In the present paper, we discuss the influence of point defects on electrical and optical characteristics of ZnO thin films grown by the atomic layer deposition (ALD) method. The films were grown on glass substrates at low temperature (100–200 °C). We used diethylzinc (DEZn) and deionized water as precursors. Room temperature photoluminescence (RT PL) spectra, secondary ion mass spectroscopy (SIMS), electron dispersive X-ray (EDX) analysis and Hall effect measurements were made for as-grown ZnO layers and for the annealed ones (in air at 300 and 400 °C as well as in N\(_2\) atmosphere at 400 °C). The air-annealed ZnO films reveal a substantial reduction of a carrier concentration (up to 4 orders of magnitude – from \(10^{19}\) to \(10^{15}\) cm\(^{-3}\)) combined with changes in intensity of the defect-related luminescence bands. PL related to deep defects is shifted towards the lower energy range (red light emission) after annealing (in air and nitrogen-rich conditions).

Keywords: zinc oxide, atomic layer deposition (ALD), electrical properties, photoluminescence.

1. Introduction

Zinc oxide (ZnO) is nowadays extensively studied as a very attractive material for electronic, photovoltaic and optoelectronic applications. The main advantages of some crucial features of this material, such as its wide direct bandgap (3.37 eV at \(T = 300\) K) or high exciton binding energy (60 meV at \(T = 300\) K) have already been widely discussed in numerous papers and reviews (see, e.g., [1–5]).

In electronic devices (including piezoelectric transducers, thin film transistors (TFTs), cross-bar memories or transparent conductive oxides (TCOs)), where zinc
oxide can be used, one requires stable and controllable doping in the wide range of values of electrical parameters. This problem still remains a vital one for ZnO [1, 2, 5].

The free carriers’ concentration can be quite easily regulated in this compound, for instance, by obtaining “as-grown” ZnO thin films and crystals with substantially reduced level of electrically active unintentional defects, which introduce donor levels under the conduction band and therefore increase \( n \)-type conductivity. These defects can either be native (e.g., oxygen vacancies, zinc interstitials [1, 2]) or incorporated ones (such as hydrogen atoms [5–9]). The low carrier concentration \( n \), desired for many ZnO applications, can be achieved also by different ways of post-growth treatment, such as annealing at high temperatures [10, 11]. This is unfortunately excluded when ZnO is predicted for an active element in cross-bar memories [12] or deposited onto temperature sensitive organic substrates [13].

For ZnO based Schottky junctions, high carriers’ mobility is desired simultaneously with possibly low level of \( n \). Fulfilling these two requirements enables one to obtain a high forward current (due to high mobility) and a low reverse current (as a result of a low \( n \) concentration) [14].

However, obtaining a satisfactory level of mobility in ZnO requires more efforts than it was in the case of \( n \) concentration. The mobility values achieved in many growth methods are very diverse (particularly, for ZnO thin films, where they are at most at the level of 50 cm\(^2\)/Vs or lower, as in the case of the PLD technique) and strongly dependent on the substrates and growth conditions [15]. Thus, in order to ensure the control of concentration and mobility, the deposited layer should have both appropriate chemical composition [16] and highly ordered crystalline structure as scattering processes (e.g., on grain boundaries) are often regarded to be the key factor limiting Hall mobility [17].

In this work, we analyzed the influence of growth conditions as well as post-growth treatment on the behavior of defect-related luminescence and defects, strongly affecting electrical properties of ZnO layers obtained.

### 2. Experimental details

ZnO films discussed in this paper were grown using the low temperature (LT) ALD process as it provides uniform, continuous coating of surfaces with developed morphology, irregular shape and quite big dimensions [18]. This limitation cannot be avoided, e.g., in MBE and PLD methods, which are also widely used for ZnO growth.

Our ZnO layers were deposited in the Cambridge NanoTech Savannah 100 reactor on a glass substrate. Here, taking DEZn as a zinc precursor and H\(_2\)O as an oxygen source, we involved a double exchange reaction as follows:

\[
\text{Zn(C}_2\text{H}_5\text{)}_2 + \text{H}_2\text{O} \rightarrow \text{ZnO} + 2\text{C}_2\text{H}_6
\]

