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(Zn,Cu)O Films by Atomic Layer Deposition — Structural, Optical and Electric Properties

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ZnCuO thin films have been deposited on silicon, glass and quartz substrates by atomic layer deposition method, using reactive organic precursors of zinc and copper. As zinc and copper precursors we applied diethylzinc and copper(II) acetyloacetonate. Structural, electrical and optical properties of the obtained ZnCuO layers are discussed based on the results of scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction, atomic force microscopy, the Hall effect and photoluminescence investigations.

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1. Introduction

Several potential applications of ZnO for novel optical devices as, for instance blue light emitters, lasers devices or UV sensors [1] were proposed. In addition, ZnO doped with transition metal (TM = Co, Cu, Mn, ...) ions is intensively studied for spintronics applications [2]. A theoretical prediction by Dietl et al. [2] suggested that room temperature ferromagnetism (RT FM) should exist in heavily p-type doped alloys of ZnMnO. Cu^+ can be used as an additional p-type dopant into naturally n-type ZnO samples to obtain ferromagnetic ZnCuO films [3–5]. Even in studies where RT FM is reported, the effect of carrier type on the ferromagnetic properties is unclear [5]. So the research on high-quality (Zn,TM)O alloys systems is becoming fairly important.

2. Experimental

All discussed ZnCuO samples were grown between 200 °C and 300 °C by the atomic layer deposition (ALD) technique using the F-120 Microchemistry reactor and double exchange reactions. In our experiments we applied diethylzinc (DEZn) as a zinc precursor, copper (II) acetylacetonate ($Cu(acac)_2$) as a copper 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. The use of these precursors allows us the significant reduction of a growth temperature to 300 °C and below, which proved to be very important for the growth of uniform films of (Zn,TM)O [6]. ZnCuO samples were grown with different Zn-to-Cu ratios of the ALD cycles, which turned out to be crucial to obtain uniform ZnCuO layers, as already indicated in Refs. [6, 7].

Different substrates were used depending on experiment requirements — Si for structural and optical investigations, quartz or glass for electrical measurements. The surface morphology was analyzed from the results of atomic force microscopy (AFM, Bruker Dimension Icon) investigations, using the PeakForce Tapping and silicon nitride probes with sharp tips (a tip radius: 2 nm). 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 ZnCuO. SEM measurements were performed using scanning electron microscope Hitachi SU_70 equipped with a GATAN MonoCL System.

The structure and the crystallographic orientation of ZnCuO layers were measured by the X-ray diffraction (XRD) using the X'Pert MPD diffractometer in a full angular range. Quality of the layers was investigated by a high resolution X'Pert MRD diffractometer equipped with the X-ray mirror, a two-bounce monochromator at the incident beam and a Pixcel detector at the diffracted beam.

3. Results

The results of XRD measurements are shown in Fig. 1. We optimized the ALD cycles (ratio of ZnO to CuO ALD cycles) in order to obtain depth and in-plane homogeneous ZnCuO films. The X-ray diffraction measurements of ZnCuO films deposited on silicon substrate showed

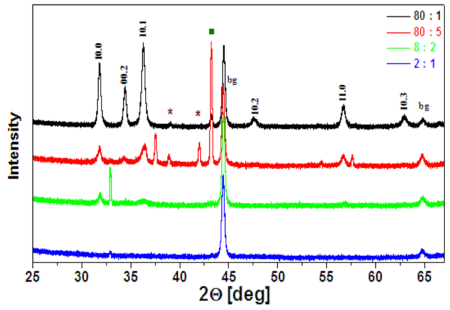

Fig. 1. 2θ XRD spectra of the polycrystalline ZnCuO samples grown at 250 °C with different ratio of ZnO to CuO ALD cycles. The peaks (*) belong to the CuO phase and the one marked with (■) is due to Cu metal inclusions.

that the Cu doping (for Cu doping concentration below 10%) does not change the wurtzite structure of ZnO.

The XRD investigations indicate however that foreign phases and metal inclusions are formed even for relatively low Cu fractions in ZnCuO. At growth temperature 250 °C and Cu concentration of 3% the films show segregation of a second phase (the XRD peaks marked with *) due to CuO [3, 8] and of (the XRD peaks marked with ■) Cu metal inclusions. When the Cu concentration is higher than 20% we observed amorphous structure of the films obtained.

