OPTICAL SPECTRA OF THIN INTRINSIC AND AL DOPED NANOCRYSTALLINE ZNO THIN LAYERS DEPOSITED BY PULSED LASER DEPOSITION ON FUSED SILICA GLASS SUBSTRATES

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Abstract

Zinc oxide (ZnO) is a low-cost and environmentally friendly material with unique optical properties and a variety of nano and microstructures imposing challenges for energy conversion, scintillators, photocatalytic wastewater treatment, electrochemical energy storage, or sensing applications. In this work, the nominally undoped and Al-doped nanocrystalline ZnO thin layers were pulsed laser deposited (PLD) on fused silica glass. The samples were characterized by photothermal deflection (PDS) and photoluminescence (PLS) spectroscopy. Excitons were observed at low temperature in both samples at about 3.4 eV. The intrinsic samples show the red PL in near infrared region at about 1.9 eV related to zinc vacancies. The results show that optical properties can be evaluated from optical spectra of very thin nanocrystalline ZnO layers with the thickness below 100 nm.

Keywords: Pulse laser deposition, wide band gap semiconductors, optical properties, doping

1. INTRODUCTION

Zinc oxide is a low-cost and environmentally friendly material with unique optical properties and a variety of nano and microstructures imposing challenges for energy conversion, scintillators, photocatalytic wastewater treatment, electrochemical energy storage or sensing applications [1-3]. A number of typical dopant elements such as F, B, Al, Ga, In and Sn have been used so far to produce conducting ZnO films. It is worth underlining that among all the group III elements, Al is a cheap, abundant and non-toxic material [4]. Thus Al-doped ZnO films are prominent, low-cost substitutes for indium tin oxide films as transparent conducting films in the photovoltaic and sensor applications [5-7].

In this paper, we use the PLD setup [8] to deposit very thin nanocrystalline intrinsic and Al-doped ZnO films on fused silica glass substrates to prove that the optical parameters can be evaluated even from the optical spectra of very thin polycrystalline ZnO films with thickness below 100 nm.

1.1 Pulse laser deposition (PLD)

Polycrystalline ZnO and Al-doped ZnO layers were prepared on fused silica substrates by pulsed laser deposition (PLD) setup from TSST B.V. equipped with KrF (λ = 248 nm) excimer laser COMPex 50. After reaching a base pressure of 10^{-4} Pa, oxygen was introduced with process pressures of 10 Pa with a flow rate

of 10 cm^3/min. The substrates were placed into a rotating holder (5 rpm). The excimer laser was focused to a spot of the area of 2 mm^2 and set up at the repetition rate of 20 Hz for target ablation. For the deposition from the stoichiometric targets, the pulse energy (measured inside the chamber) was kept at about 24 mJ giving the fluence of 1.2 J/cm^2, respectively. The number of pulses was 20 000 (sample A) and 40 000 (sample B) throughout the experiment, yielding in both cases layers with thickness about 80 nm, see **Table 1**. After the deposition, samples were cooled inside the chamber. We previously discovered a strong effect of the atmosphere during this cool-down step [10].

Table 1 The nanocrystalline ZnO films deposited by PLD on fused silica glass substrates, including the thickness (*d*), the dielectric constant (ε_∞), the parameters of the Lorenc (A, E_0 and E_1) and Drude models (E_p and E_2) as well as the optical absorption coefficient at 1 eV (α)

Sample	*d* (nm)	ε_∞	*A*	E_0(eV)	E_1(eV)	E_p(eV)	E_2(eV)	α (cm^{-1})
A (undoped)	85	3.32	1.21	3.61	0.17	0.18	0.59	< 10
B (Al-doped)	77	3.28	1.41	3.82	0.05	0.39	0.11	730

1.2 Photothermal deflection spectroscopy (PDS)

The transmittance, reflectance and absorptance spectra were measured simultaneously in the 300–1400 nm spectral range by photothermal deflection spectroscopy (PDS) setup with 150 W Xe lamp, SpectraPro-150 monochromator (150-mm focal length, f/4-aperture, slits 1/1mm) equipped with two gratings: a UV holographic (1200 /mm) and a ruled (600 /mm) blazed at 500 nm. The spectral resolution was 5 nm with the UV holographic grating and 10 nm with the ruled grating. Samples were immersed into liquid (Florinert FC72) to measure the relative temperature of the illuminated sample independently for selected photon energies using deflection of probe laser beam. The spectra were spectrally calibrated by measuring PDS of a black carbon sample.

