Characterization of MgZnO epitaxial layers with high Mg concentration

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# Table of Contents

INTRODUCTION ....................................................................................................................................................... 3

1. PROPERTIES OF MGZNO................................................................................................................................... 4
   1.1 STRUCTURAL PROPERTIES OF \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) ................................................................................................................. 4
   1.2 OPTICAL PROPERTIES OF \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \)........................................................................................................................................ 7

2. SAMPLES AND EXPERIMENTAL TECHNIQUES ........................................................................................ 10
   2.1 SAMPLES ................................................................................................................................................................ . 10
   2.2 ATOMIC FORCE MICROSCOPY (AFM) ...................................................................................................................... 11
   2.3 TIME RESOLVED PL MEASUREMENT TECHNIQUE .......................................................................................... 12
   2.4 LIGHT MEASUREMENT SYSTEM .......................................................................................................................... 14
   2.5 SCANNING NEAR FIELD OPTICAL MICROSCOPE (SNOM) .............................................................................. 15

3. RESULTS AND DISCUSSION ............................................................................................................................ 17
   3.1 SURFACE TOPOGRAPHY MEASUREMENTS .............................................................................................................. 17
   3.2 PHOTOLUMINESCENCE MEASUREMENTS UNDER TEMPERATURE ........................................................................ 20
   3.3 TIME-RESOLVED PHOTOLUMINESCENCE MEASUREMENTS ....................................................................................... 23
   3.4 SNOM MEASUREMENTS........................................................................................................................................... 25

4. SUMMARY AND CONCLUSIONS .................................................................................................................... 29

5. SUGGESTIONS FOR FUTURE WORK ............................................................................................................ 29

6. REFERENCES ...................................................................................................................................................... 30
Abstract

In this work, a series of Mg$_{x}$Zn$_{1-x}$O epitaxial layers with different Mg mole fraction ($x = 0.025; 0.166; 0.303; 0.318$) grown by MBE has been investigated. Time-resolved photoluminescence (TRPL) measurements and scanning near field optical microscopy (SNOM) technique have been implemented in order to obtain PL spectra and decays as well as spatial distribution of the PL intensity and peak wavelength. Atomic force microscopy technique has been chosen to evaluate structural properties. Images of epitaxial layer surface profile, obtained by AFM technique, have revealed distinct characteristics for all samples and a strong surface roughness dependence on Mg concentration. Analysis of the PL spectra has shown nonmonotonous PL peak wavelength dependence on temperature for three MgZnO samples with the highest Mg mole fraction. Arrhenius plots for the PL intensity dependence on temperature have been drawn and parameters have been evaluated. Samples with higher Mg mole fraction show higher value of activation energy. Time-resolved PL decays have revealed a biexponential shape for all four samples at low temperatures. Three samples with the highest Mg mole fraction show an increase of the PL decay time at low temperature. The PL intensity mappings, obtained by SNOM technique, have revealed considerable spatial variation of this parameter. Variation of the PL peak wavelength has been observed only for three samples with the highest Mg mole fraction.
Introduction

Compound semiconductors are commonly used for constructing optoelectronic devices. These materials are composed of elements from two or more different groups of the periodic table and are classified according to the periodic table groups of their constituent atoms (IV, III-V, II-VI, etc). Modern light emitting diodes (LEDs), emitting from ultraviolet (UV) to green light, are often made from III-N semiconductors such as InN, GaN, AlN and alloys of these. However, the production of these materials is difficult and expensive. Furthermore, indium and gallium are very rare metals and the demand of these is growing rapidly. This stimulates the research for alternative solutions, and II-VI group semiconductors such as ZnO, MgZnO and CdZnO, which show a great potential in replacing the nitrides.

For the meantime, the growth of MgZnO layers is difficult because of low thermodynamic solubility of MgO in ZnO. However, recent works show a high improvement in growing techniques for MgZnO layers and it makes possible to accurately investigate luminescence properties of this material. Finally, according to the recent research, MgZnO shows high potential to become extensively used material for production of optoelectronic devices where wide band gap semiconductor is required.

In this thesis, the results of the investigation of the structural and optical properties of ternary MgZnO layers grown by MBE are presented.
1. Properties of MgZnO

1.1 Structural properties of Mg\textsubscript{x}Zn\textsubscript{1-x}O

Zinc oxide is a well-known and widely used material. Research of its semiconducting properties was started in 1930 [1], but interest in this material dropped soon because of difficulties to make p-type ZnO layers. Undoped ZnO has electron-conducting properties because of naturally occurring oxygen vacancies. The zinc atom adjacent to the vacancy has a free bond and acts like a donor. Interest in ZnO has recently risen again because of the improvement in growth techniques. Those improvements have made the production of UV-emitting MgZnO layers possible.