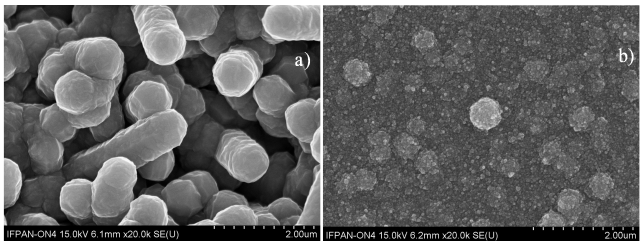

Fig. 2. SEM images of the ALD grown ZnCuO films on silicon substrate for samples with different ratios of ZnO to CuO ALD cycles: (a) 80:1 and (b) 8:2.

The surface morphology of ZnCuO films was investigated with the scanning electron microscopy (SEM) and atomic force microscopy (AFM). Figure 2 shows the SEM images of the ZnCuO films grown at 250 °C by the ALD with (a) eighty to one and (b) eight to two ratios of ZnO to CuO ALD cycles. Flakes-like or nanorods structure of ZnCuO films was often observed for thin films with Cu concentration above 5%. It turned out that it is by far more difficult (than for ZnMnO or ZnCoO) to find optimal growth conditions to get films of a good structural quality grown in 2D mode.

Root mean square (RMS) value of roughness of the films ranged between 6 nm and 25 nm, depending on the Cu fraction. AFM investigation indicates that roughness of these layers grows with an increase of Cu concentration in ZnCuO films (see Fig. 3). Clearly 3D growth

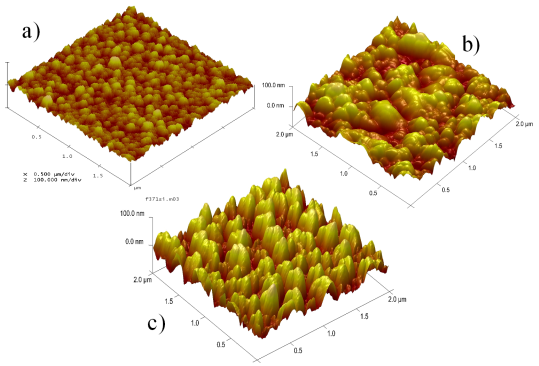

Fig. 3. AFM images of ZnCuO films for: (a) Cu = 1.5% (RMS — 7.5 nm), (b) Cu = 10% (RMS — 22 nm), and (c) Cu = 25% (RMS — 25 nm).

mode dominates, as also observed in the SEM investigations. We do not observe correlations between a growth temperature and layers thickness (number of the ALD cycles) and roughness of ZnCuO films. We observed such correlation for ZnCoO films, as reported in our previous work [7].

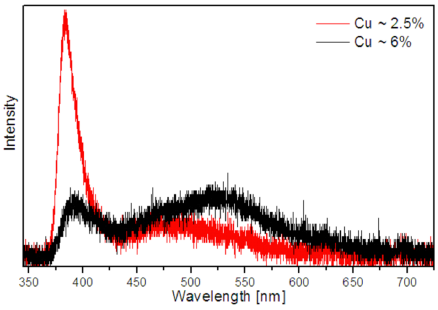

Fig. 4. Room temperature PL spectra for ZnCuO thin film grown at 250 °C. We show the data for the as-grown samples with two different Cu concentrations.

The room temperature PL spectra of the ZnCuO samples are shown in Fig. 4. The 382 nm peak is assigned to the ZnO near-band edge transition. The PL spectra show that introduction of Cu to ZnO quenches visible PL around 382 nm. This effect is clearly Cu related. In turn, the broad and intense green emission at about 520 nm rises in intensity with Cu concentration. Likely this PL band is associated with Cu doping, since this PL increases with Cu concentration in ZnCuO.

The Hall-effect measurements show that most of the ZnCuO films are of n-type with carrier concentration up to 4×10^{19} cm^{-3}. Surprisingly n concentration does not depend on Cu concentration and on growth temperature.

4. Conclusions

ZnCuO films were grown at low temperature by the ALD method using organic zinc and copper precursors.

The highest Cu concentration achieved in the present work was about 25%. Most of the films studied show n-type conductivity. Formation of foreign phases and inclusions of Cu metal are detected for the films with and increased Cu concentration.

Acknowledgments

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