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Photoluminescence Dynamics and Quantum Yield of Intrinsically Conductive ZnO from Atomic Layer Deposition

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Abstract

Zinc oxide (ZnO) thin films deposited by atomic layer deposition (ALD) and a (0001)-oriented bulk-ZnO single-crystal are compared by ultrafast time-resolved and spectral photoluminescence spectroscopy as well as by luminescence quantum yield (QY) measurements. While the ALD-ZnO is intrinsically conductive, bulk-ZnO is electrically rather insulating. Nevertheless, PL spectra of both materials reveal similarities: A peak in the near-UV originating from inter-band transitions and a defect peak in the green-yellow spectral region associated to deep trap states. We investigate the dynamics and efficiency of these luminescence emissions to understand the interdependency of defects and the yet insufficiently understood conductivity mechanism of ALD-ZnO. Spectrally, a PL blueshift of the trap-mediated peak is observed for the transition from poor to good conductivity, which
occurs with increasing ALD-deposition temperature. The quantum yield of ALD-ZnO is shown to be \( \sim 18 \)-times lower and the luminescence lifetime of the UV-peak is \( \sim 14 \)-times shorter compared to bulk-ZnO. We conclude that these properties are related to a significantly higher density of non-radiative defects, which might also represent electrically active scattering centers. These results indicate a new direction for further optimization of ALD-ZnO towards indium tin oxide (ITO)-compatible electrical conductivities by reducing or passivating these defects.

**Keywords:** zinc oxide; time-resolved photoluminescence; atomic layer deposition; quantum yield

### I. INTRODUCTION

ZnO is a wide bandgap semiconductor (~3.3 eV) with the potential to replace tin-doped indium oxide (ITO) as the standard transparent conductive oxide (TCO). Beside its high transmittance of around 90 \% [1-3], ZnO also exhibits a high intrinsic conductivity of \( 5 - 100 \) m\( \Omega \)cm (depending on the deposition temperature) [3, 4] which is most probably based on hydrogen [5]. The intrinsic conductivity can be further enhanced towards the mid-\( 10^{-4} \) \( \Omega \)cm range by adding Al as dopant in ALD-ZnO/Al\(_2\)O\(_3\) nanolaminates [6-8]. However, supercycle processes involving two materials would impede the use of high throughput spatial ALD systems that allow for industrially relevant deposition speeds [9, 10]. Therefore, it is desirable to achieve the conductivities of Al-doped ALD-ZnO by pure ALD-ZnO. Apart from TCO-applications highly conductive ALD-ZnO was also suggested for carrier-selective tunneling contacts in high-efficiency silicon solar cells [11].
Generally, defects are useful in a TCO to increase the conductivity, if they provide charge carriers or contribute to the charge transport by offering unoccupied states near the conduction band. On the other hand, defect states can also contribute to charge carrier recombination or cause scattering of the charge carriers and hence increase the electrical resistance. Therefore, a deeper knowledge of the nature and function of defects is generally desirable for TCO optimizations.

ALD-ZnO deposited at low temperature shows a well-known defect-PL peak in the PL spectra at around 500-600 nm [12]. This defect peak seems to have a correlation with both, the deposition temperature and the conductivity of the ZnO films, hence, suggesting a connection of the radiative defects involved in this peak with the electrical properties [4]. The question arises if any change in the concentration of radiative defects with varying deposition temperature appears due to a different free charge carrier density or a different number of non-radiative defects, or alternatively, if a different deposition temperature simply generates a different concentration of radiative centers in the ALD-ZnO layer.

