THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

Luminescence Properties of Nitrogen-Doped ZnO

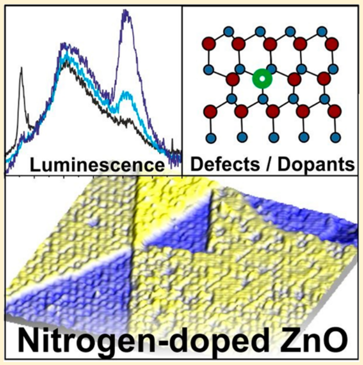
Fernando Stavale,[†,‡] Leandro Pascua,[†] Niklas Nilius,*[,†,§] and Hans-Joachim Freund[†]

[†]Fritz-Haber-Institute, Max-Planck-Society, Faradayweg 4-6, D-14195 Berlin, Germany

[‡]Centro Brasileiro de Pesquisas Físicas - CBPF/MCTI, Rua Dr. Xavier Sigaud 150, 22290-180 Rio de Janeiro, Brazil

[§]Institute of Physics, Carl von Ossietzky University, D-26111 Oldenburg, Germany

ABSTRACT: Pure and nitrogen-doped ZnO films are prepared on a Au(111) single crystal and characterized by luminescence spectroscopy in a scanning tunneling microscope. In both cases, a 730 nm defect peak is revealed in addition to the band recombination peak at 373 nm. The intensity of the defect peak increases when growing the film at reducing conditions or inserting nitrogen into the oxide lattice. Our finding suggests that not the nitrogen impurities but O vacancies are responsible for the defect emission and that the nitrogen incorporation only facilitates the formation of O defects.



1. INTRODUCTION

Zinc oxide (ZnO) is expected to play an important role as transparent conductor in thin-film solar cells and in optoelectronic devices.[1,2] Three fundamental properties render this material suited for high-end optical applications, namely, its direct band gap in the near UV (3.3 eV), its high electron mobility, and the large exciton binding energy that promotes radiative recombination of electron−hole pairs.[3,4] However, the breakthrough in technological applications is still hindered by problems to fabricate *n*- and *p*-type oxide phases. So far, most studies have reported spontaneous *n*-doping, a phenomenon that relates to the uncontrolled incorporation of hydrogen into the wurtzite lattice.[5,6] In contrast, *p*-doping turned out to be difficult and many doping strategies were unsuccessfully tested to fabricate a *p*-conductive isomorph.[7,8] The problems were traced back to various physical limitations, for example, to the abundance of excess electrons in the as grown material, the facile formation of native defects canceling the *p*-type character, and the improper position of acceptor levels that are often too deep in the band gap to enable thermal activation at room temperature.[9]

Nitrogen doping was considered to be a promising approach to achieve *p*-type conductivity of ZnO.[10−15] Although continuous progress has been reported over the years, fabrication of a genuine *p*-doped material is still not in sight. In principle, nitrogen insertion should be feasible in the wurtzite lattice without strain, as oxygen and nitrogen have similar atom radii and electronic structures. The N ion is expected to enter the lattice in two distinct configurations, either as substituent on the oxygen site (N_O) or as defect complex in combination with Zn (N_O-V_{Zn}) or O vacancies ($N_{Zn}-V_O$).[16,17] According to theory, the impurity ions induce a deep acceptor level in the ZnO band gap, giving rise to a broad luminescence peak at ~730 nm.[18,19] The respective peak has indeed been observed in ZnO single crystals altered by traces of nitrogen.[20] Unfortunately, the N-doped samples featured low carrier mobility and could not be used as *p*-type semiconducting oxide.

In this Article, we revisit the optical and electronic properties of nitrogen-doped ZnO films, using luminescence spectroscopy with a scanning tunneling microscope (STM). Our experiments reproduce the characteristic 730 nm peak; however, they are in conflict with earlier interpretations that N-dopants are responsible for the emission. Instead, we provide evidence that the red luminescence is due to O vacancies, being produced by the insertion of N ions into the wurtzite lattice.

