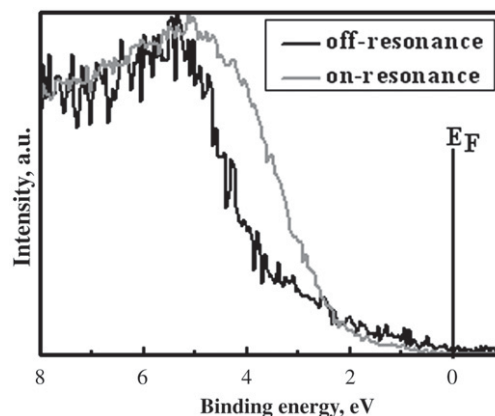Fig. 7. Experimental Co $L_{2,3}$ NEXAFS spectra of $Zn_{1-x}Co_xO$ samples: a) x 0.12, b) x 0.22, c) x 0.3, d) x 0.5.

Fig. 9. On-resonance ($h_v \approx 774$ eV) and off-resonance ($h_v \approx 770$ eV) valence band photoemission spectra of $Zn_{0.88}Co_{0.12}O$ sample. Inset: corresponding difference curve showing the Co 3d PDOS.

in MOCVD process. All films obtained show ferromagnetic behavior at room temperature. It is suggested that Co^{2+} ions are responsible for magnetism in the samples. The method proposed is a perspective for deposition of other ZnO-based thin epitaxial films.

Acknowledgements

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