II. EXPERIMENTAL

ZnO films were deposited on wet-chemically cleaned Si wafers and quartz glass pieces. The substrates were coated with a 100 nm thermal ZnO ALD film at different deposition temperatures in the range of 100°C to 250°C. The used precursors were diethylzinc (DEZ; at room temperature) and deionized water (H₂O). More detailed information about the preparation process and the ALD process parameters can be found in Ref. [4]. For comparison to bulk single-crystalline ZnO a double-side polished, c-plane-cut, (0001)-oriented ZnO sample (purchased from CrysTec GmbH, Berlin) was used. PL spectroscopy was
performed at room temperature with excitation by a cw-HeCd laser (3.8 eV). The spectra were recorded by a grating spectrograph with CCD detector (Andor). EQY was measured in a setup based on a 10 cm-diameter integrating sphere, which was coupled via a silica fibre-bundle to a spectroscope with \( f = 30 \text{cm} \) a LN\(_2\)-cooled DD-BI-CCD camera. The EQY setup was calibrated using a tungsten-halogen standard lamp. More details on the method can be found in [13]. For the time-resolved PL (TR-PL) measurements, the samples were excited by a femtosecond laser (100 fs) at 360 nm. The PL signal was collected and focused by two lenses \( f = 10 \text{cm} \) on the entrance slit of the spectrograph attached to streak-camera (Hamamatsu) which enables to record spectro-temporal evolution of PL with a time resolution of about 4 ps. An 385 nm long-pass filter was used to suppress reflections of the excitation beam.

### III. RESULTS AND DISCUSSION

In Fig. 1(a) the room-temperature PL spectra of the ALD-ZnO samples deposited at various temperatures and the single-crystalline (0001)-bulk-ZnO are shown. All spectra are normalized for better visibility, although this obscures the fact that especially the 100°C and 125°C sample have rather weak UV-peak intensities (~20% compared to the other ALD-samples). Apart of that, the UV-peak position of all ALD-samples is virtually invariable at 381 ± 1 nm, whereas the UV-peak of the bulk-ZnO sample is located at 375 nm. The full width at half-maximum (FWHM) of the bulk-ZnO UV-peak is roughly half compared to the ALD-samples (11 nm vs. 24 nm on average). It does not really come as a surprise that single-crystalline ZnO exhibits a sharper peak than the polycrystalline low-temperature deposited ALD-ZnO. However, the ~50 meV redshift of the PL peak is probably of different origin. As
demonstrated recently by ultraviolet photoelectron spectroscopy (UPS) and low-temperature Hall-measurements [5], ALD-ZnO behaves like a quasi-metallic semiconductor with a free electron density of up to $\approx 5 \times 10^{19}$ cm$^{-3}$ and a vanishing energetic difference between the Fermi level and the conduction band. The donor level (most likely induced by hydrogen in ALD-ZnO) merges with the conduction band (Mott transition), which in turn lowers the ground state of thermalized, optically excited electrons in the conduction band. Hence, a radiative transition does not take place from the conduction band edge but from the donor level and its tails, which naturally extend some-ten meV into the bandgap. This could explain both, the slight PL redshift and the broader FWHM of radiative interband transitions in ALD-ZnO.

The deposition temperature dependence of the defect-PL peak is very significant (cf. Fig. 1(a)). The lowly conductive samples (100°C, 125°C) have a broad band at 630-650 nm, which vanishes almost completely for ALD films in the electrical conductivity transition region (150°C). Starting from 175°C another band at 510-520 nm emerges, which reaches a maximum intensity at 225°C, before decreasing again for 250°C. Apart from slight variations in peak width the latter band is also found in the bulk-ZnO sample, i.e. a deposition temperature of 175°C or higher is required for ALD-samples to obtain an energetically similar configuration of the radiative levels deep in the bandgap. Most notably, that implicates that the radiative trap states are initially (at low deposition temperature) located at $\approx 1.9$ eV (not far from the mid-gap region at 1.625 eV) and shift towards a position of $\approx 2.4$ eV from the respective band edges for $T_{\text{depo}} \geq 175$°C, as schematically shown in Fig. 2. According to literature the PL-band peaked at 630-650 nm (100°C and 125°C samples) is caused by acceptor-like zinc vacancy defects [14-16], while the 510-520 nm band occurring at higher deposition temperature is related to deep-donor oxygen vacancy defects [16, 17]. Hence, in
Fig. 2 for the red PL-band the right schematic and for the green-yellow PL-band the left schematic appears to represent most likely the true recombination paths. It remains ambiguous whether there is a direct physical connection between the structural changes that enable the apparent switching of the defect-PL center and the more than one order of magnitude increase in conductivity when increasing the deposition temperature from 100 – 175°C or whether that is purely coincidental. It is noteworthy that the PL spectra shown here were recorded using a setup with a focused excitation laser beam, which implicates high excitation power densities. In contrast, our previous PL spectra as shown in Ref. [4] were recorded at only 0.16 W/cm². While differences in the PL-peak ratios of UV-peak and defect-peak are readily explainable by the vastly different excitation power dependencies, the ~1.9 eV PL-peak was not observed before under low excitation conditions. Further investigations spanning an even broader excitation power density range will have to clarify the origin of this observation.