2. EXPERIMENTAL SECTION

The experiments were performed in an ultrahigh vacuum STM operated at 100 K. Our setup consists of a Beetle-type microscope head, placed inside of a parabolic mirror. The latter collects photons from the tip−sample junction and guides them to a grating spectrograph (150 lines/mm) outside the vacuum chamber. The luminescence spectra were acquired by retracting the STM tip from the surface for a few 100 nm, applying a voltage of −150 V, and drawing an electron current of 5 nA from the tip by means of the STM feed-back loop. Emitted photons were accumulated for 300 s by a liquid-nitrogen cooled CCD detector. Our approach enables reliable detection of weak photon sources with 100 nm spatial and 4 nm spectral resolution. The experimental setup can be found in ref 21.

Received: April 11, 2014
Revised: May 27, 2014
Published: May 28, 2014

dx.doi.org/10.1021/jp5035536 | *J. Phys. Chem. C* 2014, 118, 13693−13696

ZnO films of 25 monolayer (ML) thickness were prepared by evaporating ZnO pellets for 10 min in 2×10^{-5} mbar of oxygen onto an Au(111) single crystal at room temperature. Annealing in O_2 at 700 K stimulated ordering of the film, as deduced from a sharp, hexagonal (1 × 1) LEED pattern indicative for the $(000\bar{1})$ surface of ZnO.[22] The crystalline nature was confirmed by STM images, displaying wide terraces delimited by straight steps along the high symmetry directions of the wurtzite lattice (Figure 1a). The surface was homogeneously covered with angstrom-sized protrusions, being assigned to individual hydroxyl (−OH) groups. Hydroxylation is the common pathway to remove the polarity of O-ZnO,[23] which is the expected termination of our Au(111)-supported films grown in oxygen excess.[22] Doping was realized by adding atomic nitrogen, produced by an ion gun, to the O_2 ambience used for film growth. The nitrogen flux was varied between 1×10^{14} and 1×10^{12} ions/s to fabricate strongly and weakly doped films, respectively. The doped films were crystallized by gentle annealing to 700 K in a gas mixture comprising 1×10^{-5} mbar N_2 and 1×10^{-5} mbar O_2. Film doping via direct insertion of N_2 molecules turned out to be unsuccessful, as the molecular species left the sample in subsequent annealing steps, restoring the properties of the nondoped material.

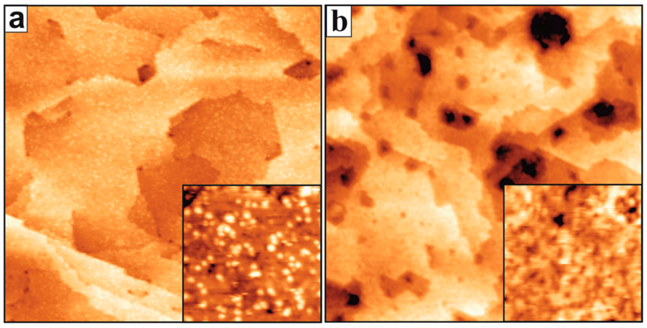


Figure 1. Overview STM images of (a) pristine and (b) nitrogen-doped ZnO films of 25 ML thickness grown on Au(111) (1 nA, 3.8 V, 200×200 nm^2). The inset in (a) shows nanosized protrusions that are assigned to hydroxyl groups on O-terminated ZnO. The surface irregularities in (b) result from a mixture of OH groups and N-related surface defects (both 25×25 nm^2).

3. RESULTS AND DISCUSSION

Figure 1 shows STM topographic images of two 25 ML thick ZnO films, prepared with and without addition of atomic nitrogen to the growth atmosphere. The overall film morphology is similar in both cases, apart from the growth pits that are larger in the doped films. We explain these holes with nitrogen-induced defects that develop during N exposure and coalesce into large pits in the subsequent annealing step. Also on the near-atomic scale, nitrogen incorporation leaves morphological fingerprints in the STM images. Whereas pristine ZnO is homogeneously covered with Å-sized protrusions due to the hydroxyl groups, the doped oxide features faint depressions on the surface that grow in number at higher nitrogen exposure (Figure 1, insets).[24,25] Given our finite spatial resolution, we are unable to decide whether those minima represent the dopants or emerge as secondary defect during nitrogen treatment. Note that the electron diffraction patterns of pristine and doped films are indistinguishable and no evidence for the formation of nitride or oxonitride phases is revealed.

