Impact of air-exposure on the chemical and electronic structure of ZnO:Zn$_3$N$_2$ thin films

M. Bär[*][1], K.-S. Ahn[2], S. Shet[2], Y. Yan[2], L. Weinhardt[1], O. Fuchs[3], M. Blum[3], S. Pookpanratana[1], K. George[1], W. Yang[4], J.D. Denlinger[4], M. Al-Jassim[2], and C. Heske[1]

[1]*Department of Chemistry, University of Nevada, Las Vegas (UNLV), 4505 Maryland Parkway, Box 454003, Las Vegas, Nevada 89154-4003, U.S.A.*

[2]*National Renewable Energy Laboratory (NREL), 1617 Cole Boulevard, Golden, Colorado 80401, U.S.A.*

[3]*Experimentelle Physik II, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany*

[4]*Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, 1 Cyclotron Rd., Berkeley, California 94720, U.S.A.*

The chemical and electronic surface structure of ZnO:Zn$_3$N$_2$ ("ZnO:N") thin films with different N contents was investigated by soft x-ray emission spectroscopy. Upon exposure to ambient air (in contrast to storage in vacuum), the chemical and electronic surface structure of the ZnO:N films changes substantially. In particular, we find that the Zn$_3$N$_2$/(Zn$_3$N$_2$+ZnO) ratio decreases with exposure time and that this change depends on the initial N content. We suggest a degradation mechanism based on the reaction of the Zn$_3$N$_2$ content with atmospheric humidity.

[*]Corresponding author. Email: baerm2@unlv.nevada.edu. Phone: 001-702-895-5078. Fax: 001-702-895-4072

In the past, ZnO has been used in a large variety of applications[1]. For example, its wide band gap (E_g^{ZnO} = 3.3 eV[2]) and large exciton binding energy make it a promising material for UV optoelectronic devices[1,3]. Recently[4], ZnO has also been suggested as a candidate material for photoelectrochemical (PEC) applications such as hydrogen production. Since ZnO possesses similar or even better optical and electronic properties than TiO_2 (which has received much PEC attention in the past[5]), it is expected to result in good PEC performance if chemical stability can be achieved. As in the case of TiO_2, E_g^{ZnO} is too large to effectively use the full spectrum of solar irradiation. It is therefore critical for PEC applications to reduce E_g^{ZnO}. One possible approach is to mix ZnO with Zn_3N_2. Despite the reported wide range of optical band gap energies for Zn_3N_2 ($\sim 1.0 - 3.2$ eV[6]) a reduction of E_g is expected. Since the chemical activity of O is much higher than that of N[7], it is difficult to incorporate N into ZnO even in the case of much lower N concentration (as used for p-type doping[1,3,8]). However, theoretical studies[9] show that the incorporation of N in ZnO can be enhanced by increasing the "chemical potential" of the N source.

Recently, a corresponding reactive radio frequency (RF) sputter technique-based deposition method[10] was developed at NREL. It uses the RF sputter power as parameter to control the incorporation of N. Such layers show an increasing N content with increasing sputter power and the (expected) corresponding E_g reduction down to 1.76 eV for a N content of approx. 35 at%.[10] This confirms that $ZnO:Zn_3N_2$ ("ZnO:N") thin films can be prepared by this approach. Corresponding layers show a higher photo response than pure ZnO[4], which is promising for their application in PEC. However, indications were found that the ZnO:N films are not stable in the electrolyte, which is critical in terms of PEC application. Furthermore, we observe discoloration of ZnO:N films with high N content after prolonged storage in ambient air.

We have therefore used soft x-ray emission spectroscopy (XES) to study the chemical and electronic (surface) structure of ZnO:N layers with different N contents. In particular, we focus on electronic and

chemical changes upon ambient air exposure in order to identify instabilities and their underlying mechanisms.

ZnO:N thin films (approx. 500 nm thick) were deposited on F-doped SnO_2/glass substrates by reactive RF sputtering using a Zn metal target in mixed O_2 and N_2 ambient [$O_2/(O_2+N_2O) = 5$ % , see Ref. 10 for more details]. Two sets of samples were investigated. For the first (second) set, the RF power was varied between 80 and 200 W (100 and 150 W). The sample sets were each complemented by pure ZnO layers prepared in O_2 atmosphere using an RF power of 80 W. The first set was exposed to air for approx. one month before XES characterization. For the second sample set the time between preparation and initial characterization was minimized (to a few hours) and great care was taken that the samples were not exposed to ambient air before initial characterization. The latter was accomplished by using N_2-filled glovebags for sample transfer, packaging/sealing (in polyethylene bags), and mounting. Note also that the second sample set was prepared using a significantly modified sputter system (different sputter gun as well as geometry). The XES measurements were conducted at the ALS using the SXF x-ray spectrometer at Beamline 8.0.1. The energy scale of the O K emission window was calibrated using the literature value[11] for the Zn L_2 emission (1034.7 eV). The composition of the samples was determined by quantitative energy dispersive spectroscopy (EDS) on respective cross sections using the nano probe in an FEI Tecnai F20 transmission electron microscope (TEM).

