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Cathodoluminescence Profiling for Checking Uniformity of ZnO and ZnCoO Thin Films

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We employ scanning electron microscopy and cathodoluminescence for evaluation of uniformity of ZnCoO films obtained by the atomic layer deposition. Cathodoluminescence quenching by Co ions allows us to detect (regions of weaker light emission) Co accumulations, with the resolution limited by diffusion length of secondary carriers.

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1. Introduction

ZnO is emerging material for electronic and photovoltaic applications. In turn, ZnCoO and ZnMnO are very intensively studied for spintronic applications, as possible ferromagnetic (FM) materials at room temperature [1–3]. After initial theoretical predictions many reports claimed FM properties of ZnMnO and ZnCoO (see [1, 2] and references given there). Present understanding is that the reported FM is not related to "volume properties" of ZnTMO (TM stands for transition metal ions, Mn or Co in our investigations), but due to inclusions of foreign phases or metal accumulations [1–3]. Such inclusions can be of nm sizes and thus difficult to be detected. For example could not be detected in our XRD investigations.

In the present work we demonstrate use of cathodoluminescence (CL), which is a non-destructive and high resolution method, to the studies of uniformity of ZnCoO. ZnCoO films obtained by atomic layer deposition (ALD) are investigated with a scanning electron microscope (SEM) (surface topography), energy dispersive X-rays spectroscopy (EDS) (elements distribution) and cathodoluminescence (CL). In the latter method we utilize the fact that TM ions, such as manganese and cobalt, quench visible light emission of ZnO [4, 5]. EDS resolution is about 1 μm, which is much larger than CL in-plane resolution of about 50–100 nm for a GaN [6] and also ZnO, which is determined by diffusion length of secondary electrons [6].

2. Measurement method

In our investigations we used two properties of the CL measurements — first is the possibility of the two-dimensional CL mapping, when detection is set at the selected wavelength. Such maps together with the SEM studies can give information not only about surface morphology, but also on the interlink between the sample structure and its light emission properties.

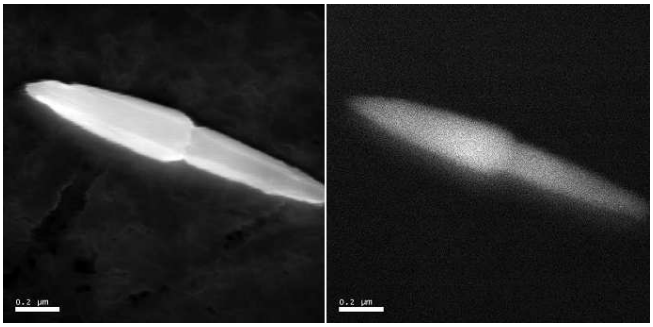

Fig. 1. Left — SEM image taken at 15 kV with secondary electron detector, right — CL map taken with detection set at about 580 nm.

Example of such studies is shown in Fig. 1 for ZnO-based nanorods. Structure seen in CL image corresponds to a microstructure of the sample, with emission coming mostly from volume of the rod and slightly deactivated at surface, due to the increased defect concentration there.

In Fig. 2 we demonstrate the basics of the CL depth-profiling investigations, used by us to study depth distribution of TM ions in the studied films. The data shown in Fig. 2 were calculated by us for a density of ZnO, based on a method described in [6]. The results shown in Fig. 2 indicate that by selecting accelerating voltage we can de-

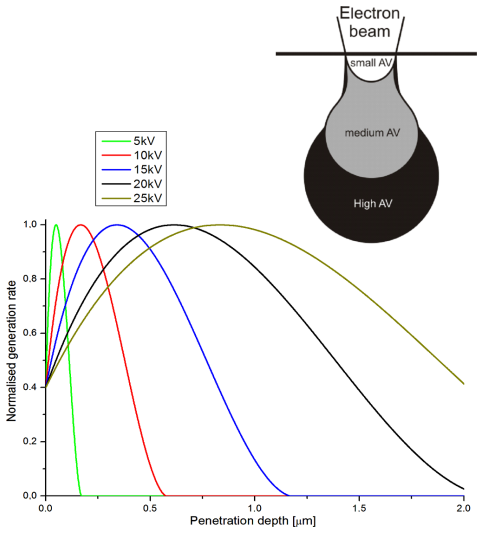

Fig. 2. Interaction area shape and dependence of the depth from which the CL signal comes on the accelerating voltage.

tect CL coming from given depth of the sample. In turn in-plane resolution is limited by diffusion length of secondary electrons [7] and weakly depends on accelerating voltage (see Fig. 2). Thus, the CL study can yield crucial information on the defects distribution.

Combining various CL experiments — profiling and two-dimensional mapping, we can obtain information on the sample uniformity in three dimensions. Additionally, using the fact that transition metals like Co and Mn very efficiently quench luminescence of ZnO, the method seems to be perfect for testing the homogeneity of the DMS samples based on ZnO [4].

Unfortunately, the method has its drawbacks — the test samples must be of a good quality (good emitters), and the level of impurities cannot exceed a few percent, otherwise CL emission is totally quenched [4, 5].

3. Results and discussion

We studied two types of samples grown with the ALD method. First, ZnCoO samples characterized by a relatively high crystal quality and low Co content (less than 1%). Second, the reference ZnO samples with similar characteristics and quality. CL maps at the large and small magnifications and for different accelerating voltages (AVs) were measured, with the CL detection set at 380 nm, i.e., at the band edge emission. CL maps (and also SEM images) taken at low magnifications, not shown here, show high homogeneity of the samples. We concentrate here on the results obtained at the increase magnification of 50 000×, which allows us to search for sample nonuniformities.