In contrast to the morphology, the ZnO electronic structure as probed with STM conductance spectroscopy reveals distinct differences between pristine and doped films. Spectra of bare ZnO are characterized by a wide band gap, extending from the valence-band onset at −2.0 to the conduction band at +0.75 V (Figure 2). The total gap size is therefore slightly smaller than in the bulk material. The proximity of the conduction band to the Fermi level proves the *n*-type character of our films. Upon nitrogen doping, the onset of the valence states undergoes a pronounced upshift toward the Fermi level, rendering the band gap smaller and more symmetric. At high doping levels, the band gap collapses to 1.0 eV, indicating a massive inducting of electronic gap states by the nitrogen impurities (Figure 2).

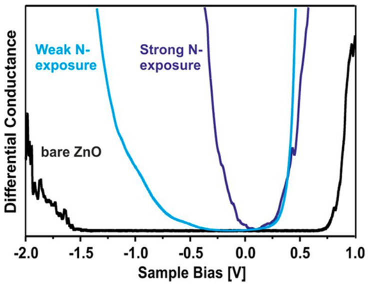


Figure 2. Differential conductance spectra taken on bare and nitrogen-doped ZnO films. Note the gradual reduction of the band gap with increasing nitrogen exposure.

In further experiments, we have employed STM-assisted luminescence spectroscopy to compare the optical response of pristine and nitrogen-doped ZnO (Figure 3). The spectra of the pristine films feature four major emission bands that slightly vary in their relative intensity from sample to sample. The prominent peak at 373 nm (3.3 eV) is readily assigned to the band-recombination mediated by excitonic modes in ZnO. The excitonic fine-structure is not resolved in our data due to the relatively high experimental temperature of 100 K. The high-wavelength bands are related to defects in the oxide lattice and have been analyzed in detail in an earlier paper.[26] In short, the 730 nm peak (1.7 eV) is found to develop upon thermal, optical, or chemical reduction of the oxide. In the example

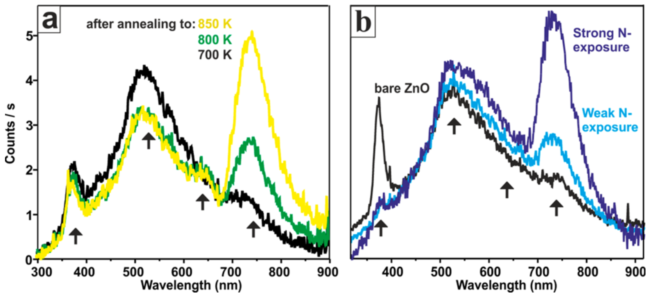


Figure 3. (a) STM luminescence spectra of bare ZnO prepared either via oxygen annealing at 700 K or vacuum annealing at higher temperature to stimulate thermal reduction. (b) Similar spectra of doped ZnO films, grown at different nitrogen exposure and postannealed at 700 K in a mixture of N_2 and O_2. The four main peaks are marked by arrows; the intensity scale is identical in both panels.

shown in Figure 3a, the ZnO film has been vacuum annealed to increasing temperatures, stimulating the gradual loss of oxygen and the formation of V_O defects in the wurtzite lattice. The associated defect levels give rise to new radiative recombination channels for either hot electrons in the conduction or hot holes in the valence band, both of them generated by the injected electrons from the tip. The 535 nm peak (2.3 eV), on the other hand, has been connected to Zn vacancies, because the emission diminishes in the presence of metallic Zn during film growth. The Zn vacancies are particularly stable in *n*-type ZnO, as they compensate for the abundance of excess electrons in the lattice.[27] Finally, two scenarios were proposed for the weak 595 nm peak (2.1 eV). A moderate rise of the emission intensity after adding atomic oxygen to the reaction gas suggested that O interstitials might provide the new recombination pathway.[22] Conversely, the report of a particularly intense 595 nm band in nano-ZnO (clusters, rods, tubes, coils, etc.) points to an involvement of low-coordinated Zn−O units, whose emission properties are governed by a surface gap that is smaller than the respective bulk value.