Since the ionic radius of Mg\textsuperscript{2+} (0.57 Å) is close to that of Zn\textsuperscript{2+} (0.6 Å), the replacement of Zn by Mg should not cause a significant change of the lattice constant. However, a large crystal structure difference between the wurtzite-hexagonal ZnO (\(a = 3.25\) Å and \(c = 5.21\) Å) and the rock-salt-cubic MgO (\(a = 4.21\) Å) can cause unstable phase mixing [2]. Depending on growth conditions, MgZnO may have a cubic or a hexagonal lattice (Fig. 1.1).

![Figure 1.1](image.png)

Figure 1.1 The structural models of the hexagonal (a) and cubic (b) MgZnO alloys [2].

It is important to know which growth conditions lead to a specific lattice of MgZnO layer. Despite the similarity between the Zn\textsuperscript{2+} and Mg\textsuperscript{2+} ionic radii, the thermodynamic solubility limit of MgO in ZnO is less than 4 mol%. It is possible to produce Mg\textsubscript{x}Zn\textsubscript{1-x}O with a higher Mg percentage by using a non-equilibrium thermodynamic growth condition, however, a phase separation of the lattice can occur under the following condition [3]. In this case, Mg\textsubscript{x}Zn\textsubscript{1-x}O structure is made from cubic and hexagonal microcrystals simultaneously. It was possible to produce single-phase
hexagonal structure layers with up to $x = 0.5$ Mg mole fraction by using different growth techniques and conditions [3-7]. Cubic structure layers could be produced with $x > 0.6$ Mg mole fraction [8, 9] but the production of thin $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ layer with $x = 0.33$ by using MOCVD technique was reported as well [10]. However, hexagonal structure layers with cubic lattice and low Mg mole fraction are in a metastable state, and the lattice phase separation or the phase transition could occur when temperature reaches the turning point value [2,5]. The stability of material depends on the difference between the total energies of cubic and hexagonal lattice structures. Figure 1.2 shows theoretical values of the total energies of the hexagonal and cubic $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys at temperature $T = 0$ K with different values of $x$ varying from 0 to 1 [2]. The hexagonal structure is more stable than the cubic for $0 \leq x \leq 0.69$ Mg mole fraction and vice versa, because the hexagonal structure has a lower total energy than the cubic structure at $x \leq 0.69$. The stability of the structure also depends on temperature because the total energy of different lattice structures changes at different rates with the changing temperature.

![Figure 1.2](image)

Figure 1.2 The total energies of the hexagonal (square) and cubic (circular) $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys [2].

Since $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ has the most unstable structure with $x$ values around 0.5, usually it grows with a mixed phase lattice structure at these $x$ values. Figure 1.3 shows composition tuned $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ band gap and the corresponding phases. The shaded area is the phase separated region that has no well defined band gap [8]. The same paper [8] concludes that phase segregation occurs in the interval of $0.37 \leq x \leq 0.6$. A layer with the hexagonal lattice structure grows at lower $x$ values and with the cubic lattice – at higher $x$ values. It should be noted that other papers suggest slightly different $x$ values of the mixed phase [4, 6, 11]. This can be explained by the observation that the layer structure strongly depends on growth techniques and conditions.
It is difficult to grow good structural quality Mg\textsubscript{\textit{x}}Zn\textsubscript{1-\textit{x}}O layer on ZnO buffer even with low \textit{x} value because thermodynamic solubility of MgO in ZnO is very low. In the molecular beam epitaxy (MBE), the layer initially grows uniformly, however, when it becomes thicker, the phase segregation tends to occur. Because of the phase segregation, areas with higher and lower MgO concentrations form. The surface of such layer tends to be very rough because it is composed of relatively high nanorods (figure 1.4). In Ref. 12 is is shown that a higher smoothness can be reached by lowering the thickness of the layer. Figure 1.4 shows that 38 nm thick layer has a high surface smoothness compared with the thicker layers. Thus, by lowering the thickness of the layer, it is possible to obtain a strained, single-phase and smooth layer. Such layers can be used for multiple quantum well structure production.
1.2 Optical properties of Mg\textsubscript{x}Zn\textsubscript{1-x}O

ZnO and MgO have bandgap energies of 3.3 eV [1] and 7.8 eV, respectively [13]. ZnO is a wide bandgap semiconductor and MgO is more a like a dielectric material than a semiconductor. A semiconductor alloy with a bandgap ranging from 3.3 eV to 7.8 eV can be achieved by mixing ZnO and MgO into the ternary Mg\textsubscript{x}Zn\textsubscript{1-x}O compound (Fig. 1.3). However, a big mismatch between the MgO and ZnO lattice constants creates difficulties to produce a good quality layer without the lattice segregation. The bandgap of such a material depends not only on the Mg mole fraction \(x\), but also on a type of the lattice. Mg\textsubscript{x}Zn\textsubscript{1-x}O with hexagonal lattice has a smaller bandgap than the one with cubic lattice. For example, hexagonal Mg\textsubscript{0.33}Zn\textsubscript{0.67}O has a bandgap \(E_g = 3.99\) eV [4], whereas that with the cubic lattice – \(E_g = 4.96\) eV [10]. Therefore, in order to grow a layer with the particular bandgap, it is very important to grow a layer with a proper value of Mg mole fraction \(x\) and the right type of lattice type without any lattice segregation.