The data shown in Fig. 3 indicate a direct link between microstructure of the sample and light emission intensity. Emission is weak or even quenched at grain boundaries,

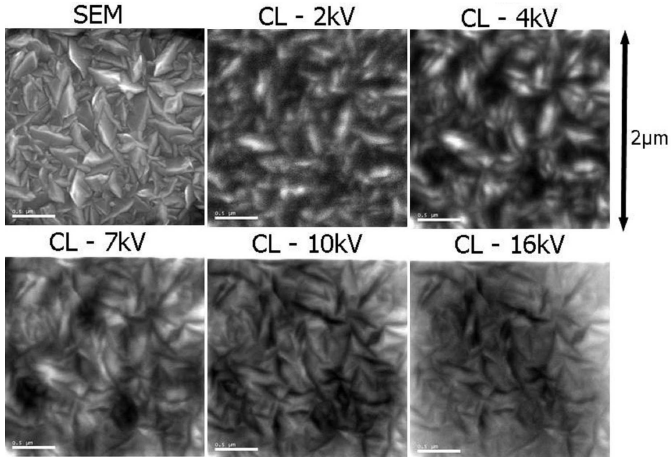

Fig. 3. SEM image taken at 15 kV with secondary electron detector and CL maps taken for different AVs for the reference ZnO film.

where large defect concentration is expected. CL is also weaker at the interface region, which reflects an increased defect concentration there. Moreover, strong defect related CL starts to dominate CL detected from the interface region. We obtained similar results for highly uniform ZnCoO film.

The next step was annealing of samples at 800 °C for 2 h in nitrogen. After annealing at 800 °C the intensity of luminescence strongly increased. This reflects an improved crystallinity (samples studied were polycrystalline) of the annealed ZnO and ZnCoO films.

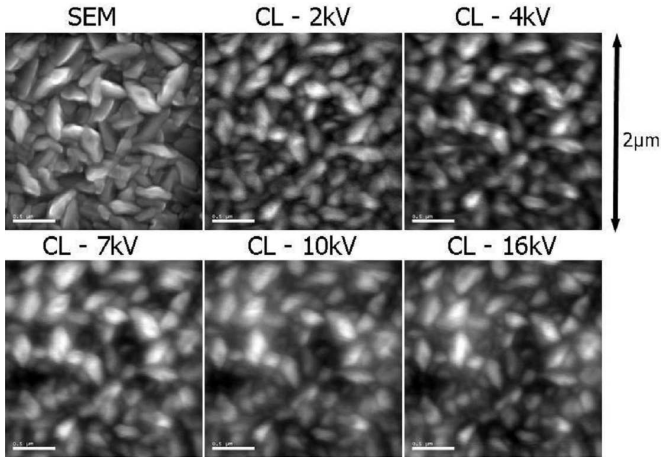

Fig. 4. SEM image taken at 15 kV width secondary electron detector and CL maps for different AVs for ZnO film after annealing at 800 °C.

Figure 4 once more shows the direct link between microstructure of the sample and its light emission. Bright emission comes from the grains (columns) and is weak from the grain boundaries.

We observe a very different situation for the annealed ZnCoO sample (see Fig. 5). We observe the appearance

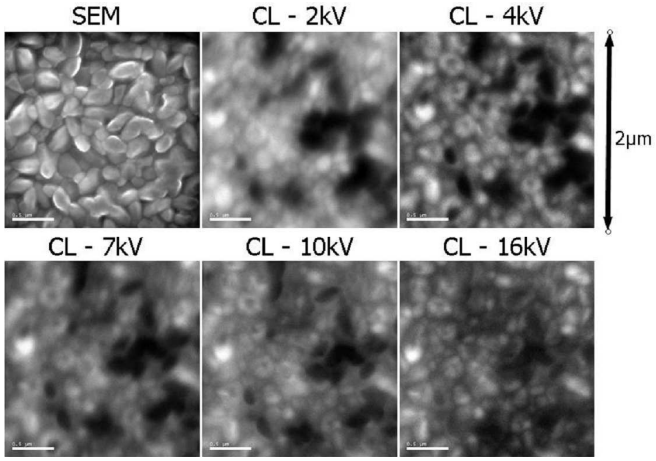

Fig. 5. SEM image taken at 10 kV with secondary electron detector and CL maps for different AVs for ZnCoO film after annealing at 800 °C.

of dark spots, observed from the same area at different AVs. CL is quenched not only at the grains boundaries, but also at some grains, which we relate to a spinodal decomposition of the sample and the appearance of Co-rich regions [1, 2]. Depth-profiling indicates that such nonuniformities have 3D character, resulting in the formation of Co-rich columns.

The spatial resolution of the CL is limited by diffusion length of secondary electrons, which we estimate to be fairly small in our ZnCoO samples, smaller than the radius of columns, as also found for GaN and InGaN samples [7]. We can only estimate the maximum size of Co-rich regions, which are less than 100 nm. Such resolution is comparable to the one obtained from the TEM investigations and better by about one order in magnitude than the XPS resolution.

4. Summary

The method based on CL mapping and profiling allows us to estimate uniformity of ZnCoO films based on the fact that emission from TM rich regions is deactivated. We demonstrate that CL profiling can give information on dopants/defects distribution in ZnO and ZnCoO with a higher resolution than the EDS measurements. Moreover, three-dimensional maps can be obtained.

Acknowledgments

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