1.3 Photoluminescence spectroscopy (PLS)

PL spectra were measured at low temperature in the spectral range 360-700 nm with a spectral resolution of 2 nm using a closed He-circle cryostat OptistatDry (Oxford Instruments, UK) and a focused UV LED (1 mW Thorlabs M340F3) equipped with narrow bandpass (BP340) and long pass (LP350) optical filters, operating in ac mode at a frequency of 307 Hz. The emitted light was collected and focused onto the 1 mm wide input slit of double gratings SPEX 1672 monochromator (220-mm focal length, f/4-aperture, 1200/mm grating, 1/1 mm slits, spectral resolution 2 nm) equipped with Peltier cooled red sensitive photomultiplier (PMT) and a current preamplifier with 10^5 V/A transimpedance (Ametex 5182) to be measured at selected photon energies independently by a lock-in amplifier (Ametex 5105) with ac noise level about 10 pA (1 μV). The whole setup was spectrally calibrated with Oriel #63358 Quartz Tungsten halogen lamp and converted from wavelength to energy scale for quantitative analysis.

2. RESULTS AND DISCUSSION

Figure 1 shows the transmittance (T), reflectance (R) and absorptance (A) spectra of the Al-doped ZnO layer (sample B). Absorptance spectrum was measured using PDS and put into the absolute scale using 1-*R*-*T* spectrum. It should be noted that unlike PDS, which measures *A* directly, the 1-*R*-*T* spectrum cannot be used to evaluate *A* below 1%. The dielectric function ε (the complex index of refraction $n + ik$) as a function of energy *E* and the film thickness *d* were evaluated from the reflectance spectra using Lorenc and Drude models [10] included in the commercial *FimWizard*(c) software (https://sci-soft.com/product/film-wizard/), see Equation 1 and **Table 1**.

$$\varepsilon(E) = (n + ik)^2 = \varepsilon_\infty \left(1 + \frac{A^2}{E_0^2 - E^2 + iE_1^2} + \frac{E_p^2}{E(E - iE_2)}\right) \quad (1)$$

The fit of *R* spectra is shown in **Figure 2**. **Table 1** also shows the shifts of the central position of the Lorenc peak (E_0) and the plasma energy (E_p) as expected. Once the index of refraction $n(E)$ and the film thickness d were known, the optical absorption coefficient $\alpha(E)$ was evaluated from PDS spectra independently at each measured photon energy E [11], see **Figure 4**.

