

The effect of annealing on spectra and decay time of X-ray luminescence of zinc oxide powders

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Abstract. The annealing effects on zinc oxide powders have been investigated. Annealing was performed at 800, 1050°C in vacuum and air for 2 h. After that, the powders were annealed in gas mixture consisted of 15% H₂ and 85% Ar for 30 min at 800°C. After vacuum annealing the powders have green luminescence band located at 515 nm and decay time curve of the luminescence has three exponential decays with time constants: 10-50 ns, 100-200 ns, and 1100 ns. After air annealing powders have green luminescence band with peak at 525 nm and decay time curve of the luminescence has three exponential decays with time constants: 5 ns, 100-200 ns, and 4000-5000 ns. Annealing in hydrogenous ambience has no effect on peak position or intensity for powders previously annealed vacuum. In air annealed powders intensity of green luminescence decreases significantly after annealing in hydrogenous ambience.

1. Introduction

Zinc oxide (ZnO) is a direct wide band gap (3.37 eV) semiconductor material with a large exciton binding energy (60 meV). It gained significant attention motivated by potential applications as an oxide electronic material, and in optoelectronic and lighting applications. Luminescence of ZnO, generally, has two bands: near band edge luminescence (NBEL), ascribed to excitons [1], and green luminescence (GL). The origin of the GL is still a matter of debates, despite a great number of studies. As a rule, GL is ascribed to native defects. Lack of reliable theoretical calculations of defect energy levels and uncertainty of interpretation of EPR data makes difficult to analyze experimental results [2]. In most cases GL is attributed to zinc [3, 4] or oxygen [5, 6] vacancies. Some authors assume that GL can be connected to both defects [7, 8].

By applying different annealing atmospheres one can indicate if an increase/decrease in the concentration of a specific intrinsic defect is correlated with the GL properties.

In this work, we present the effect of vacuum or air and H₂-Ar annealing on the shift of the emission, intensity and decay time changes of ZnO powders.



2. Experimental

Chemical purity (powder #1, 99,9%, Russia) and high purity (powder #2 99,999%, USA) powders were used. Annealing was performed at 800, 1050°C in vacuum and air for 2 h. After that, powders were annealed in gas mixture of 15% H₂ and 85% Ar for 30 min at 800°C.

The X-ray excited luminescence (XRL) spectra were measured under steady state X-ray excitation (40 kV, 10 mA) with a FEU-106 PMT and a MDR-2 grating monochromator with 1200 grooves/mm. The spectra were corrected for the quantum efficiency of the PMT and for the monochromator transmission.

The decay time curves were recorded with the experimental system described in detail in [9]. A pulsed X-ray source with 1 ns pulse duration operates at 30 kV and maximum current amplitude of 500 mA. The detection system consists of a FEU-71 PMT, operating in single photon counting mode and related electronics. The system allows measurements with time resolution better than 400 ps. The XRL spectra and decay time curves were measured in the reflection mode: the angle between X-ray beam and the PMT was 90 deg. All measurements were performed at room temperature.

3. Results

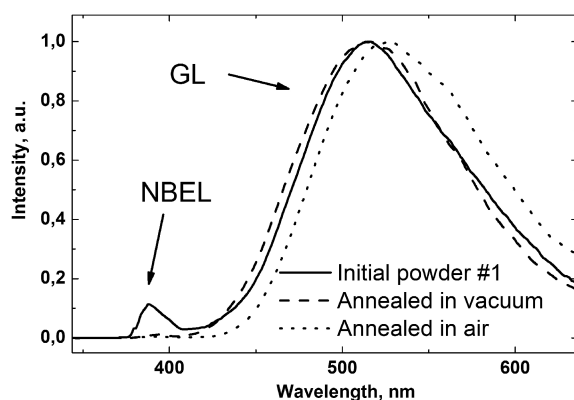


Figure 1. X-ray excited luminescence spectra of powder #1 after annealing in vacuum and air. All intensities are normalized.