Surprisingly, the very same emission bands that were found for pristine ZnO are detected for the nitrogen-doped films as well (Figure 3b). Apparently, nitrogen doping does not open up new recombination channels for hot electrons and holes generated by the STM tip. The N-ions in the lattice rather modulate the intensity of the existing peaks, as demonstrated in a spectral series measured as a function of N exposure (Figure 3b). Here, the band recombination peak at 373 nm loses intensity, probably because of an increasing disorder in the doped samples.[28] The 730 nm peak, on the other hand, intensifies with increasing doping level, while the 535 nm line assigned to Zn vacancies remains unchanged. In strongly doped films, the 730 nm peak reaches 10 times the intensity of the band-recombination peak and an even further rise of the red emission is observed after vacuum annealing to more than 700 K. Apparently, the overall emission response of doped ZnO matches the one of the nondoped but highly reduced films, suggesting that nitrogen plays only an indirect role in the emission process. As a working hypothesis, we propose that nitrogen incorporation promotes the formation of O vacancies in the wurtzite lattice, which in turn produce the red luminescence at 730 nm. We will substantiate this idea in the following.

Nitrogen insertion into ZnO has traditionally been connected with the appearance of a 730 nm luminescence peak.[20] According to recent DFT calculations,[19] the N^{2-} impurity ions produce a deep acceptor level in the ZnO band gap that enables radiative recombination of hot electrons from the conduction band. The associated transition energy, calculated under consideration of structural relaxations, has been given with 1.7 eV, in good agreement with a 730 nm emission response. On the basis of the results presented here, we want to challenge this interpretation. As evident in Figure 3a, the 730 nm peak occurs also in photoluminescence spectra of ZnO films that were never brought into contact with atomic or molecular nitrogen. This is a highly reliable statement, as our samples were prepared in an ultrahigh vacuum environment (2×10^{-10} mbar), using an oxygen source of 99.999% purity. Also the ZnO pellets were free of nitrogen, as evaluated from the peak-14 intensity in mass spectrometry. More importantly, the 730 nm emission could be reproducibly established even in nitrogen-free films, for instance, by annealing in vacuum, exposure to ultraviolet photons, or treatment with atomic hydrogen.[26] While none of these procedures are able to alter the nitrogen content of our samples, they all affect the abundance of O vacancies in the lattice. We therefore connect the red luminescence to O vacancies rather than nitrogen-related defects.

Nonetheless, the 730 nm emission shows up also when atomic nitrogen is added to the ZnO growth atmosphere (Figure 3b). A possible explanation is the enhanced O vacancy formation in the presence of nitrogen impurities, an effect that would be compatible with the valence difference between oxygen and nitrogen.[29] N atoms in substitutional O-sites of the wurtzite lattice lack one valence electron to fill their 2p shell. As a result, a localized hole-state develops in the band gap that transforms the N-ion into a deep acceptor.[19] This energetically unfavorable situation can be removed if a compensating defect forms in the oxide lattice that provides the missing electron. The ideal defect would be an anion vacancy (V_O), as shown with the following equation in Kröger−Vink notation:

$$2N_O^{\times} + O_{latt}^{\times} \rightarrow 2N_O^{-} + V_O^{2+} + \frac{1}{2}O_2(\text{desorb})$$

Here, the two extra electrons generated by the release of a neutral 1/2 O_2 molecule are used to satisfy the valence requirements of two nitrogen ions in the ZnO lattice. Note that our ionic picture oversimplifies the situation, as bonds in the wurtzite lattice have a substantial covalent contribution. The spontaneous development of compensating defects in the presence of charged impurities is a common phenomenon in oxide systems. For example, the substitution of bivalent Mg with monovalent Li ions in rocksalt materials also triggers the formation of O vacancies, according to[30]

$$2Li_{Mg}^{-} + 2O_{latt}^{+} \rightarrow 2Li_{Mg}^{-} + V_O^{2+} + O_{latt}^{\times} + \frac{1}{2}O_2(\text{desorb})$$

The scenario developed above thus connects the appearance of the 730 nm emission with the formation of O defects in N-doped ZnO. It also explains the puzzling result of a strong 730 nm line in apparently nitrogen-free ZnO films. In that case, the O vacancies are formed by other processes, such as thermal or photochemical removal of lattice oxygen.