ZnO is a specific semiconducting material because it has very a large exciton binding energy of about 60 meV. Most of semiconductors have smaller exciton binding energies compared to the room temperature thermal energy (~25 meV), eg. GaN, commonly used for in production of LEDs and laser diodes, has only the exciton binding energy of ~23 meV. It has been observed that exciton binding energy in Mg\textsubscript{x}Zn\textsubscript{1-x}O has approximately the same value like in ZnO [16, 17]. Absorption spectra for Mg\textsubscript{x}Zn\textsubscript{1-x}O at room temperature are shown in figure 1.5. Clearly expressed peak reveals that the excitonic nature of the optical transitions is preserved despite the alloy broadening. In the case of the binary compound ZnO, the \(A\) and \(B\) excitons are clearly visible [18].

![Figure 1.5 Absorption spectra for Mg\textsubscript{x}Zn\textsubscript{1-x}O thin films at room temperature [16].](image-url)
The evolution of photoluminescence (PL) peak wavelength on temperature for pure ZnO and Mg$_x$Zn$_{1-x}$O with a low Mg content normally follows the bandgap temperature dependence described by the Varshni formalism:

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{(\beta + T)}.$$  

Because $\alpha$ and $\beta$ constants have only positive values, the bandgap decreases with the rising temperature. Such dependence results in a continuous red shift in the PL peak wavelength position. However, it has been observed that with increasing Mg mole fraction the PL peak wavelength tends to have S-shaped temperature dependence. Temperature-dependent PL spectra of Mg$_x$Zn$_{1-x}$O with Mg mole fraction $x = 0.55$ show a clear S-shaped dependence of the PL peak (Fig. 1.6) [19]. Such dependence cannot be explained only by the Varshni formula.

Similar PL peak behavior has been observed in the well-known In$_x$Ga$_{1-x}$N material [20]. It has been stated that indium in the layer is distributed non-uniformly and forms high and low concentration areas. Because In-rich InGaN areas have a lower bandgap, these areas act like localization centers. Therefore, excited carriers tend to move to areas of higher indium concentration and localize there. This carrier localization model is used to describe the S-shaped PL peak dependence in InGaN [20].

Figure 1.6 Temperature-dependent PL spectra of Mg$_{0.55}$Zn$_{0.45}$O sample [19].
Because of similarities between PL temperature dependence of MgZnO and InGaN, it is considered that Mg tends to distribute non-uniformly and forms localization centers with lower Mg concentrations. The S-shaped temperature dependence of the PL peak can be explained by localization model using figure 1.7 [21]. According to the authors of this scheme, carriers can move into the localized state only by overcoming $\Delta E_1$ barrier and escape by overcoming $\Delta E_2$ barrier. At low temperature, the major part of the carriers does not have enough energy to overcome $\Delta E_1$ and especially $\Delta E_2$ barrier. With increasing temperature, the carriers have more energy and start to localize by overcoming the energetic barrier $\Delta E_1$. Therefore, the initial decrease of the PL peak energy is due to the localization process through $\Delta E_1$. Further temperature increase enhances population of the localized states, and the PL peak energy slightly increases. It continues to increase until the decrease of the bandgap, described by the Varshni’s law, overcomes the effect of population of the localized states. At even higher temperatures, the decrease of the PL peak energy is governed solely by bandgap temperature dependence.

Figure 1.7 A schematic illustration showing the processes of carrier injection into and escape out of the localized centers [21].
2. Samples and experimental techniques

2.1 Samples

In this work, a series of Mg$_x$Zn$_{1-x}$O epitaxial layers with different Mg mole fraction have been investigated. These layers have been grown on a sapphire substrate by MBE (their structure is depicted in figure 2.1). Three samples have the same layer structure and consist of a MgO buffer layer, a ZnO middle layer and a Mg$_x$Zn$_{1-x}$O upper layer. The last sample has a different buffer layer composed of undoped GaN.

