

Thin films of ZnO and ZnMnO by atomic layer epitaxy

ALEKSANDRA WÓJCIK¹, KRZYSZTOF KOPALKO¹, MAREK GODLEWSKI^{1, 2}, ELŻBIETA ŁUSAKOWSKA¹,
ELŻBIETA GUZIEWICZ¹, ROMAN MINIKAYEV¹, WOJCIECH PASZKOWICZ¹, KRZYSZTOF ŚWIĄTEK¹,
MARCIN KLEPKA¹, RAFAŁ JAKIEŁA¹, MICHAŁ KIECANA¹, MACIEJ SAWICKI¹, KRZYSZTOF DYBKO¹,
MATTHEW R. PHILLIPS³

¹Institute of Physics, Polish Academy of Sciences, al. Lotników 32/46, Warszawa, Poland

²Department of Mathematics and Natural Sciences College of Science,
Cardinal Stefan Wyszyński University, ul. Dewajtis 5, 01-815 Warszawa, Poland

³Microstructural Analysis Unit, UTS, Sydney, Australia

We discuss properties of thin films of ZnO and ZnMnO grown with atomic layer epitaxy using new, organic zinc and manganese precursors. Several characterization techniques, including X-ray diffraction, atomic force microscopy, scanning electron microscopy, cathodoluminescence, superconducting quantum interference device (SQUID) and electron spin resonance, show good topography of the films and their advantageous optical and magnetic properties.

Keywords: ZnO, magnetism, low temperature growth, organic precursors.

1. Growth method

Atomic layer epitaxy (ALE), often referred to as atomic layer deposition (ALD) [1, 2], is a deposition method in which growth precursors are alternatively introduced to a growth chamber. Pulses of precursors are separated by purging periods with a neutral gas, which was nitrogen in our system. Purging gas removes remaining vapors of the first precursor from a growth chamber. Only those which saturated surface of a growing film are left. Then vapors of a next precursor are introduced. In the consequence, precursors react only on a surface of a film, *i.e.*, very reactive precursors can be used [1, 2].

Formally, each sequence of exposures (precursor 1 – purging – precursor 2 – purging) should saturate the surface with a monomolecular layer. This should result in a unique self-limiting growth mechanism of thin films in the ALE method. Such situation is however very rarely realized. We needed several (up to 10) sequences to grow 1 monolayer of various II-VI compounds studied by us [3–6]. We managed

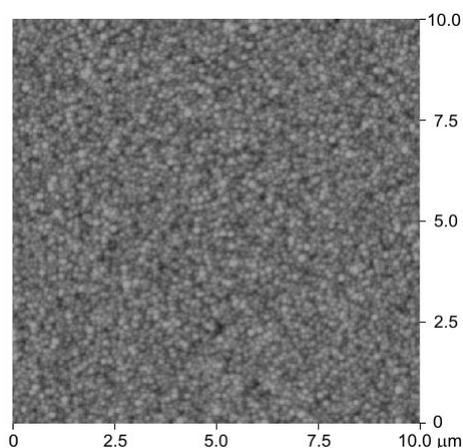


Fig. 1. AFM image of ZnO film grown using acetate on sapphire.

to obtain a monolayer cover only in the present study by using organic precursors of zinc.

In the present project we used organic zinc precursors: zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$) and deionized water (H_2O) as ZnO precursors. ZnO films were obtained due to a double exchange chemical reaction: $\text{Zn}(\text{CH}_3\text{COO})_2 + \text{H}_2\text{O} \rightarrow \text{ZnO} + 2\text{CH}_3\text{COOH}$ at a substrate temperature of 300–360°C and precursor temperature of 230–250°C. The growth rate was about 0.5 nm/cycle, *i.e.*, 1 monolayer per cycle was deposited.

Atomic force microscopy (AFM) investigations (see Fig. 1) indicate the reduced structural quality of the films grown with zinc acetate, as compared to the quality of those grown with ZnCl_2 . Properties of the latter films are discussed in [6]. Mean roughness (RMS) of the film studied in Fig. 1 was 6.5 nm, as compared to 0.92 nm for a film grown with ZnCl_2 . Films grown with zinc acetate show a well resolved granular microstructure, which was often not resolved for films grown with inorganic zinc precursors.