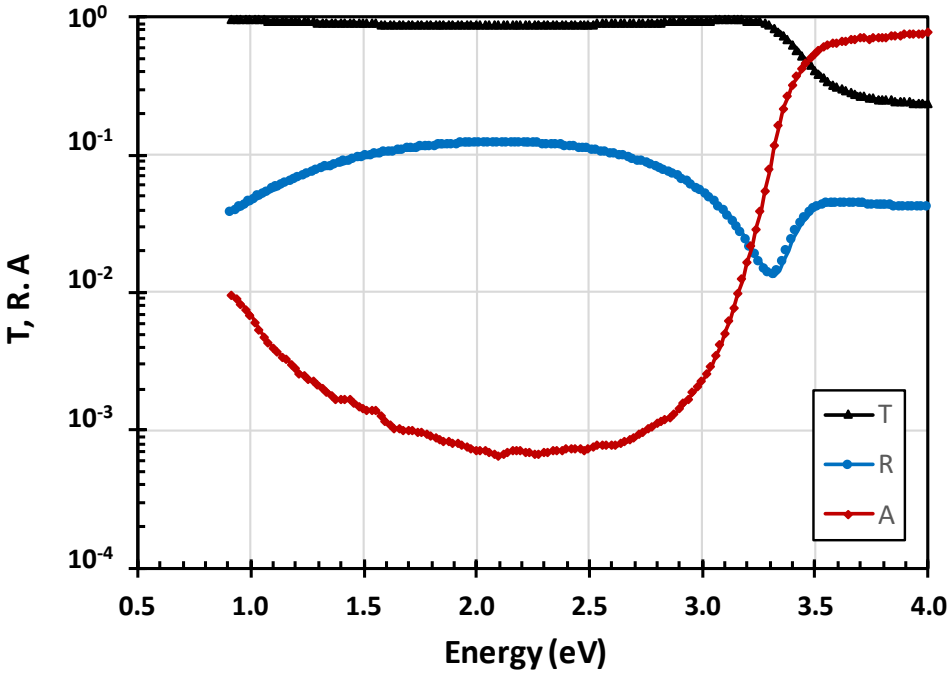

Figure 1 The transmittance (*T*), reflectance (*R*) and absorptance (*A*) spectra of the Al-doped ZnO layer (sample B)

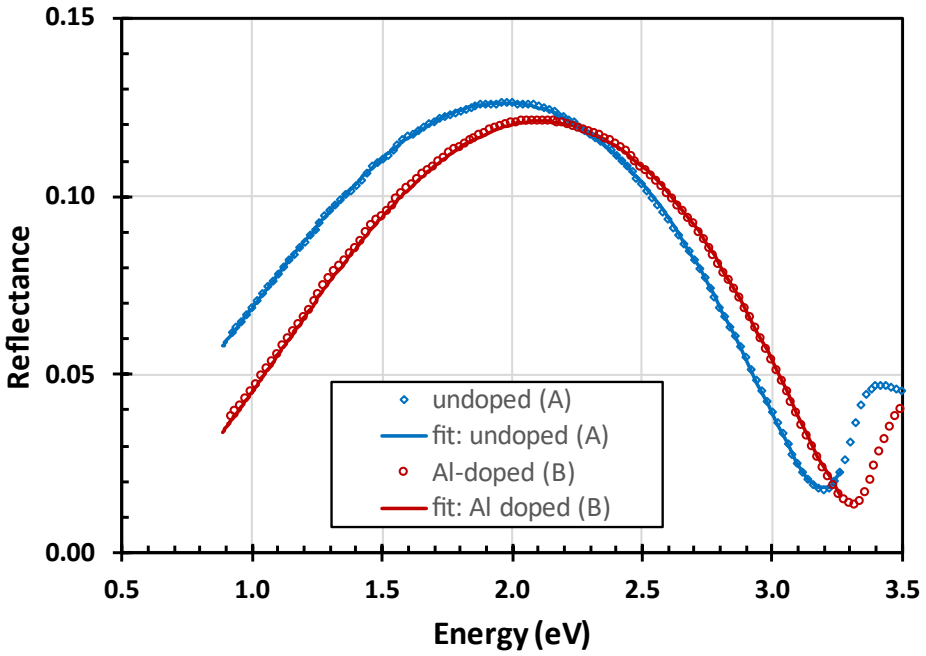

Figure 2 The measured (points) and fitted (solid line) reflectance spectra of the undoped (sample A) and Al-doped (sample B) ZnO layers