Fig. 1a shows the O K XES spectra of the first (i.e., air-exposed) sample set. The spectra are dominated by four distinct features A-D. A, B, and C are ascribed to hybridized O 2p – Zn 4p, Zn 4s, and Zn 3d states[12], respectively, decaying into the O 1s core hole. Feature D, in contrast, is attributed to the Zn L_2 emission (excited and detected in 2nd order). In the following, we thus use feature C as an indicator for oxygen atoms in O-Zn bonds, while feature D is a measure for the entire Zn content irrespective of chemical environment. Comparison of the O K XES spectra for ZnO and the different ZnO:N layers up to 120 W reveals that the position of the maximum shifts from approx. 526.6 to 526.4 eV with increasing RF power (the spectrum for 150 W will be discussed below). Furthermore, the

shoulder at approx. 523.9 eV (feature B) becomes less pronounced but increases in intensity (with respect to feature A). Close inspection of features C and D (Fig. 1b) as well as of the onset at high emission energies (i.e., the region near the valence band maximum, VBM, Fig. 1c) shows that the D/C intensity ratio increases with increasing RF power and that the onset of the O K spectra is shifted towards higher emission energies (i.e., opposite to their maximum). The latter is in good agreement with theoretical considerations[10] showing that the incorporation of N into ZnO (and hence the presence of N 2p states) shifts the VBM towards lower binding energies (here: higher emission energies). Theory also suggests that this VBM shift is primarily responsible for the E_g reduction, since no shift of the position of the conduction band minimum (CBM) was observed in corresponding calculations[10]. An analysis of the onsets of respective x-ray absorption spectra (not shown) indeed shows no significant CBM shifts, corroborating the theoretical predictions.

The O K XES spectra of the 150 W and 200 W ZnO:N samples (spectrum of the latter not shown), are very similar and present a very different behavior compared to the low RF power samples. The O K XES maximum is shifted back to approx. 526.6 eV, the shoulder B is more pronounced and reduced in intensity, the D/C ratio is reduced (not shown), and the onset of the spectrum shifts back to lower emission energy (not shown). The spectra of the 150 W and 200 W samples hence closely resemble that of the pure ZnO layer in Fig. 1.

In order to shed light on this observation, we derived the $Zn_3N_2/(Zn_3N_2+ZnO)$ ratio of the ZnO:N samples from our XES data. To avoid quantification uncertainties induced by determination of the excitation intensity and optimization of the sample positions for each measurement, intensity *ratios* rather than absolute intensities were used. As mentioned above, feature C (hybridized O 2p – Zn 3d states) is directly indicative for oxygen atoms in O-Zn bonds, while feature D (Zn L_2 emission) is a measure for all Zn atoms in the probed volume. Thus, assuming that the investigated samples are exclusively composed of Zn_3N_2 and ZnO and using the D/C intensity of the pure ZnO sample [D/C(ZnO)] as reference, one can use the D/C intensity ratio of the different samples to determine their

$Zn_3N_2/(Zn_3N_2+ZnO)$ ratio as $\{1-[D/C : D/C(ZnO)]\}$. The corresponding $Zn_3N_2/(Zn_3N_2+ZnO)$ values are shown in Fig. 2a in comparison to the composition derived by EDS (Fig. 2b presents the dependence of $Zn_3N_2/(Zn_3N_2+ZnO)$ on air-exposure time and will be discussed in conjunction with Fig. 3). We observe an increasing $Zn_3N_2/(Zn_3N_2+ZnO)$ ratio with increasing RF power up to 120 W. The XES data for the 150 W and 200 W ZnO:N samples, however, suggests a composition similar to the pure ZnO sample (as expected from the respective spectra in Fig. 1a). Note that this composition trend was also observed when using the absolute intensities of the O K and N K XES spectra to determine the $Zn_3N_2/(Zn_3N_2+ZnO)$ ratios. Up to an RF power of 120 W, the composition deduced from XES agrees (within the error bars) well with the composition derived by EDS. For the 150 W sample, the EDS data indicates a $Zn_3N_2/(Zn_3N_2+ZnO)$ ratio of 52.5 %, while the XES data suggests – as already mentioned – a composition similar to that of pure ZnO. We ascribe this difference to the fact that the EDS characterization was performed right after sample preparation, while significant air exposure occurred prior to the characterization by XES[13]. This finding points to an air exposure induced modification of the chemical surface structure of ZnO:N samples prepared by RF powers > 120 W. Hence, the instability mechanism apparently depends on the initial $Zn_3N_2/(Zn_3N_2+ZnO)$ ratio of the ZnO:N sample.