![Figure 2.1 Structures of Mg$_x$Zn$_{1-x}$O samples.](image)

All samples have been grown with different Mg$_x$Zn$_{1-x}$O layer thickness and Mg mole fraction by changing the temperature of the Mg source. Growth of the upper layer in samples A, B and C has taken 2 hours. The Mg mole fraction has been measured by energy dispersive X-ray spectroscopy technique. The parameters of each sample are listed in Table 2.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature of Mg source (°C)</th>
<th>Thickness of Mg$<em>x$Zn$</em>{1-x}$O layer (nm)</th>
<th>Mg mole fraction $x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>310</td>
<td>~100</td>
<td>0.025</td>
</tr>
<tr>
<td>B</td>
<td>345</td>
<td>~110</td>
<td>0.303</td>
</tr>
<tr>
<td>C</td>
<td>370</td>
<td>~130</td>
<td>0.166</td>
</tr>
<tr>
<td>D</td>
<td>-</td>
<td>~320</td>
<td>0.318</td>
</tr>
</tbody>
</table>
2.2 Atomic force microscopy

AFM is a high resolution scanning probe microscopy technique. It is used for very accurate surface topography measurements. AFM can achieve resolution on the order of fractions of a nanometer, but it requires extraordinary conditions such as ultra high vacuum, liquid helium temperature and excellent suppression of the environment noise. Principal scheme of an atomic force microscope is depicted in figure 2.2. It consists of a piezoelectric scanner, a cantilever with a very sharp tip, a measurement system of the cantilever deflection and a feedback loop system.

The tip must be very sharp because the resolution of the AFM predominantly depends on its size. Usually the tip has a radius with a curvature on the order of nanometers. The principle of AFM operation can be explained using figure 2.2. Firstly, the cantilever is being brought very close (on the order of nanometers) to the surface of the sample and then atomic forces (van der Waals or Coulomb force) between the tip and the sample start to deflect the cantilever. This deflection of cantilever is being used for registration of the distance between the tip and the surface of the sample. Usually this distance is kept at a constant value by using a feedback loop mechanism. Thus, a topography image is obtained by scanning the surface of the sample and measuring the deflection of the cantilever. There are two main operation modes in AFM: contact mode and dynamic mode [22]. In the contact mode, the tip is steady and the topography is obtained by measuring the static deflection of the cantilever. In the dynamic mode, the cantilever is externally oscillated at its

![Figure 2.2 Principal scheme of an AFM [22].](image-url)
resonance frequency. The oscillation parameters depend on the tip-sample interaction forces. Therefore, the change in the oscillation of the tip provides information about its position with respect to the sample surface.

Usually the deflection of the cantilever is very small, on the order of fraction of a nanometer. Thus, the registration of such deflection values requires a very sensitive measurement system. One of the most sensitive and reliable methods is an optical level detection illustrated in figure 2.2. A laser beam, which is deflected from the backside of the cantilever, is directed to a 4-segment positional photodetector, which is divided into segments for measurements of normal and lateral deflections of the cantilever [22].

The resolution of the AFM can be separated into two distinct parts: lateral and vertical resolutions. The lateral resolution depends on many factors, but the most important one is the size of the tip. Hence the lateral resolution can be improved by using a sharper tip. However, it is difficult to produce high quality tips with a very small curvature radius. Besides, interaction of sharper tips with a surface is weaker, and it becomes increasingly complicated to accurately detect such a weak interaction. Usually the lateral resolution of the AFM is considered not to exceed the size of the tip. The vertical resolution is determined mostly by the accuracy of the registration of the cantilever deflection. Because interaction force between the tip and the surface is usually very weak, these deflections are small and hard to measure. It is possible to choose a cantilever with lower stiffness, but this raises probability for the probe to crash into the surface. However, despite all the difficulties, vertical resolution as high as 0.1 nm has been demonstrated [23].

2.3 Time resolved PL measurement technique

Experimental set-up used in this work (depicted in figure 2.3) consists of a laser system, a closed loop helium cryostat, a second and third harmonics generator and a light measurement system. The laser system generates femtosecond pulses allowing to obtain high temporal resolution. It is composed of a solid state pump laser and a titanium doped sapphire (Ti:Al₂O₃) pulsed laser. The solid state laser is a Nd:YAG laser, the output wavelength of which is up-converted in a high efficient frequency doubling unit. It emits a single frequency continuous wave (CW) beam at 532 (green visible light) at a power of 10 W. The CW beam excites a Ti doped sapphire crystal situated inside a resonant cavity. The crystal absorbs the green light and emits coherent infrared light (tunable between 700 and 980 nm) via stimulated emission, giving rise to the lasing process inside the cavity. The key feature of the Ti:sapphire crystal is its high nonlinear refractive index, responsible for the Kerr lens effect inside the active medium [24]. The interplay between this focusing effect and the losses in the cavity produces strong intensity maxima with reduced
transverse size. They are eventually enhanced and built up to pulses, overcoming the continuous wave (CW) regime. In this experiment, the pulse length was equal to 130 fs (FWHM), the repetition frequency was 76 MHz and the maximum emission power of the Ti:sapphire laser was 1.3 W.