Despite rougher surfaces, films grown with zinc acetate have several advantageous properties. First of all, growth rate is significantly increased. We could grow films of several μm thicknesses, reaching saturation limit, *i.e.*, one monolayer of ZnO obtained after each growth sequence. Further advantageous properties of these films are discussed below.

XRD investigations show a puzzling property of ZnO films grown with zinc acetate. Whereas films grown on GaN/sapphire, *i.e.*, lattice matched substrate, have *c*-axis normal to a film surface, those grown with zinc acetate directly on sapphire show *c*-axis in plane of a film, as shown in Fig. 2. For such films (00.2) reflection in XRD is missing. This reflection was dominant for films grown with *c*-axis normal to a film surface. We further noticed that this growth mode can be changed back to a “normal” (*c*-axis normal to a surface of a film) by changing growth temperature and upon Mn doping.

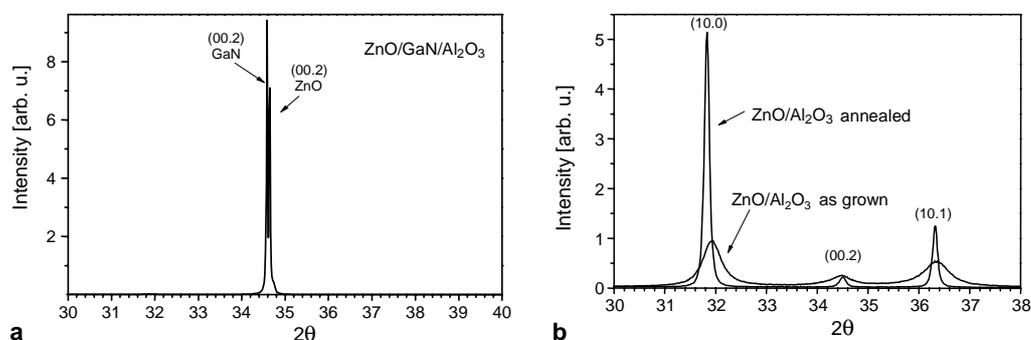


Fig. 2. XRD spectra taken for two types of ZnO films grown with zinc acetate. The first (a) was grown on sapphire covered with GaN, the second (b) directly on sapphire.

XRD investigations indicate also that structural quality of ZnO films is improved upon post-growth annealing in oxygen. Samples were annealed at a temperature of about 550°C. Annealing time was 48 hours. The resulting significant narrowing of XRD reflections is shown in Fig. 2b for a film grown directly on sapphire.

Such annealing improves also optical properties of the films. Edge luminescence of an excitonic origin was resolved, often not observed before post-growth annealing. In Fig. 3 we show cathodoluminescence (CL) emission of two types of ZnO films grown with zinc acetate. Strong edge emission is observed even at room temperature indicating good quality of our films. This emission is about 10 times more intensive in a film grown on a lattice matched substrate.

Edge emission is accompanied by a defect-related red emission. In most of our samples this emission is relatively enhanced, when excited from a region close to an interface region of the film, and becomes relatively (as compared to the intensity of the edge CL) less efficient when excited from the regions of a film with an improved structural quality. Such in-depth property of the red emission we studied with CL.

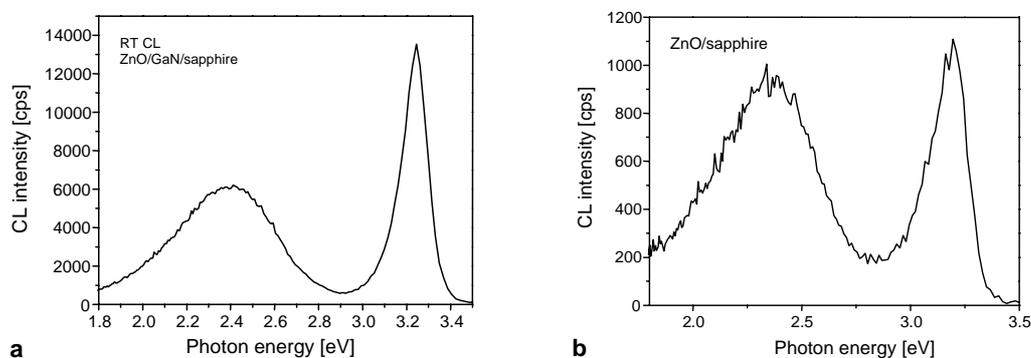


Fig. 3. Room temperature cathodoluminescence spectra of ZnO films grown on GaN/sapphire (a) and directly on sapphire (b). CL spectra were taken at optimized accelerating voltages and e -beam densities.