To further investigate the impact of air exposure, a second ZnO:N sample set was characterized. The samples were not exposed to ambient air (before initial characterization) and immediately measured after preparation. The corresponding spectra are shown in both panels of Fig. 3 (black dots). In comparison to the corresponding spectra of the first sample set, we observe that the (initial) D/C intensity ratio is higher, indicating that the ZnO:N samples of the second set have a higher $Zn_3N_2/(Zn_3N_2+ZnO)$ ratio. After initial characterization, the ZnO:N samples were cut into two pieces. One set was stored in ambient air and the other one was stored in the vacuum of the load-lock chamber attached to the SXF analysis chamber. Note that the latter set was hence occasionally (and very briefly) exposed to dry-nitrogen, which is used to vent the load-lock chamber for sample transfers. After five days, the samples were re-characterized (red spectra in Fig. 3). While no significant spectral changes can

be observed for the pure ZnO samples or the ZnO:N samples stored in vacuum[14], the O K spectra of the ZnO:N samples exposed to ambient air show substantial changes. Compared to the initial O K spectra, the D/C intensity ratio as well as the intensity of feature B is decreased, and the onset at high emission energy is shifted to lower emission energies. All of this indicates a decrease of the $Zn_3N_2/(Zn_3N_2+ZnO)$ ratio at the sample surfaces (see discussion above). An additional re-characterization after 196 days of air exposure (blue spectra, Fig. 3, left) shows a continuation of this trend. Furthermore, we observe that these changes are more pronounced for high RF powers. The quantification of the $Zn_3N_2/(Zn_3N_2+ZnO)$ ratio (using the above-described D/C intensity ratio approach) reveals that the "loss" of N indeed depends on the RF power and thus on the initial $Zn_3N_2/(Zn_3N_2+ZnO)$ ratio of the ZnO:N layer, as shown in Fig. 2b.

According to the enthalpy of formation of ZnO (-350.5 kJ/mol[15]) and Zn_3N_2 (-22.6 kJ/mol[16]), ZnO is significantly more stable than Zn_3N_2. Thus, an explanation for the "loss" of N and hence the decrease of the $Zn_3N_2/(Zn_3N_2+ZnO)$ ratio observed for the air exposed ZnO:N samples could be based on the (thermodynamically likely) conversion of Zn_3N_2 to ZnO in ambient air, but not in vacuum. Already in 1875[17], it was reported that Zn_3N_2 is stable under "exclusion of air" (i.e., vacuum), and that it will heavily decompose when brought into contact with H_2O (i.e., $Zn_3N_2 + 3H_2O \rightarrow 3ZnO + 2NH_3$).[18] Thus, we speculate that the humidity in the ambient air is already sufficient to initiate this process for our air-exposed ZnO:N samples explaining the observed decrease of the $Zn_3N_2/(Zn_3N_2+ZnO)$ ratio.

In summary, we have utilized soft x-ray emission spectroscopy for the (quantitative) investigation of the chemical and electronic surface structure of ZnO:N layers. It was found that while the ZnO:N layers are stable in vacuum, they degrade (presumably due to the humidity) in ambient air. The observed change in surface composition is dependent on exposure time and initial $Zn_3N_2/(Zn_3N_2+ZnO)$ ratio of the ZnO:N layer. Thus, the large range of reported band gap values for Zn_3N_2[6] may – based on our data – in fact very well be explained by a different degree of degradation. Even though the N content is much higher in our case, the findings might provide also new insight on the variety of findings[8] and

instability[19] reported for N-doped p-type ZnO. In the context of PEC for hydrogen production, the findings demonstrate the susceptibility of ZnO:N to ambient conditions and show that XES is a uniquely suited tool to monitor such influences, possibly even under *in-situ* conditions.

[1]C. Klingshirn, Phys. Stat. Sol. B 244, 3027 (2007).

[2]J.I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971).

[3]Ü. Özgür, Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, and H. Morkoç, J. Appl. Phys. **98**, 041301 (2005).

[4]K.-S. Ahn, Y. Yan, S.-H. Lee, T. Deutsch, J. Turner, C.E. Tracy, C.L. Perkins, and M. Al-Jassim, J. Electrochem. Soc. **154**, B956 (2007).

[5]B. O'Regan and M. Grätzel, Nature **353**, 737 (1991).