A third harmonic was produced in two steps. Firstly, a second harmonic was produced and then the output from the SHG was separated into the first and the second harmonic by dichroic mirror. Finally, those two laser beams were aligned precisely in the nonlinear crystal by adjusting the mirrors and the delay stage. Laser wavelength was tuned to about 810 nm, thus producing a third harmonic at 270 nm, which in turn was used to optically excite the sample structures. The power of excitation beam was about 7 mW and was focused into 30 µm size area on the sample, thus providing average excitation power density of 1 kW/cm².

Measurements of time-resolved PL spectra spectrally-integrated PL transients were accomplished simultaneously by using a combination of a spectrograph and a streak camera.

Figure 2.3 Schematics of the time-resolved PL measurement set-up.
2.4 Light measurement system

The light measurement section includes the spectrometer and an ultrafast streak camera. The luminescence emitted by the sample is collected by a lens, which focuses the light into the entrance slit of the spectrograph. The spectrograph has a diffraction grating, which disperses different spectral constituents of the incoming radiation in the horizontal plane. The dispersed light enters the streak camera tube through an entrance slit.

The streak camera – spectrometer system delivers intensity versus time versus wavelength information. The synchroscan mode is used in this experiment to detect very weak signals by means of integrating large number of pulses. The accumulation of many pulses requires their correct temporal alignment: this is done by means of the synchroscan trigger. The trigger unit detects a portion of the laser beam from the mode-locked laser (see figure 2.3) and generates the synchroscan signal at the same frequency as the laser repetition rate.

![Figure 2.4 Principal scheme of the streak camera.](image)

Figure 2.4 depicts the streak camera tube operation. The luminescence emitted from the sample passes through a spectrograph and enters the instrument. The amount of light entering the instrument is controlled by a horizontal slit. Lenses focus the incident light onto a photocathode which converts the photons into electrons and accelerates the photoelectrons through a chamber. Two sweep electrodes activated by the trigger unit span the electron path in the chamber. The electrodes create a linear voltage across the traversing electrons so that electrons arriving at different times end up at different vertical positions on the image plane. Hence, a conversion from time to space is obtained. The photoelectrons hit the micro channel plate (MCP), which converts them into an electric signal. The signal is read by a single processor.
2.5 Scanning near field optical microscope (SNOM)

The angular representation of the electric field in a plane \( z = z_0 \) near an arbitrary object can be written as:

\[
E(x, y, z_0) = \iiint A(k_x, k_y) \exp \left( ik_x x + ik_y y + iz_0 \sqrt{\left( k_0^2 - k_x^2 - k_y^2 \right)} \right) dk_x dk_y.
\]  

where \( A(k_x, k_y) \) represents the complex amplitude of the field, and \( k_0 = \frac{\omega}{c} \) is the vacuum wave vector [22]. Equation (1) is basically the sum of plane waves and evanescent waves propagating in different spatial directions. Typically, a lens of a microscope collects wave vectors that are confined to \([0..k_{\text{max}} = n \omega \sin \theta / c]\), where \( \theta \) is the semi-aperture angle of the lens and \( n \) is the refractive index.

According to Rayleigh’s criterion, the minimum resolvable distance between two points is defined by this equation [25]:

\[
d = 0.61 \frac{\lambda}{NA},
\]

where \( NA = nsin\theta \) represents a numerical aperture. According to equation (2), the minimum resolvable distance \( d \) can be decreased by using shorter illumination wavelengths, or by increasing the index of refraction or by increasing the collection angle \( \theta \).

However, the collection of evanescent waves with high spatial frequencies \((k_x, k_y > k_0)\) allows to overcome the resolution limit defined by Rayleigh’s criterion. Evanescent waves can be converted to propagating radiation by local scattering. The smaller the scatterer is and the closer it is placed near the surface of an object, the better the conversion will be. The collection of evanescent waves is achieved in a scanning near field optical microscope.

SNOM technique belongs to the family of scanning probe microscopies along with AFM. A principal scheme of SNOM is depicted in figure 2.5. Basically, a SNOM consists of a near-field
probe confining an optical interaction to dimensions smaller than the wavelength, a scanning stage permitting to move the sample or the tip laterally, a laser providing an excitation beam to the sample (not shown), a light detecting system to collect the response of the optical probe-sample interactions, acquisition software to reconstruct an optical image, and a feedback mechanism, which controls the distance between the tip and the sample.