The advantage of using DEZn is its high vapor pressure (>10 torr at 300 K), which allows to the growth temperature to be decreased even below 100 °C.
The electrical parameters of our ZnO samples were collected from RT Hall effect measurements involving the RH2035 PhysTech GmbH system equipped with a permanent magnet producing a magnetic field $B = 0.426$ T. The measurements were performed in van der Pauw geometry (widely described in [19, 20]). The available DC range was $10^{-8} - 10^{-3}$ A, which allowed us to detect the carriers’ concentration between $10^{14}$ and $10^{22}$ cm$^{-3}$. Thus, for measurable layers contact resistance should not be higher than $10^8$ Ω. As an ohmic contact to ZnO, the e-beam evaporated bi-layer of Ti(100 Å)/Au(400 Å) was used. The room temperature photoluminescence (PL) spectra of ZnO layers were obtained using a CM2203 spectrometer with the Xe lamp used for excitation. The excitation wavelength was 300 nm, whereas the emission spectrum was measured within the wavelength range of 340–820 nm. The sample composition was measured by the electron dispersive X-ray (EDX) analysis method using the scanning electron microscope (Hitachi SU-70).

3. Results and discussion

The samples were obtained on a glass substrate in similar growth conditions at the temperature range between 100 and 200 °C. Figure 1 presents the PL spectra for as-grown ZnO layers deposited at different temperatures.

![Fig. 1. Room temperature PL spectra obtained for ZnO layers deposited at temperature range between 100 and 200 °C (as indicated).](image)

It can be observed that the wide defect-related luminescence band (the one peaked at about 1.9 eV) decreases in intensity at higher growth temperature, as already reported for ZnO films grown by ALD at slightly different conditions [12]. Moreover, the decrease in PL intensity is accompanied by its maximum shifted towards the deep red emission area. We relate this effect to the smaller concentration of deeper native defects in a given ZnO layer. This suggestion can be supported by the data shown in Tab. 1, which gives a view on composition analysis of the layers discussed and indicates that as-grown samples reveal an evident surplus of oxygen atoms in
comparison with zinc ones. Disproportion in composition becomes balanced with increasing growth temperature, which can be related to the improved stoichiometry of the ZnO films obtained.

Table 1 shows surprisingly large concentration of carbon (decreasing with growth temperature) and nitrogen (likely as N$_2$ molecules), which was purging gas in ALD processes. Their influence on electrical properties of ZnO still remains a topic for discussion. The most important native defects, which affect ZnO electrical and optical properties, are interstitial zinc and oxygen and zinc and oxygen vacancies. Hydrogen in turn is a shallow donor in ZnO [1, 5, 6].

We observed that the hydrogen concentration in the layers decreases from $1 \times 10^{21}$ to $2 \times 10^{20}$ cm$^{-3}$ with increasing growth temperature (see Fig. 2 and Tab. 1). Hydrogen atoms can be incorporated into the ZnO film during the growth process (from OH groups of water precursor) or directly from air. Reduction of the quantity of hydrogen atoms in the sample composition is particularly important when low $n$ concentration is desired. This result also means that some other shallow donor, not hydrogen, dominates in samples grown at higher temperature.

Table 1. Composition analysis of as-grown ZnO/glass layers.

<table>
<thead>
<tr>
<th>ZnO layer number/ Growth temperature</th>
<th>O [atoms]</th>
<th>Zn (O=1) [atoms]</th>
<th>C [%]</th>
<th>N [%]</th>
<th>H [cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/100 °C</td>
<td>1</td>
<td>0.76</td>
<td>2.1</td>
<td>0.7</td>
<td>$1 \times 10^{21}$</td>
</tr>
<tr>
<td>2/100 °C</td>
<td>1</td>
<td>0.80</td>
<td>1.8</td>
<td>0.5</td>
<td>$1 \times 10^{21}$</td>
</tr>
<tr>
<td>3/130 °C</td>
<td>1</td>
<td>0.81</td>
<td>1.8</td>
<td>0</td>
<td>$7 \times 10^{20}$</td>
</tr>
<tr>
<td>4/160 °C</td>
<td>1</td>
<td>0.85</td>
<td>1.3</td>
<td>2.2</td>
<td>$4 \times 10^{20}$</td>
</tr>
<tr>
<td>5/200 °C</td>
<td>1</td>
<td>0.89</td>
<td>0.5</td>
<td>0</td>
<td>$2 \times 10^{20}$</td>
</tr>
</tbody>
</table>