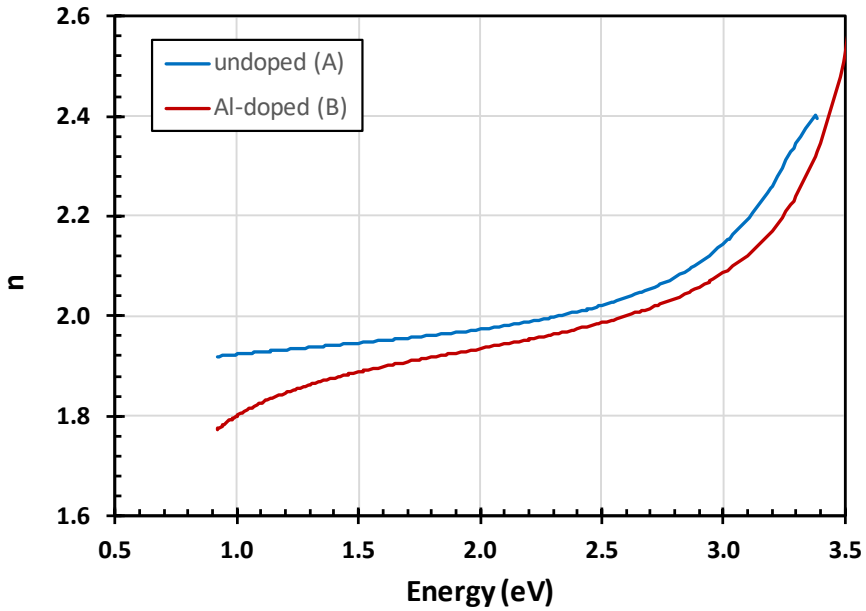

Figure 3 The spectra of the index of refraction of the nominally undoped (A) and Al-doped (B) ZnO layers

The direct bad gap of ZnO [12] is not clearly visible in **Figure 4** because of the Urbach edge [13], localized states below the optical absorption edge related to deep defects and the free carrier absorption in IR region in the case of Al-doped sample. The perturbation imposed by Al atom incorporation leads to the atomic relaxation. This phenomenon influences atomic rearrangement near Al impurity and generates a free electron in the conduction band, which can be considered as a large radius electron polaron increasing the n-type electrical conductivity in the crystal in agreement with the known experimental data [14]. The Burstein–Moss shift, in which the apparent band gap of a semiconductor is increased because of populated states close to the conduction band is also observed [15].

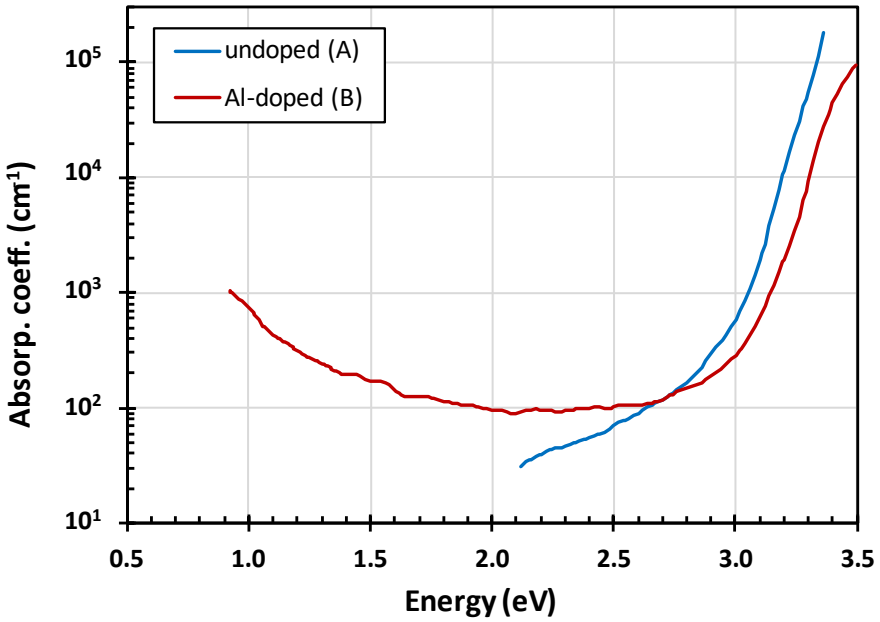

Figure 4 Optical absorption coefficient spectra of the intrinsic and Al-doped ZnO layers. The optical absorptance of the undoped ZnO was below 2.1 eV too low to evaluate the absorption coefficient

There was no measurable PL at room temperature. **Figure 5** shows the PL spectra of the intrinsic and Al doped ZnO layers measured at low temperature under UV LED excitation (340 nm, 1 mW). Excitons observed in both samples at low temperature at about 3.4 eV are more pronounced in Al doped ZnO layer. The intrinsic sample shows the vacancy related PL in near infrared region at about 1.9 eV as it was explained in our previous paper [16].

