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# Thermal Treatment for Elimination of Impurities in ZnO Thin Films

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We investigated the photoluminescence of ZnO sol–gel films coated on glass substrates using a spincoating method and then annealed in temperatures ranging from 230°C to 600°C. The primary purpose of the heat treatment was the elimination of organic waste products and polycrystalline layer formation. The temperature dependence of photoluminescence was investigated. Gaussian deconvolution was performed for measurements done in T = 12 K. This procedure provides insights into optically active defects formed in the material. The method of the Gaussian deconvolution was discussed, along with information regarding the control of fitting parameters and a comparison between different spectra. We demonstrated that luminescence properties could be tuned by changing the annealing conditions of deposited sol–gel films. Moreover, the positions of the emission peaks were discussed concerning specific defects such as vacancies or interstitials. In addition, organic waste products remain in a batch after the synthesis can be transferred to the glass substrate. Obtained ZnO films show significant differences in emission spectra associated with hydrogen, carbon, and nitrogen impurities elimination. Higher temperatures and longer annealing times benefit exciton emissions, linked with improved crystallinity of films.

topics: ZnO, thin films, thermal annealing, photoluminescence

## 1. Introduction

Zinc oxide is a commonly discussed wide bandgap semiconductor ( $E_{\rm g} = 3.37$  eV) with high exciton binding energy ( $E_{\rm XB} \approx 60$  meV), promising a wide range of applications, including roomtemperature laser actions, use as transparent conductive oxide, or down-shifting of UV radiation [1]. The number of its applications is still limited due to the lack of viable p-type doping and the existence of native defects that manifest themselves mainly in the visible part of photoluminescence (PL) [1]. Defects levels at 1.65, 1.96, 2.51 eV below the conduction band minimum (CBM) are among the most common defects in ZnO [2].

The list of commonly discussed impurities starts with neutral and charged zinc vacancies  $V_{Zn}^q$  with  $q = \{-2, -1, 0\}$ , responsible for mentioned levels.

A complimentary set of defects in ZnO consists of oxygen interstitials  $O_i$ , oxygen vacancies V, and oxygen incorporation at zinc sublattice  $O_{Zn}$ , with energy levels of 1.62, 2.28, 2.38 eV below CBM, respectively [3]. Wet chemical methods such as spincoating, while widely used, raise additional concerns regarding the elimination of nitrogen, carbon, and hydrogen from films created with the use of organic precursors. However, partial removal of impurities allows tunability of the PL spectra.

## 2. Samples preparation

Sol-gel method used for deposition of discussed thin films was prepared in a batch synthesis using 1 M zinc acetate (Zn(CH<sub>3</sub>CO<sub>2</sub>)2 · 2H<sub>2</sub>O) solution in 2-methoxyethanol (C<sub>3</sub>H<sub>8</sub>O<sub>2</sub>), stabilised with diethyleneamine (DEA, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NH). Constant stirring was employed under an ultrasonic bath for t = 1 h to ensure proper mixing of all reagents. Additionally, the solution was aged at T = 50°C for a t = 24 h before the deposition was performed.

Each of 8 layers of ZnO was spin-coated, applying t = 30 s long spinnings with 600 RPM and 1000 RPM in the subsequent steps, followed by layer drying in an oven (10 min, 100°C). The final step in the samples' fabrication was annealing in an ambient atmosphere lasting 2–10.5 h in a temperature range from 230 to 600°C. These parameters were deliberately changed to study their influence on the properties of ZnO films.

## 3. Methods

All PL spectra were collected under continuous constant band-to-band excitation with a Cd–He laser line of  $\lambda_{\rm EX} = 325$  nm ( $E_{\rm EX} = 3.815$  eV) with nominal power of  $P_{\rm EX} = 25$  mW. Spectra were collected using a silicon CCD camera in the wavelength domain, which was later recalculated, using Jacobian transformation, into the energy domain. There were no corrections for both the sensitivity curve of the camera or the light reflection of gratings mounted within the spectrometer.