The lateral resolution is determined mostly by the size of the optical probe. The fabrication of optical probes with sub-wavelength dimensions is technically challenging. There are several techniques how to produce SNOM probes. We used uncoated sharp fiber tips produced by etching the non-solarizing pure silica core fiber with a 50% concentration hydrofluoric acid (figure 2.6). This technique was chosen because of its simplicity and low cost. A fiber was submerged into a hydrofluoric acid and was kept for 3.5 hours. For the protection of the fiber’s top part, the surface of the acid was covered with iso-octane. Mean diameter of produced tips was about 100 nm.

![Figure 2.6 Production of SNOM tip scheme.](image-url)
3. Results and discussion

3.1 Surface topography measurements

Surface topography measurements can provide important information about the growth processes, structure of the layer, its quality, etc. Surface topography of \( \text{Mg}_{x}\text{Zn}_{1-x}\text{O} \) samples was measured by the AFM technique. AFM images of each sample are shown in figure 3.1. These images have 10x10 \( \mu \text{m} \) dimensions and consist of 25x25 nm pixels each.
Figure 3.1 Mg$_{x}$Zn$_{1-x}$O layer’s AFM topographies and cross-sections from marked areas.

Surface topographies show distinctive characteristics in all four samples. High smoothness of sample A shows that the low Mg mole fraction does not have a big effect on the lattice structure of the layer and the layer retains the hexagonal ZnO lattice structure. AFM image of sample B indicates totally different characteristics. Surface of this layer consists of relatively high columns, which can reach 120 nm in height and 400nm in diameter of the base. Such structure of Mg$_{x}$Zn$_{1-x}$O layers has also been observed in other works [12]. Such nanorods form when the layer is growing in the Stranski-Krastanov mode. Usually, layers grow in this mode when the growing layer has a different lattice constant or structure compared to the substrate. Clustering occurs and growth of nanorods starts when the surface, growing in this mode, reaches the critical thickness. Parameters of Stranski-Krastanov growth strongly depend on the chemical and physical properties, such as surface energies and lattice parameters, of the substrate and the film. It is likely that Mg$_{x}$Zn$_{1-x}$O layer of sample B has grown in the Stranski-Krastanov mode.
Surface topography of sample C shows structure similar to sample B. However, this surface is more granular with smaller height variations. The higher concentration of the nanorods shows increase of the number of clustering centers. It is possible that such an increase is determined by the higher Mg source temperature during the growth, which increases the mobility of Mg atoms on the surface of the layer.

The surface of sample D is very smooth (a deep scratch on the right side of the scan is mechanical) and comparable to that of sample A. Although this sample has the highest Mg mole fraction of all samples, it does not exhibit nanorod structure seen in sample B. The shape of vertical profile for sample D is similar to the shape for sample C but the magnitude of bumps is few times smaller. The smoothness of the surface can be determined by different sample structure and growth conditions.

A statistical evaluation of AFM images was performed, and the calculated roughness dependence on the Mg molar fraction is shown in figure 3.2. Arithmetic average of absolute values (SA) was chosen for the roughness parameter:

$$SA = \frac{1}{LH} \int_{0}^{H} \int_{0}^{L} |h(y, x)| dx dy,$$

where $L$ and $H$ are the length and the width of the surface image, and $h(y, x)$ – the height at the point with coordinates $x$ and $y$. Figure 3.2 shows that roughness of the first three samples grows linearly with increasing Mg mole fraction. However, sample D, which has the highest Mg concentration, shows a low roughness comparable with sample’s A roughness.

![Figure 3.2 Surface roughness dependence on Mg mole fraction.](image)
3.2 Photoluminescence measurements at different temperatures

For characterization of optical properties, photoluminescence measurements were carried out under various temperatures. The samples were excited by the third harmonic of the Ti:sapphire laser and two-dimensional images (spectrally- and time-resolved) were obtained by the streak camera (experimental setup described in chapter 2.4).

Figure 3.3 PL spectra dependence on temperature. Dots are experimental data and solid lines – FFT smoothing.

In figure 3.3 some PL spectra of all four samples are depicted. All samples have distinctive spectra. Low temperature spectra of sample A exhibit similar excitonic nature like pure ZnO. It is likely that short-wavelength peak represents radiative recombination of free excitons and long-wavelength peak – radiative recombination of bound-exciton complexes [1]. Long-wavelength peak decreases with increasing temperature and practically disappears at 80 K. The bandgap shrinkage, described by Varshni’s law, causes the shift of the PL spectrum peak to a longer wavelength.
The long-wavelength spectral peak caused by bound exciton complexes is not visible in the PL spectra of other three samples. The PL spectra of samples B, C and D have relatively broad shape even at low temperature. Such broadness can be caused by inhomogeneities of the structure, which causes bandgap fluctuations.