Fig. 2. Contribution of hydrogen (thick solid line) in ZnO as-grown layers deposited at 100 °C (left) and 200 °C (right).
A good stoichiometry (oxygen-to-zinc ratio) is likely to be one of crucial reasons for increasing free carriers’ mobility in our samples grown at higher temperature or after annealing. In fact, for specific growth parameters, mobility drops for lower $n$ concentration (Fig. 3), which suggests the existence of self-compensation phenomenon in films obtained at lower temperature (already mentioned, e.g., in [11, 21]). In such a case, the decrease of mobility is a result of simultaneously increasing concentration of electrons and holes. Otherwise, one would observe the increasing mobility with decreasing carriers’ concentration (decreasing number of native defects in ZnO layer). Figure 3 shows that for the temperature between 100 °C and 160 °C the mobility increases with increasing electron concentration and the sample obtained at 160 °C reveals the highest mobility parameter (37 cm$^2$/Vs). The electrical conductivity grows up faster than a carrier concentration, which can be regulated in a wide range of $n$ ($10^{16} – 10^{20}$ cm$^{-3}$) mainly by adjusting the deposition temperature [11, 16, 21]. This makes the as-grown zinc oxide films under investigation very perspective ones for many applications, including TCO materials [22, 23].

Moreover, as presented in Tab. 1 and Figs. 2 and 3, possibly incorporated hydrogen atoms do not show any dominant influence on electrical parameters of the ZnO samples, as free electron concentration grows up with a decreasing hydrogen contribution.

In order to have a better insight into the behavior and nature of point defects in the ZnO layers obtained we decided to perform an annealing of the samples in air (at 300 °C and 400 °C) and in the N$_2$ atmosphere (at 400 °C). Table 2 summarizes the electrical properties of the ZnO samples before and after 30 minutes of annealing in air.

In some cases, marked in Tab. 2 as “–”, the electron concentration was too small (below $10^{14}$ cm$^{-3}$) to be measured. Therefore, only the films’ resistance $R$ [GΩ] could be given.
Table 2. Electrical parameters of ZnO/glass layers before and after annealing in air. For non-measurable (highly resistive) films their resistance $R$ [GΩ] is given.

<table>
<thead>
<tr>
<th>Sample number/Growth temp.</th>
<th>As-grown layers</th>
<th>Layers annealed at 300 °C</th>
<th>Layers annealed at 400 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n$ [cm$^{-3}$]</td>
<td>$\mu$ [cm$^2$/Vs]</td>
<td>$\rho$ [Ωcm]</td>
</tr>
<tr>
<td>1/100 °C</td>
<td>$4.5 \times 10^{16}$</td>
<td>1.6</td>
<td>86.7</td>
</tr>
<tr>
<td>2/100 °C</td>
<td>$2.9 \times 10^{17}$</td>
<td>3.0</td>
<td>7.2</td>
</tr>
<tr>
<td>3/130 °C</td>
<td>$3.9 \times 10^{18}$</td>
<td>8.6</td>
<td>0.2</td>
</tr>
<tr>
<td>4/160 °C</td>
<td>$2.5 \times 10^{19}$</td>
<td>36.9</td>
<td>$6.8 \times 10^{-3}$</td>
</tr>
<tr>
<td>5/200 °C</td>
<td>$1.2 \times 10^{20}$</td>
<td>28.3</td>
<td>$1.8 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Fig. 4. RT PL spectra for as-grown sample denoted as 1 in Tabs. 1 and 2, deposited at 100 °C (solid line), then annealed for 30 min in air at 300 °C (dashed) and 400 °C (dotted). A shift ($\Delta E = 0.11$ eV) of defect-related luminescence peak towards red emission area is observed.

Fig. 5. RT PL spectra measured for as-grown sample deposited at 100 °C (solid line), then annealed for 30 min in air at 400 °C (dotted) and in N$_2$ at 400 °C (dashed). The sample is denoted as 1 in Tabs. 1 and 2.
As can be seen from Tab. 2, annealing in air results in a substantially decreased (up to 4 orders of magnitude) level of \( n \) concentration. Comparing this with Fig. 4 and Tab. 1 we assume that annealing in air leads to a decrease in concentration of oxygen atoms located in interstitial positions. PL investigations indicate that the wide defect-related maximum of PL spectrum is moved towards lower energies (from orange-red to red emission), when the role of interstitial oxygen atoms responsible for orange-red emission [24] is reduced – see Fig. 4. According to the results presented in [25, 26], the observed red light emission occurs due to interstitial zinc atoms. The effect of decreasing mobility together with a lower level of \( n \) concentration in ZnO layers deposited at 160 °C and 200 °C was noticed after annealing in air (contrary to the behavior of this parameter observed for the samples annealed in N\(_2\) atmosphere, shown later on), which confirms the assumed self-compensation mechanism in air-annealed films.