Three out of four measured spectra are subjects to Gaussian deconvolution. Sample 2h\_230C was not subject to Gaussians deconvolution due to weak near-bandgap emission. That procedure used a set of 13 Gaussians fitted with the least square method to the experimental spectra. The first fitting step includes a heuristic guess of initial parameters, with Gaussians' Means situated mainly at the local maxima of curves yet to be fitted. Peaks' positions (En [eV]), amplitudes (Am), and broadenings (Br [eV]) were calculated using the least square method. Initial tests show the existence of many local minima of fits' residuals, so the approach was changed as described in steps:

- 1. A Mean photons' flux "Mean\_ZnO" for 2h\_500C, 3h\_600C and 10.5h\_600C was calculated.
- 2. Artificial "Mean\_ZnO" spectrum was fitted, keeping peaks' broadenings roughly in a range of 40–400 meV, to obtain Mean\_ZnO's parameters. That is to prevent nonphysical results that can arise from heuristically chosen initial values.
- 3. Fitted parameters (Am, En, Br) were fed into the fitting script, as initial values for each measured sample fitted separately in that step. Allowed changes in peaks' position were artificially kept below 0.01 meV per iteration, so amplitudes and broadenings were adjusted the most until the relative shift in peaks' amplitudes dropped below  $\Delta Am < 0.1$  per iteration.
- 4. Iteratively changed parameters were fed into the fitting script again, but allowed changes of Gaussians' Means was increased to 1.0 meV per iteration. Another stopping criterium of peaks' energies changes ( $\Delta En < 0.1 \text{ meV}$ ) was added in conjunction with  $\Delta Am < 0.1\%$ to accommodate all 39 parameters being fitted at that step.

Steps 3 and 4 took roughly 50–70 iterations regardless of the sample.

### 4. Results

Four photoluminescence spectra of ZnO thin films were measured in T = 12 K, and are presented in Fig. 1. Zinc oxide was prepared each time with



Fig. 1. PL spectra collected at T = 12 K, for 10.5h\_600C, 3h\_600C, 2h\_500C and 2h\_230C normalized emission.



Fig. 2. Gaussian deconvolution of PL spectra of  $2h_{500C}$  ZnO thin film, measured at T = 12 K. The lowest energy peak (p.1) was marked with a dotted line.

the same batch composition and deposition procedure. The difference in spectra proves that annealing times and temperatures can change the PL emission of the thin films. We attribute this to the selective elimination of organic impurities from films under annealing in air, although some deposition of air molecules cannot be excluded.

Sample 2h\_230C did not show excitonic emission connected to high crystallinity. Still, this sample showed emission in a 1.7–2.4 eV range, which can be attributed to  $V_{Zn}^{-1}$ ,  $O_i$ ,  $O_{Zn}$  native defects proving oxygen-rich growth conditions. However, we noted a weak emission of  $E(N_O^{-1}) = 1.7$  eV that can be linked to free-electron recombination to  $N_O^{-1}$  defects ground states as pointed in [4]. That emission is relatively more potent Thermal Treatment for the Elimination...

p.#	Mean_ZnO		2h_500C		$3h_{600C}$		10.5h_600C	
	En	Br	En	Br	En	Br	En	Br
p.1	1.619	0.262	1.609	0.259	1.602	0.246	1.648	0.279
p.2	1.776	0.192	1.782	0.189	1.755	0.212	1.790	0.175
p.3	1.898	0.182	1.907	0.183	1.887	0.199	1.900	0.163
p.4	2.062	0.235	2.068	0.228	2.051	0.236	2.066	0.240
p.5	2.258	0.290	2.268	0.290	2.240	0.289	2.265	0.290
p.6	2.518	0.366	2.551	0.367	2.494	0.374	2.508	0.356
p.7	2.947	0.333	3.017	0.357	2.918	0.331	2.907	0.311
p.8	3.084	0.181	3.115	0.190	3.066	0.174	3.070	0.178
p.9	3.178	0.105	3.168	0.079	3.177	0.116	3.188	0.120
p.10	3.242	0.056	3.233	0.053	3.252	0.067	3.241	0.049
p.11	3.302	0.071	3.291	0.080	3.304	0.051	3.309	0.028
p.12	3.314	0.029	3.316	0.029	3.318	0.031	3.313	0.082
p.13	3.358	0.036	3.359	0.032	3.357	0.043	3.357	0.032

Fitted values of 13 peaks (p.#) of En and Br from deconvolutions of PL spectra, together with Mean\_ZnO parameters used as initial for fitted samples.

![](_page_2_Figure_4.jpeg)

Fig. 3. Deconvolution of 3h 600°C spectrum.

in the 2h\_500C sample, the spectrum's deconvolution of which is shown in Fig. 2. In our case,  $N_O^{-1}$  emission can be attributed to the peak with En(p.2) = 1.776 eV, leaving En(p.1) = 1.619 eV being attributed to the V<sub>O</sub> defect that was introduced during annealing. For the sake of clarity in this paper, the given peak number will be referenced with p.#.