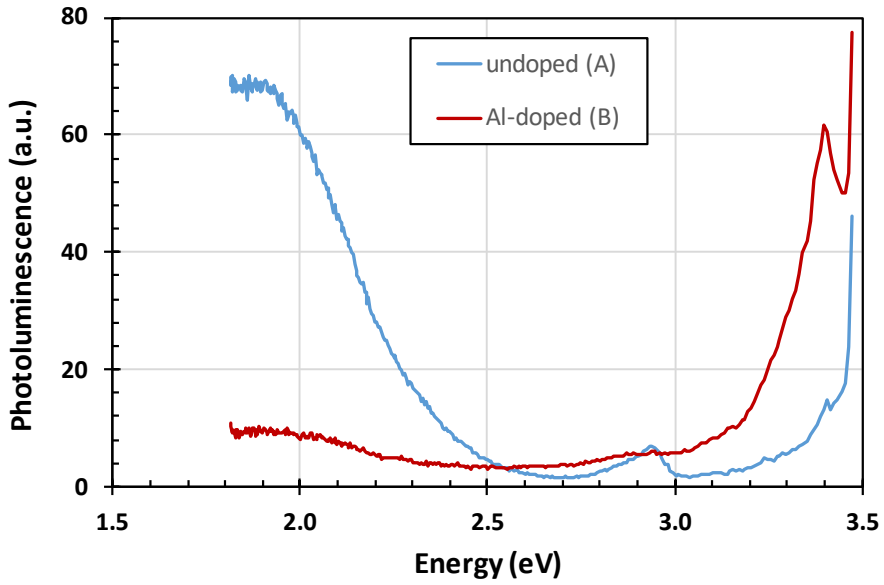

Figure 5 Photoluminescence spectra of the intrinsic (sample A) and the Al-doped ZnO layers (sample B) measured at low temperature (nominally 4 K) under UV LED excitation

3. CONCLUSION

The thin intrinsic and Al-doped nanocrystalline ZnO layers were deposited by PLD on fused silica substrates. The effect of Al doping on the optical properties was investigated. The complex index of refraction and the film thickness were evaluated from the reflectance spectra using Lorenc and Drude models and the commercial *FimWizard* software. The optical absorption coefficient was evaluated from PDS spectra independently. Excitons were observed in photoluminescence spectra at low temperature in both samples at about 3.4 eV. The PLS in near infrared region at about 1.9 eV is related to vacancies. The results show that optical properties can be evaluated from optical spectra of very thin nanocrystalline ZnO layers with the thickness below 100 nm.

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REFERENCES

[1] KLINGSHIRN, C. F., ed. *Zinc Oxide: from fundamental properties towards novel applications*. B.m.: Springer, 2010. Springer series in materials science, 120. ISBN 978-3-642-10576-0.

[2] KLINGSHIRN, Claus, J. FALLERT, H. ZHOU, J. SARTOR, C. THIELE, F. MAIER-FLAIG, D. SCHNEIDER a H. KALT. 65 years of ZnO research - old and very recent results. *physica status solidi (b)* 2010, vol. 247, no. 6, pp. 1424–1447. Available from: https://doi.org/10.1002/pssb.200983195

[3] KLINGSHIRN, Claus F. *Semiconductor optics*. 3rd ed. Berlin New York: Springer, 2007. ISBN 978-3-540-38347-5.