The annealing process performed at 400 °C in the N\(_2\) atmosphere for 0.5 hour caused a further shift of the defect-related PL maximum towards the deep red emission area (in comparison with the one observed after annealing the ZnO films in air at 400 °C). This effect is presented in Fig. 5. Simultaneously, green luminescence became more intensive.

With regard to suggestions given in [25, 27–30] the enhanced intensity of green PL after annealing in N\(_2\) may occur in so-obtained oxygen deficient ZnO samples [27] and originate from uncompensated oxygen vacancies: either singly (\( V_O^+ \)) [28, 29] or doubly (\( V_O^{2+} \)) [30] charged ones.

As in the case of optical properties we also noticed substantial changes in electrical parameters of the ZnO layers after annealing them in N\(_2\). This process was performed for four samples deposited at 100 °C. Table 3 presents their electrical parameters before and after annealing in nitrogen. One of the samples from Tab. 3 (marked therein with (*) and denoted as 1 in Tabs. 1 and 2) was also annealed in air – the PL results are compared in Fig. 5. As we noticed, the longer annealing results in a larger reduction of electron concentration (this effect is not shown here). Secondly, annealing in the nitrogen-rich conditions for 30 minutes was applied in order to compare the influence of oxygen and nitrogenous environments on the electrical parameters of our ZnO specimens.

As can be noticed in Tabs. 2 and 3, annealing in N\(_2\) causes a smaller reduction of \( n \) concentration than the same process carried out in air (this is especially visible in

<table>
<thead>
<tr>
<th>Sample number/Growth temp.</th>
<th>As-grown layers</th>
<th>Layers annealed at 400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n ) [cm(^{-3})]</td>
<td>( \mu ) [cm(^2)/Vs]</td>
</tr>
<tr>
<td>6(*)/100 °C</td>
<td>4.5×10(^{16})</td>
<td>1.6</td>
</tr>
<tr>
<td>7/100 °C</td>
<td>4.4×10(^{15})</td>
<td>14.1</td>
</tr>
<tr>
<td>8/100 °C</td>
<td>5.1×10(^{15})</td>
<td>3.8</td>
</tr>
<tr>
<td>9/100 °C</td>
<td>3.7×10(^{18})</td>
<td>3.8</td>
</tr>
</tbody>
</table>
the case of sample 6 from Tab. 3, which should be directly compared with sample 1 from Tab. 2). Simultaneously, we observed an evident increase of carriers’ mobility, which may suggest that annealing in N$_2$ results in a decreased number of native defects in the ZnO layers discussed (self-compensation phenomenon is in this case not a dominant factor leading to a lower free electron concentration).

4. Summary

In this paper, we showed that both electrical and optical properties of ZnO layers obtained at low temperature by the ALD technique can be controlled depending on future film’s applications (only by adjusting basic growth parameters such as deposition temperature and precursor doses). Composition analysis, together with electrical and optical studies after annealing in air and N$_2$, pointed to a possible dominant kind of native defects in the grown ZnO films. The three most important ones are: oxygen vacancies (responsible for green emission), oxygen atoms in interstitial positions (emission in orange-red area) and zinc interstitials (giving a PL maximum in deep red range).

Every type of annealing resulted in substantially reduced free electron concentration (up to 4 orders of magnitude) and low energy shift of the defect-related PL maximum. However, Hall mobility decreases after annealing in air, but increases (up to 105 cm$^2$/Vs) as a result of annealing in N$_2$ atmosphere. Therefore, we consider that either the self-compensation mechanism or lower number of defects is responsible for the reduction of $n$ concentration, in the respective cases under study.

We have also noticed that hydrogen atoms in ZnO samples do not dominate their electrical properties as electron concentration increases with decreasing hydrogen contribution in as-grown layers.

To conclude, the ZnO layers obtained with controlled PL spectra as well as adjusted electrical parameters may have many applications in modern electronics and optoelectronics, e.g., thin film transistors (TFTs) [31] and other devices in which low thermal budget is strongly required (such as cross-bar memories, $p$-$n$ junctions organic material/ZnO, etc.) [12, 32–34].

Acknowledgements – The research was partially supported by the European Union within the European Regional Development Fund, under the grant Innovative Economy (POIG.01.01.02-00-008/08). The F-120 ALE reactor of Microchemistry was bought using SEZAM grant of the Foundation for Polish Science.

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Received June 19, 2009
in revised form October 7, 2009