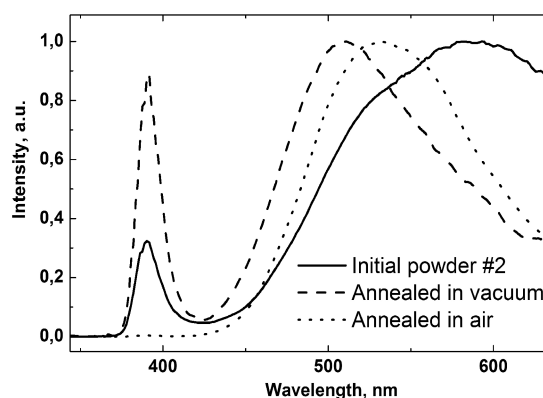


Figure 2. X-ray excited luminescence spectra of powder #2 after annealing in vacuum and air. All intensities are normalized.

The XRL spectra of powder #1 are shown in Fig. 1. Spectrum of initial powder has broad GL band at 513 nm and peak of NBEL at 389 nm with low intensity. After vacuum annealing GL maximum of powder #1 is around 513 nm (same as initial powder) and intensities of GL are about 10 (for 800°C) and 20 (for 1050°C) times greater than the initial one. GL maximum of both air annealed powders is around 525 nm and intensity is 5 times greater than the initial one.

The XRL spectra of powder #2 differ from that of powder #1 (Fig.2). Initial powder #2 has peak of GL intensity at 585 nm. After vacuum annealing NBEL intensity grows up towards to GL ones, but complete intensity of luminescence didn't change significantly. GL maximum of vacuum annealed powder is at 510 nm. Air annealing provides result completely the same to powder #1: rise of GL intensity and its maximum at 525 nm. Powder #2 had very weak luminescence intensity, so for further research we used powder #1.

Decay time curves of air and vacuum annealed powders are presented in Fig. 3. All the powders have complex decay time curves that consist of several exponential decays. Decay curves of air annealed powders are identical. One can see that slow component becomes faster for vacuum annealed powders. Decay time curve of air annealed powders have three clearly separable components. The estimated decay time constants are 5 ns, 100-200 ns, and 4000-5000 ns. Decay time curves of vacuum annealed powders can be approximated by two exponential decays but if we take into account the case of air

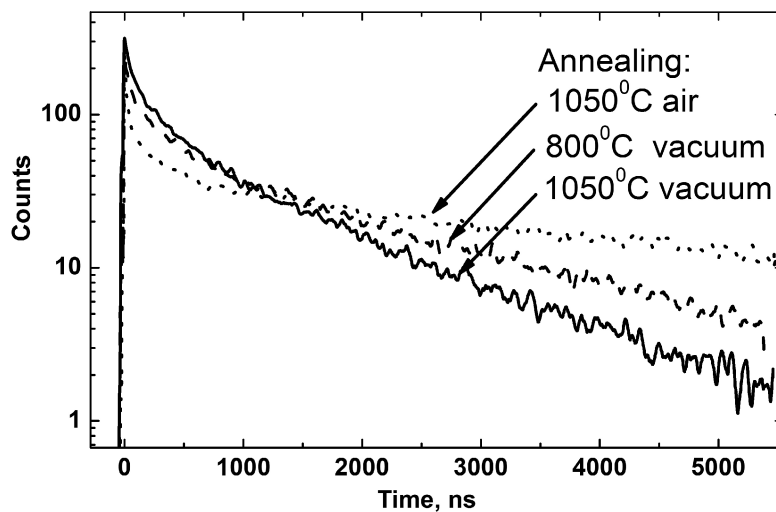


Figure 3. Decay time curves of powder #1 after annealing in vacuum and air.

annealed powders we should expect at least three decay times. Approximation by three exponential decays gives time constants of: 10-50ns, 100-200ns, and a slow decay time constant. For powder annealed at 800°C decay time of slow component is about 1600 ns and for powder annealed at 1050°C decay time of slow component is about 1100 ns.

Results of annealing in hydrogenous ambience are completely different for powders previously annealed in vacuum and air (Fig.4). For vacuum annealed powders annealing in hydrogenous ambience has no effect on peak position or intensity. Intensities of GL decrease significantly in air annealed powders and at the same time NBEL intensities grow up to GL ones.

Comparing decay time curves before and after annealing in hydrogenous ambience (Fig. 5) it can be seen that fast components of decay time curves have some differences and slow components are the same. So it can be clearly seen that decay time curves of vacuum annealed powders contained fast component which is quenched by annealing in hydrogenous ambience. Obviously, this component can produce inaccuracy in estimating of decay times for other components.