[4] GÜRBÜZ, Osman, İsmail KURT, Serkan ÇALIŞKAN a Sadık GÜNER. Influence of Al concentration and annealing temperature on structural, optical, and electrical properties of Al co-doped ZnO thin films. *Applied Surface Science* 2015, vol. 349, pp. 549–560. Available from: https://doi.org/10.1016/j.apsusc.2015.04.233

[5] HAO, Ming, Xianhang LU, Fei SUN, Yunhe FU, Yaoshuai BA, Yuanhua XIE a Kun LIU. Optoelectronic effect of Al-based buffer layers on Al-doped ZnO thin transparent conductive films on flexible substrates. *Optical Materials* 2024, vol .157, 116179. Available from: https://doi.org/10.1016/j.optmat.2024.116179

[6] BENAMARA, Majdi, Pedro RIVERO-ANTÚNEZ, Hassen DAHMAN, Manel ESSID, Souhir BOUZIDI, Marc DEBLIQUY, Driss LAHEM, Víctor MORALES-FLÓREZ, Luis ESQUIVIAS, José P. B. SILVA a Lassaad EL MIR. Selective and rapid detection of acetone using aluminum-doped zno-based sensors. *Journal of Sol-Gel Science and Technology* 2023, vol. 108, no. 1, pp. 13–27. Available from: https://doi.org/10.1007/s10971-023-06197-5

[7] YOO, Ran, Andreas T. GÜNTNER, Yunji PARK, Hyun Jun RIM, Hyun-Sook LEE a Wooyoung LEE. Sensing of acetone by Al-doped ZnO. *Sensors and Actuators B: Chemical*. 2019, vol. 283, pp. 107–115. Available from: https://doi.org/10.1016/j.snb.2018.12.001

[8] HOLOVSKÝ, Jakub, Eva HORYNOVÁ, Lukáš HORÁK, Katarína RIDZOŇOVÁ, Zdeněk REMEŠ, Lucie LANDOVÁ a Rupendra Kumar SHARMA. Pulsed laser deposition of high-transparency molybdenum oxide thin films. *Vacuum* 2021, vol. 194, 110613. Available from: https://doi.org/10.1016/j.vacuum.2021.110613

[9] HORYNOVÁ, Eva, Oleksandr ROMANYUK, Lukáš HORÁK, Zdeněk REMEŠ, Brianna CONRAD, Amalraj PETER AMALATHAS, Lucie LANDOVÁ, Jana HOUDKOVÁ, Petr JIŘÍČEK, Tomáš FINSTERLE a Jakub HOLOVSKÝ. Optical characterization of low temperature amorphous MoOx, WOX, and VOx prepared by pulsed laser deposition. *Thin Solid Films.* 2020, vol. 693, 137690. Available from: https://doi.org/10.1016/j.tsf.2019.137690

[10] TOMPKINS, Harland G. *Spectroscopic ellipsometry and reflectometry: a user's guide*. New York: Wiley, 1999. ISBN 0-471-18172-2.

[11] FOWLES, Grant R. *Introduction to modern optics*. 2nd ed., Dover ed. New York: Dover Publications, 1989. ISBN 978-0-486-65957-2.

[12] PANKOVE, Jacques I. *Optical processes in semiconductors*. Unabridged republication, with slight corr. Mineola [NY]: Dover, 1975. ISBN 978-0-486-60275-2.

[13] URBACH, Franz. The Long-Wavelength Edge of Photographic Sensitivity and of the Electronic Absorption of Solids. *Physical Review* 1953, vol. 92, no. 5, pp. 1324–1324. Available from: https://doi.org/10.1103/PhysRev.92.1324

[14] MALDONADO, Frank a Arvids STASHANS. Al-doped ZnO: Electronic, electrical and structural properties. *Journal of Physics and Chemistry of Solids.* 2010, vol. 71, no. 5, pp. 784–787. Available from: https://doi.org/10.1016/j.jpcs.2010.02.001

[15] BURSTEIN, Elias. Anomalous Optical Absorption Limit in InSb. *Physical Review.* 1954, vol. 93, no. 3, pp. 632–633. Available from: https://doi.org/10.1103/PhysRev.93.632

[16] BURYI, M., V. BABIN, Y.-Y. CHANG, Z. REMEŠ, J. MIČOVÁ a D. ŠIMEK. Influence of precursor age on defect states in ZnO nanorods. *Applied Surface Science* 2020, vol. 525, 146448. Available from: https://doi.org/10.1016/j.apsusc.2020.146448