Figure 1: (a) Room-temperature PL spectra of all samples excited with a laser excitation power of 316 W/cm². (b) Excitation power dependence from 10 to 1000 W/cm² of the UV-peak and the defect peak at 520 nm, exemplarily shown here for the 250°C-sample, which is representative for all other ALD-samples. Dashed lines are linear fits.
Figure 1(b) shows the excitation power dependence of both peaks and proves that no saturation occurs, not even for an excitation flux of 1000 W/cm², since both curves can be fitted linearly. This indicates that both peaks have very high recombination rates that easily cope with even the highest optical generation rates. However, the slope of the UV-peak is ~4-times higher than that of the defect peak, i.e., the excitation of interband transitions is significantly more efficient than radiative transitions mediated by trap states deep in the bandgap. In the range of approximately 100-1000 W/cm² the power dependence of the PL-intensities \( I \) can also be fitted with a power law function \( (I^\alpha) \), which results in exponents \( \alpha_{UV} \approx 1.2 \) and \( \alpha_{defect} \approx 0.9 \), which are similar to those found for ZnO-nanowires in Ref. [18].

Figure 2: Schematic of ZnO-bandgap according to the results from PL spectroscopy: The deep levels (dark blue areas where the black line indicates the PL-peak energy) causing the radiative recombination (green arrows) are located near mid-gap (dashed red line) for low ALD deposition temperatures and shift further away from mid-gap to the positions typically observed for bulk-ZnO for \( T \geq 175^\circ C \). At the transition between both regimes (150°C) almost no defect-PL is observed. For both bands both recombination options are shown: radiative transitions between the trap levels and photo-excited holes in the VB (left respectively) vs. radiative transitions between the trap levels and photo-excited electrons in the CB (right respectively). Please see text for a discussion of the origin of the defect-PL.
The very low absorption in the visible range of the ALD-ZnO for all deposition temperatures (absorption coefficients around $10^3$ cm$^{-1}$) [19] indicates that the radiative defects causing the defect peak have very small absorption cross sections, as usual for point defects. Instead of direct absorption of incident light, these defects are more likely to be populated by absorption of UV photons over the band gap, followed by a non-radiative relaxation into the respective defect state deep in the band gap and finally the radiative recombination. The number of photons generated by radiative recombination (interband and trap-mediated) with respect to the amount of absorbed UV-photons is described by the external quantum yield (EQY). In Fig. 3 the EQY under cw-laser excitation at 330 nm and with luminescence detection over the whole spectral range of the ZnO-PL peaks is shown. The ALD-ZnO samples have on average EQY values of only 0.37% without any dedicated trend with deposition temperature. In contrast, the single-crystalline bulk-ZnO sample has an EQY of 6.8%, i.e., its quantum yield is on average a factor of 18 higher compared to ALD-ZnO. We propose as explanation for this observation that the PL-competing non-radiative recombination is pronounced in ALD-ZnO and that the material is rich in non-radiative centers.
Figure 3: External quantum yield of the total PL-emission (350 – 1100 nm) from ZnO as function of ALD-deposition temperature in comparison with single-crystalline (0001)-ZnO. The bulk-ZnO sample is on average 18-times more efficient in PL emission than the ALD-ZnO samples.