Dependence of the PL peak wavelength on temperature is depicted in figure 3.4. Wavelength of the PL peak for sample A increases monotonously with increasing temperature. The PL peak from 5 K to 280 K shifts ~55 meV and it is close to the peak shift value (~62 meV) for pure ZnO [17, 19]. It is likely that this PL peak shift is caused mainly by the bandgap shrinkage. However, other samples show different tendencies of the PL spectrum peak shift. Peak wavelength in sample B decreases in the temperature interval from 30 K to 100 K. Peak wavelength in sample C decreases slightly at temperatures from 40 K to 100 K and at 160K. Peak wavelength in sample D sharply decreases at 160 K and 260K. The S-shaped peak wavelength dependence in sample B can be explained by the localization model. However, peak wavelength dependence in sample D has two sharp decreases and it requires more complex explanation.

Figure 3.4 PL spectra spectrum peak position dependence on temperature.
In order to compare yield of PL emission, the spectrally-integrated PL intensity was analyzed in the temperature range from 5 K to 300 K and Arrhenius plots of the integrated PL intensities was depicted in figure 3.5. Arrhenius plot of sample A shows quite strong decrease of the PL intensity at high temperatures. The PL intensity of the other three samples practically remains the same with increasing temperature until the critical point. It shows good suppression of non-radiative recombination processes at low temperature in samples with the high Mg mole fraction. The PL intensity for samples B and D even rises a little bit before the strong decrease in PL intensity starts. The optimal localization of excitons, which suppresses non-radiative recombination, can cause such increase in the PL intensity [19, 20].

In order to evaluate activation energy in the thermal quenching process, a fitting on the curves’ linear parts (plotted on a semi-log scale) was performed. It should be noted that Arrhenius plot for sample B does not show linear dependence even at the highest temperatures. It can be explained by assuming that sample B has more than one thermal quenching process with different activation energies. Therefore, in order to evaluate activation energies at temperatures at which the PL intensity starts to decrease and at the room temperature, two tangent lines at a given points were drawn.

![Figure 3.5 Arrhenius plots of integrated PL intensities. Inset shows magnified image of dependence at high temperatures.](image-url)
Values of the activation energies in the thermal quenching process and other parameters for Arrhenius plots are listed in table 3.1. As mentioned above, two activation energies for sample B were evaluated. Samples with higher Mg concentration show considerably higher activation energies.

It should be noted that the ratio of PL intensity at 5 K and room temperature is different for all the samples. The PL intensity ratio $I_{5K}/I_{300K} = 27$ for sample D is the lowest for all four samples. It seems that, despite the good suppression of the non-radiative recombination at low temperatures, the PL intensity for sample C decreases the most. The PL intensity for sample D decreased $e$ times at the highest temperature, which, along with the structural data, confirms the high quality of this sample.

Table 3.1 PL intensity ratios $I_{5K}/I_{300K}$, activation energies in the thermal quenching process and temperatures at which the PL intensity decreases $e$ times

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_{5K}/I_{300K}$</th>
<th>Activation energy</th>
<th>$T(I = I_{5K}/e)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>63</td>
<td>22 meV</td>
<td>30 K</td>
</tr>
<tr>
<td>B</td>
<td>105</td>
<td>8 meV, 161 meV</td>
<td>135 K</td>
</tr>
<tr>
<td>C</td>
<td>468</td>
<td>82 meV</td>
<td>85 K</td>
</tr>
<tr>
<td>D</td>
<td>27</td>
<td>120 meV</td>
<td>190 K</td>
</tr>
</tbody>
</table>

3.3 Time-resolved photoluminescence measurements

Figure 3.6 depicts some time-resolved PL decay measurements at different temperatures. At low temperatures, the signals for all samples exhibit a clear biexponential decay. The decay shape for sample A is single exponential above 40 K. However, PL decay for sample B retains the biexponential shape even at room temperature. Visually the decay shapes for samples C and D at high temperatures seem to be single exponential, but the fitting still provides two slightly different decay times. Such biexponential shapes for PL decays of MgZnO layer are confirmed in other articles [26].
Figure 3.7 shows dependence of the PL decay time on temperature. The PL decay for sample A has two characteristic times, which clearly correspond to the two different parts of the PL spectrum (see figure 3.3). Further analysis shows that the longer decay time corresponds to the bound excitons and the shorter – to the free excitons. The longer time component disappears at 60 K. The PL spectrum (figure 3.3) at this temperature still retains a small amount of the PL intensity caused by bound excitons but it seems to have no noticeable impact on the shape of the PL decay. The PL decay time for sample A reaches its minimum value of about 12 ps at 100 K temperature.