Another important property of ZnO films grown with zinc acetate is their relatively high resistivity. A common property of ZnO films grown with other techniques is their high *n*-type conductivity. This was also observed for our films with room temperature free electron concentration reaching 10^{19} cm^{-3} . In spite of this fact, resistivities of most of our films were of about 100Ω . Origin of this increased resistivity is not understood yet.

2. Mn doping

ZnMnO is an interesting spintronics material [7]. For spintronics application we need ZnMnO alloys with Mn fractions exceeding a doping limit. Using inorganic Mn precursors we failed however to grow such alloys. We thus tried to select appropriate growth conditions and Mn precursors to grow alloys of ZnMnO with Mn fractions above 1%. In the present study we used two types of organic Mn precursors. The first precursor was $\text{Mn}(\text{thd})_3$ (Mn tris (2,2,6,6-tetramethyl-3,5-heptadionate)). The second precursor was $\text{Mn}(\text{acac})_3$, (*i.e.*, Mn(III) acetylacetonate). Growth was performed at temperatures of 160°C for $\text{Mn}(\text{thd})_3$ and $160\text{--}180^\circ\text{C}$ for $\text{Mn}(\text{acac})_3$ and at low substrate temperature of $300\text{--}360^\circ\text{C}$. Films grown with zinc acetate had *c*-axis in a plane of the film, but those co-doped with Mn changed their growth mode, *i.e.*, *c*-axis was normal to the surface.

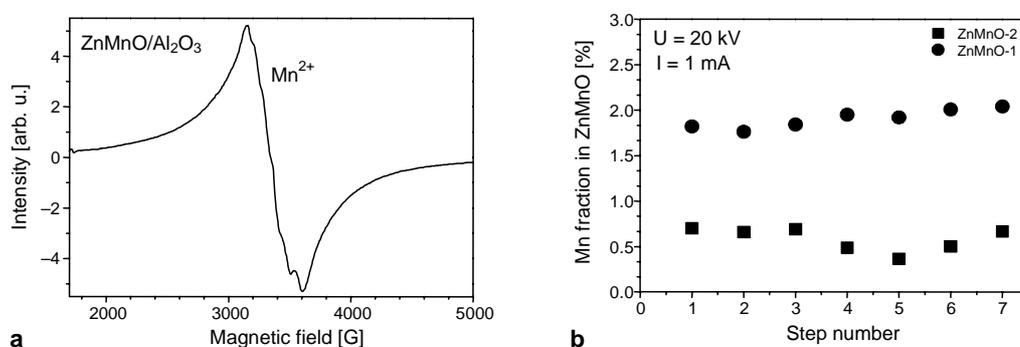


Fig. 4. Low temperature ESR spectrum (a) and EPMA (b) of ZnMnO films grown on sapphire. EPMA data were taken with a step of 0.5 mm, studying in-plane profile of Mn distribution.

The use of organic Mn precursors enabled a significant increase in Mn fraction in ZnMnO. Mn fractions reaching 10% were achieved. $\text{Mn}(\text{thd})_3$ precursor was more efficient than $\text{Mn}(\text{acac})_3$, as we concluded from X-rays studies and secondary ion mass spectroscopy (SIMS) analysis.

Mn introduction to the films was confirmed with electron spin resonance (ESR) (Fig. 4), SQUID, SIMS and electron probe microanalysis (EPMA). EPMA and SIMS investigations indicate relatively high in-plane and in-depth homogeneity of our samples. Magnetic properties of these films are under study at present.

3. Summary

We successfully employed ALE technique for growing relatively thick ZnO and ZnMnO films using organic zinc and manganese precursors. These films show good structural quality and advantageous optical and magnetic properties. Relatively flat film surfaces, intensive band edge emission, increased resistivity and lack of magnetic inclusions of Mn foreign phases are found.

Acknowledgments – This work was partly supported by grant no. PBZ-KBN-044/P03/2001 of Polish State Committee for Scientific Research (KBN). The ALE reactor was bought using SEZAM grant of the Foundation for Polish Science.

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Received June 6, 2005