The stability of the fitting model and the results was ensured using the procedure described in Sect. 3. Table I shows initial values for fitting procedure as "Mean\_ZnO" and results for films. Amplitudes, as easily identifiable from plots, are skipped.

Table I shows that changes in peaks' positions are smaller than 70 meV, which is a value obtained for a peak p.7, situated  $En(p.7) = 2.96 \pm 0.06$  eV.

![](_page_2_Figure_9.jpeg)

Fig. 4. Deconvolution of 10.5h 600°C spectrum.

Mean change in peaks' positions  $\Delta En$  equals 13.36 meV averaged across all peaks from Table I. A significant change of peaks at En(p.7) = 2.96 eV is not problematic since that part of the spectrum provides limited information for analysis. This part of the spectra is relatively flat, and Gaussians' Means can be covered with additional changes in other parameters. Amplitudes, fitted as free parameters, are skipped for clarity since the values arose from previously done normalizations of each spectrum and are not helpful for in-between-samples comparisons.

Figures 3 and 4 show deconvolution of 3h\_600C and 10.5h\_600C spectra measured at T = 12 K. Analogously, Fig. 2 proves the fitting procedure is valid for a diverse set of spectra.

#### 5. Discussion

Intense emission of p.8, p.9, p.10 peaks (3.115 eV, 3.168 eV, 3.233 eV), which are characteristic for the  $2h_{500C}$  sample, may be related to the hole ionisation energy 200 meV as calculated in [4]. It happened that p.8 and p.9 peaks have almost precisely 200 meV lower energy than excitonic transitions En(p.12) and En(p.13).

The peak position energy En(p.11) of the 2h\_500C film can be assigned as a phonon replica of the E(p.13) peak, as their energy difference of 68.4 meV is close to the usually reported value of longitudinal optical phonon E(LO) = 72 meV in ZnO [5]. However, this energy difference is not found in either 3h\_600C or 10.5h\_600C films, which is unexpected assuming that the higher temperatures of annealing cause an increase in the quality of the films by eliminating impurities. The peak p.11 with the energy En = 3.291 eV that can be assigned to the transition energy of a free electron to an acceptor hole formed by nitrogen in the oxygen site (N<sub>O</sub>) was found at 3.278 eV [5].

Samples 3h\_600C and (finally) 10.5h\_600C show weaker and weaker emissions, corresponding to the whole p.8–p.10 region, which we attribute to eliminating nitrogen by prolonged annealing. We can also deduce that our thin films initially had a relatively high concentration of hydrogen that passivated N<sub>O</sub> defects, as shown in [4], by ZnO films annealing in H<sub>2</sub> gas. Our samples, prepared in a wet chemical process, should have a high concentration of hydrogen, forming stable cationic dopants, as shown in [6]. In the case of carbon, the formation of a defect complex at the oxygen site (CN)<sub>O</sub> of sublattice was proven [7]. Most importantly, it was found that carbon interstitials (C<sub>i</sub>), acting as donors, prefer to bind with nitrogen in ZnO [7].

The above mentioned findings suggest that the unusual emission of 2h\_500C thin film is due to thermal annealing stopped in such a moment that previously passivated N<sub>O</sub> dopants become optically active in that film. This suggests that, at this temperature and time, both carbon and hydrogen impurities are mostly annealed. Films annealed at  $T = 600^{\circ}$ C prove that the annealing of nitrogen impurities requires more energy provided in the form of heat, which can be obtained with longer annealings or higher temperatures.

## 6. Conclusion

Our studies have shown that PL spectra depend strongly on annealing conditions and that changes in their shapes are strongly related to dopants and impurities within samples' volumes. We assume that ZnO films annealed in  $T = 230^{\circ}$ C possess the number of gas-forming contaminants that cause PL spectra to be rather complicated in composition and to lack near-bandgap emission.

Thermal annealing of such films can cause subsequential elimination of hydrogen, carbon, and nitrogen from ZnO. Annealing paused at different stages provides an opportunity for tunning of PL spectra, suggesting different elimination rates for gasforming impurities, which seems to align with PL spectra, up to the highest temperature of annealing  $T = 600^{\circ}$ C and the period up to t = 10.5 h. The 10.5h\_600C film mostly shows excitonic emissions and PL peaks from native points defects, with reduced organic (C, N, H) impurities influence spectra.

However, the concentration of gas-forming impurities at all the individual stages of films annealing is unknown, which leaves a place for further studies.

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