Time-resolved PL measurements were carried out to probe the optical decay dynamics of the samples and to reveal the lifetimes of the excited states for both UV peak and defect peak. In Fig. 4 the ALD-ZnO PL-decays of the UV peak are compared to bulk ZnO.

Figure 4: Normalized time-resolved PL spectra measured near the UV-peak (395 nm) of all ALD-samples and bulk-ZnO (inset). The time scale of the decay of bulk-ZnO is an order of magnitude slower than for all ALD-samples.
Obviously, the luminescence decay of the UV-peak of ALD-ZnO is very fast and especially when compared to bulk-ZnO (see inset of Fig. 4). The latter can be fitted by a single-exponential decay with a time constant of $65.1 \pm 0.6$ ps. Fitting the ALD-ZnO decay curves reveals lifetimes of on average 4.8 ps, but these values are too close to the time resolution of the streak camera (~4 ps) to allow for any precise information. Still, it can be concluded that the UV-peak lifetime of ALD-ZnO is at least an order of magnitude faster than that of bulk-ZnO (neglecting the error introduced by the time resolution of the setup the lifetimes differ by a factor of at least ~14). We note that the decay curve of the 175°C-sample is slightly offset and appears to have a few-ps longer lifetime. However, we cannot correlate this observation to any special property of this sample and neglect it therefore as an artefact of this specific measurement.

![Figure 5](image)

**Figure 5:** (a) Normalized time-resolved PL decays measured at 500 nm, i.e., on the defect peak together with exponential fits (black dotted lines); all curves are vertically offset for the sake of better visibility. (b) Lifetime values of the defect PL-peak. The average defect-PL lifetime of all ALD-samples is similar to that of bulk-ZnO.
In Fig. 5(a) the time-resolved PL data measured on the defect PL-peak are shown. It turns out that all peaks can be reasonably fitted by single exponential decay functions. In addition, there are only marginal differences between the defect-PL lifetimes of ALD-ZnO and bulk-ZnO, as shown in Fig. 5(b). In fact, the average defect-PL lifetime of all ALD-samples is 106 ps which is well comparable to the bulk-ZnO sample (100 ps). It is noted that the lifetime of the 100°C and 125°C sample, which have the red defect-PL peak, have comparable lifetimes also at 600 nm (here 105 ps and 75 ps, respectively). This indicates that the dynamics of the radiative recombination via deep trap states is similar despite of the presumably different origin of red and green-yellow PL (zinc vacancy vs. oxygen vacancy). The circumstance that the deposition temperatures which yield highest conductive samples (200-225°C) [2, 4] have the longest lifetimes, is considered purely coincidental due to the absence of other correlations with conductivity, e.g. for the medium-low resistivities (150°C, 175°C, 250°C) in comparison with the poorly-conductive samples (100°C, 125°C), which all have essentially the same lifetimes.

Comparing the properties of ALD-ZnO to bulk-ZnO, we have a much lower resistivity, lower QY, and shorter lifetimes of the interband UV-PL for ALD-ZnO, but similar defect-PL lifetimes. Hence, the configuration of the deep radiative states has apparently no influence on the conductivity and the non-radiative states in the bandgap do obviously not interact with the defect-PL emission for both ZnO materials.