[6]K. Toyoura, H. Tsujimura, T. Goto, K. Hachiya, R. Hagiwara, and Y. Ito, Thin Solid Films **492**, 88 (2005); M. Futsuhara, K. Yoshioka, and O. Takai, Thin Solid Films **322**, 274 (1998); F. Zong, H. Ma, W. Du, J. Ma, X. Zhang, H. Xiao, F. Ji, and C. Xue, Appl. Surf. Sci. **252**, 7983 (2006); K. Kuriyama, Y. Takahashi, and F. Sunohara, Phys. Rev. B **48**, 2781 (1993).

[7]B.S. Li, Y.C. Liu, Z.Z. Zhi, D.Z. Shen, Y.M. Lu, J.Y. Zhang, X.W. Fan, R.X. Mu, and D.O. Henderson, J. Mater. Res. **18**, 8 (2003).

[8]D.C. Look, D.C. Reynolds, C.W. Litton, R.L. Jones, D.B. Eason, and G. Cantwell, Appl. Phys. Lett. **81**, 1830 (2002); D.C. Look and B. Claflin, Phys. Stat. Sol. B **241**, 624 (2004).

[9]Y. Yan, S.B. Zhang, and S.T. Pantelides, Phys. Rev. Lett. **86**, 5723 (2001)

[10]K.-S. Ahn, Y. Yan, and M. Al-Jassim, J. Vac. Sci. Technol. B **25**, L23 (2007).

[11]*X-ray data booklet*, 2nd edition, Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720, 2001.

[12]T. Strunskus, O. Fuchs, L. Weinhardt, C. Heske, M. Guraya, M. Muhler, V. Staemmler, Ch. Wöll, J. Electron Spectrosc. Rel. Phenom. **134**, 183 (2004); C.L. Dong, C. Persson, L. Vayssieres, A. Augustsson, T. Schmitt, M. Mattesini, R. Ahuja, C.L. Chang, and J.-H. Guo, Phys. Rev. B. **70**, 195325 (2004).

[13]Another possible explanation could be based on the different information depths (defined as the depth from which 95 % of the signals is collected) of XES [~ 270 nm in ZnO for O K XES; B.L. Henke, E.M. Gullikson, and J.C. Davis, Atomic Data and Nuclear Data Tables **54**, 181 (1993), http://henke.lbl.gov/optical_constants/atten2.html] and EDS (in the μm-range). In our case, however, this does not apply since a TEM nano probe on sample *cross sections* was used for the here-considered EDS measurements.

[14]Close inspection of the O K spectra before and after 5 days in vacuum actually reveals a slight increase of the D/C intensity ratio. One (speculative) explanation for this observation could be the initial presence and later vacuum-dehydratization of $Zn(OH)_2$ in the ZnO:N samples (see K. Hirokawa and Y. Danzaki, Surf. Interf. Anal. **4**, 63 (1982)).

[15]David R. Lide (editor), 88th Edition of the CRC Handbook of Chemistry and Physics 2007–2008 (http://www.hbcpnetbase.com/).

[16]H.A. Wriedt, Bull. Alloy Phase Diagrams **9**, 247 (1988).

[17]K. Kraut (editor), Gmelin-Kraut's Handbuch der Chemie III., p. 33, Carl Winter's Universitätsbuchhandlung, Heidelberg (1875).

[18] H.E. Roscoe and C. Schorlemmer, *A Treatise on Chemistry: Volume II, The Metals*, 4th edition, London*:* Macmillan*,* 650 (1907)*.

[19]Z.Y. Xiao, Y.C. Liu, R. Mu, D.X. Zhao, and J.Y. Zhang, Appl. Phys. Lett. **92**, 052106 (2008).

Fig. 1 (a) O K XES spectra of the first ZnO:N sample set. The main features are labeled A – D. (b) Detailed presentation of features C and D (0-120W). (c) Detailed presentation of the onset at high emission energies (0-120W).

Fig. 2 $Zn_3N_2/(Zn_3N_2+ZnO)$ ratios of the investigated ZnO:N samples (first set), derived from XES and EDS (a) and of the second ZnO:N sample series (derived from XES) as a function of air exposure time (b).

Fig. 3 Initial O K XES spectra (black dots in both panels) of the second ZnO:N sample set, compared to corresponding spectra of samples stored in air (left) and vacuum (right). Red spectra were taken after 5 days, blue spectra after 196 days of storage.

(a) O K - XES
$h\nu = 560$ eV

A
B
C
D

ZnO
80 W
100 W
120 W
150 W

Normalized Intensity

Emission Energy [eV]

(b)

D
C

(c)

120 W
ZnO

Emission Energy [eV]