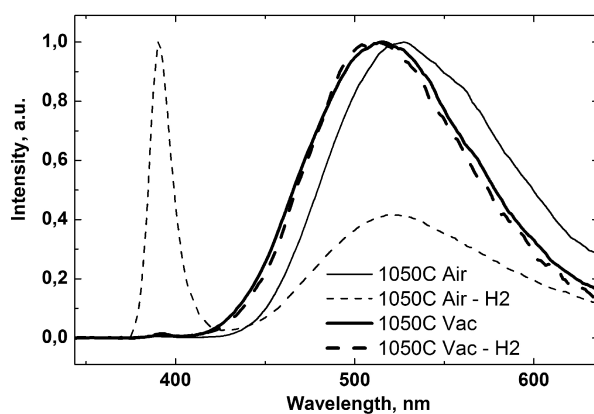


Figure 4. X-ray excited luminescence spectra of air and vacuum annealed powders #1 after annealing in hydrogenous ambience. All intensities are normalized.

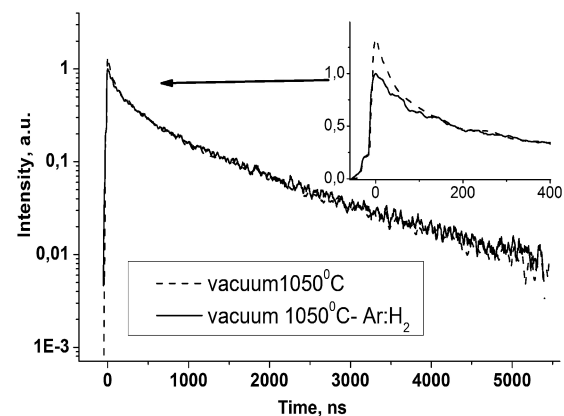


Figure 5. Comparison of the decay time curves of vacuum annealed powder #1 before and after annealing in hydrogenous ambience.

4. Discussion

The effects of annealing in vacuum and air should be caused mainly by creation of native defects: oxygen vacancies and zinc vacancies, respectively. For certain, there are a lot of other types of native defects in the zinc oxide but they have high formation energy [10] and cannot have a great influence

except of interstitial zinc. Interstitial zinc has low formation energy [10] and acts as a shallow donor, so it can participate in energy transfer processes.

Hydrogen can extract an excess of oxygen; as it comes from DFT calculations [11], it can passivate zinc vacancies by creation of $(V_{Zn}-H_2)^0$ centers and it can act as shallow donor.

Changes in X-ray luminescence spectra that come after annealing can be explained by assuming that GL with peak at 510-515 nm is related to oxygen vacancies and GL with peak at 520-530 nm is related to zinc vacancies.

Annealing in vacuum creates oxygen vacancies therefore intensity of GL increases. After that, annealing in hydrogenous ambience can't produce significant effect.

Annealing in air reduces number of oxygen vacancies and it creates zinc vacancies. Formation energy of zinc vacancies is higher [10, 12], so the GL has lower intensity. The following annealing in hydrogenous ambience reduces the excess of oxygen and passivates zinc vacancies. As a result, GL intensity decreases dramatically.

Powders #1 and #2 had great difference in GL intensity after vacuum annealing. Oxygen vacancies have to have specific charge state to take part in the luminescence process. As shown in [13], they should be singly or doubly ionized vacancies. Charge state of the vacancies is determined by the Fermi level [10], which is dependent on presence of donor or acceptor impurities. We suppose that powder #1 had acceptor impurities that led to creation of singly ionized vacancies and strong GL.

Decay time curves are not clearly understood yet. They have complex structure that consists of several components with similar decay times, so it is hard to clearly resolve them. In addition, it is unclear why the change of the slow component decay time occurs after annealing. As a hypothesis, an appearance of a new nonradiative decay channel or changes in the properties of a complex luminescence center can be assumed. It should be noted that if donor-acceptor pairs had taken part in the luminescence then decay time curves would have had hyperbolical decay.

5. Conclusions

Vacuum and air annealing of ZnO powders causes rise of green luminescence with peaks at 510-515 nm and 525-530 nm, respectively. Despite the fact that peaks have very small difference in position, luminescence has different origins. Luminescence band with maximum at 510-515 nm is connected with oxygen vacancies and luminescence band with maximum at 525-530 nm is connected with zinc vacancy. However, complex decay time curves show that luminescence cannot be associated with single vacancies.

6. References

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