In order to explain the huge difference in QY (factor of ~18) and UV-peak lifetime (factor of ~14), we considered initially the free electron density which was recently determined by Hall measurements to range from $0.5 - 5 \times 10^{19} \text{ cm}^{-3}$ as function of ALD deposition temperature [5]. However, in this case there should be a dependence of QY and UV-peak lifetime on
Deposition temperature as the free carrier density increases by one order of magnitude from 100 to 200°C deposition temperature. Since no dependence with deposition temperature is observed, the high free carrier density represents, if at all, just one part of the explanation. The much shorter lifetimes of the UV-PL-peaks can be also explained by a high density of trap states quenching the luminescence, similar to the ZnO nanorods described in [20]. The lifetime of the UV peak of bulk-ZnO is more than an order of magnitude longer than for the ALD samples. Therefore, the non-radiative recombination rate for ALD-ZnO must be considerably higher than for bulk ZnO. The relation between quantum yield and the measured lifetime ($\tau_{\text{meas}}$) of a PL peak is given by:

$$QY = \frac{\tau_{\text{meas}}}{\tau_{\text{rad}}},$$

where $\tau_{\text{rad}}$ denotes the radiative lifetime of the luminescing state. The relation between this lifetime and the non-radiative lifetime ($\tau_{\text{non-rad}}$) is given by:

$$1/\tau_{\text{meas}} = 1/\tau_{\text{rad}} + 1/\tau_{\text{non-rad}}.$$

Given that the internal lifetime of the interband transition ($\tau_{\text{rad}}$) is the same for all kinds of ZnO, i.e. $\tau_{\text{rad,ALD}} = \tau_{\text{rad,bulk}}$, the following relation is deduced:

$$\frac{QY_{\text{bulk}}}{QY_{\text{ALD}}} = \frac{\tau_{\text{meas,bulk}}}{\tau_{\text{meas,ALD}}}.$$

The measured QY shown in Fig. 3 is 6.8 % for bulk and 0.37 % for the ALD samples which gives an QY ratio of ~18. Comparing this value with the ratio of the bulk lifetime and the approximated ALD UV-peak lifetime of at least ~14, we find a reasonable agreement. The shorter UV-peak lifetimes and the significantly lower QY of the ALD-samples can be explained by much higher non-radiative recombination rate, or in other words, an at least one order of magnitude higher density of non-radiative defect states in ALD-ZnO. Taking into account the poly-crystalline morphology of ALD-ZnO these defects could reside on the abundant grain boundaries or simply at the thin film surface, which is generally a highly
defective part in a semiconductor. Alternatively, the very low deposition temperature of ALD does not allow for significant surface diffusion during growth and hence a high intrinsic point defect density is also likely. On the other hand, a significantly higher ALD-deposition temperature is incompatible with high conductivities, due to the maximum observed around 200°C [5]. Also, any kind of thermal post-deposition treatment just decreases the conductivity, irrespective of the ambient or atmosphere used [21]. Therefore, one possible route of optimization of the conductivity aims at improving the poly-crystalline quality by the choice of substrate material. Owing to circumstances, a crystalline surface with suitable lattice parameters could result in larger crystalline grain sizes and thereby less grain boundary defects than the amorphous silicon oxide surface used so far. Besides, the ALD-process parameters such as precursor dose time or pump/purge time might have influence on the point defect density of ALD-ZnO and should be critically reviewed in future for their optimization potential.
IV. CONCLUSIONS

The quantum yield and the dynamics of the photoluminescence of both single-crystalline bulk-ZnO and ALD-ZnO thin films were measured. The EQY of bulk-ZnO was found to be ~18-times higher than for ALD-ZnO and the lifetime of the interband transition (UV-peak) was found to be at least ~14-times faster. This can be explained by an approximately one order of magnitude higher density of non-radiative states in ALD-ZnO. Although the conduction electron density varies significantly with increasing deposition temperature only little influence of that on the PL dynamics is observed, while spectrally the red defect-PL band disappears and the green-yellow band emerges. We conclude that the optical and electrical properties of ALD-ZnO are not directly correlated, i.e., neither QY nor TR-PL measurements allow to estimate the conductivity or free carrier density. On the other hand, the comparison of the optical properties to single-crystalline (0001)-ZnO reveals that further potential of improving ALD-ZnO conductivity might reside in the optimization of the poly-crystalline quality by a suitable choice of substrate or the ALD-process parameters apart from the temperature.

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