The decay time dependence on temperature for sample B shows a different tendency. The time increases with increasing temperature below 40 K. This effect can be explained by intensification of the exciton localization. According to the localization model presented in reference [20], excitons need to overcome the effective energetic barrier in order to localize, and the higher temperature increases probability of this process. With further increase in temperature, the probability of the non-radiative recombination overcomes that of the other processes, and the PL decay time tends to decrease. The PL decay time dependence on temperature for sample D has a similar shape but the increase in lifetime continues even to 60 K. The lifetime curve for sample C shows practically no increase but the shape differs from the curve of sample A. The shorter PL lifetime is almost
constant at the low temperature interval for all samples except sample A. These results fit with the integrated PL intensity dependence on temperature and further confirm the exciton localization model.

![Figure 3.7 PL decay time dependence on temperature.](image-url)

### 3.4 SNOM measurements

In order to analyze PL peculiarities with a high spatial resolution, measurements by SNOM technique were carried out. SNOM technique provides a possibility to directly confirm the exciton localization model. According to this model, the material composition of the layer is not evenly distributed and it causes bandgap fluctuations. Because the peak position of near-band edge PL depends on the bandgap energy, its uneven distribution should be seen in the peak position mapping obtained by the SNOM technique.
SNOM measurement results of all four MgZnO samples are shown in figure 3.8. As expected, non-homogenous distribution of the PL intensity and peak wavelength were obtained. Distribution of the PL peak wavelength is practically homogenous only for sample A. It fits with other experimental results confirming the uniform composition of MgZnO layer. Slight variation in the PL intensity can be caused by uneven distribution of non-radiative recombination centers.
Figure 3.8 The PL intensity, peak wavelength mappings and PL spectra from marked areas. Dots are experimental data and solid lines – FFT smoothing.

Other three samples exhibit clearly uneven distribution of the PL peak wavelength. The maps of sample B exhibit the largest variations, which suggest a high composition inhomogeneity of the MgZnO layer. According to the localization model, areas with the high PL intensity should
correspond to the longer wavelength areas. However, an opposite tendency is apparent for sample B. Considering the surface topography of this sample (see figure 3.1), it is likely that the PL with longer wavelength is emitted from nanorod structure areas. A poor collection efficiency of the near-field PL from nanorod areas can explain the low PL intensity.

The PL intensity and peak wavelength mappings for sample C do not correlate significantly. Slight variation of the PL peak wavelength has opposite correlation than predicted by localization model, and can be caused by the band-filling of tails of density of states (DOS). Small variation in composition, not observable by SNOM technique because of insufficient resolution, can form such tails of DOS. Two areas with the longest wavelength correspond to a slightly elevated PL intensity and can be caused by higher Zn mole fraction in these areas.

The PL wavelength mapping for sample D has small but clear variations. The PL intensity and peak wavelength variations correlate similarly to the slightly varying parts of the maps of sample C, thus, it can be explained by the band-filling for tails of DOS.
4. Summary and conclusions

Characterization of MgZnO epitaxial layers with various Mg mole fractions was performed by means of AFM, time-resolved PL and SNOM techniques. Surface topographies, spectrally- and time-resolved PL at different temperatures, PL intensity and peak wavelength mappings were obtained and analysis of these experimental results was performed. The conclusions of the analysis are listed below:

- Roughness of the MgZnO layer surface strongly depends not only on Mg mole fraction but also on the structure of the sample and the growth conditions.
- Three MgZnO samples with the highest Mg mole fraction show nonmonotonous PL peak wavelength dependence on temperature, which can be caused by the exciton localization.
- Time-resolved PL decays have a biexponential shape for all four samples, but only samples B, C and D retain such shape at room temperature. The PL spectra and temporal transients allow ascribing different lifetimes for free and bound excitons. It is likely that the longer lifetime corresponds to the localized excitons for sample B, C and D.
- Almost constant PL intensity and an increase of the PL decay time at low temperatures for samples B, C and D show good suppression of non-radiative recombination centers, which can be caused by efficient exciton localization at low temperatures.
- The PL intensity mappings for all samples show considerable spatial variation of this parameter. However, only samples B, C and D have a variation of PL peak wavelength. The variation of PL peak wavelength confirms the localization model.
- Performed investigation shows that Sample D, which differs from other samples by buffer layer and by thickness, has the best optical ant structural properties and can be used for fabrication of MgZnO based optoelectronic devices.

5. Suggestions for future work

In order to gain more information about the radiative recombination efficiency, measurements on external quantum efficiency could be made. The comparison of external quantum efficiency for all samples could provide deeper understanding of the radiative and non-radiative processes in MgZnO layers with various Mg mole fractions.

Similar experiments could be further performed on MgZnO quantum well structures. It could provide important information about PL peculiarities in structures commonly used in optoelectronic device fabrication.
6. References