Finally, we discuss our experiments in the light of potential strategies to produce either *p*-conductive ZnO or low band gap materials for optoelectronic and photovoltaic applications. Our conductance measurements indicate a gradual decrease of the band gap upon nitrogen incorporation. We explain this effect with the induction of new electronic states into the oxide gap, originating from both nitrogen substitutes and compensating O defects. At high doping levels, the reduced gap size allows for electron transport even at negative and low positive bias, an effect that is not observed for stoichiometric ZnO. Band gap reduction via excessive nitrogen doping seems thus to be feasible. However, we have not observed a switch between *n*- and *p*-type conductivity, as the Fermi level was found to remain constant with respect to the conduction band and only new states emerged in the lower part of the gap. This trend will not lead to a genuine *p*-type conductivity, and we doubt that N-doping is a promising approach to realize hole conductivity in ZnO.[19,31]

4. CONCLUSIONS

Luminescence spectra of ZnO thin films revealed a 730 nm emission peak with and without nitrogen doping. Our observation suggests that the red luminescence cannot be explained with electron transitions involving the N-induced defects. We rather assign the 730 nm peak to O vacancies in the wurtzite lattice, being stabilized by different processes, one of them being the insertion of aliovalent N-ions.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: nilius@fhi-berlin.mpg.de. Telephone: 0049.30.8413.4191.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

F.S. thanks the “Alexander v. Humboldt Stiftung” for financial support. The authors acknowledge support from the DFG Cluster of Excellence “UniCat”.

■ REFERENCES

(1) Sanchez, S.; Berson, S.; Guillerez, S.; Lévy-Clément, C.; Ivanova, V. Toward High-Stability Inverted Polymer Solar Cells with an Electrodeposited ZnO Electron Transporting Layer. *Adv. Energy Mater.* **2012**, *2*, 541−545.

(2) Huang, J.; Yin, Z.; Zheng, Q. Applications of ZnO in organic and hybrid solar cells. *Energy Environ.* **2011**, *4*, 3861−3877.

(3) Ryu, Y.; Lee, T.-S.; Lubguban, J. A.; White, H. W.; Kim, B.-J.; Park, Y.-S.; Youn, C.-J. Next generation of oxide photonic devices: ZnO-based ultraviolet light emitting diodes. *Appl. Phys. Lett.* **2006**, *88*, 241108-1−3.

(4) Könenkamp, R.; Word, R. C.; Godinez, M. Ultraviolet Electroluminescence from ZnO/Polymer Heterojunction Light-Emitting Diodes. *Nano Lett.* **2005**, *5*, 2005−2008.

(5) Zhang, S. B.; Wei, S.-H.; Zunger, A. Intrinsic n-type versus p-type doping asymmetry and the defect physics of ZnO. *Phys. Rev. B* **2001**, *63*, 075205-1−7.

(6) Du, M. H.; Biswas, K. Anionic and Hidden Hydrogen in ZnO. *Phys. Rev. Lett.* **2011**, *106*, 115502-1−4.

(7) Look, D. C.; Farlow, G. C.; Reunchan, P.; Limpijumnong, S.; Zhang, S. B.; Nordlund, K. Evidence for Native-Defect Donors in n-Type ZnO. *Phys. Rev. Lett.* **2005**, *95*, 225502-1−4.

(8) Hapiuk, D.; Marques, M. A. L.; Melinon, P.; Flores-Livas, J. A.; Botti, S.; Masenelli, B. p Doping in Expanded Phases of ZnO: An Ab Initio Study. *Phys. Rev. Lett.* **2012**, *108*, 115903-1−4.

(9) Kobayashi, A.; Sankey, O. F.; Dow, J. D. Deep energy levels of defects in the wurtzite semiconductors AIN, CdS, CdSe, ZnS, and ZnO. *Phys. Rev. B* **1983**, *28*, 946−956.

(10) Lautenschlaeger, S.; Hofmann, M.; Eisermann, S.; Haas, G.; Pinnisch, M.; Laufer, A.; Meyer, B. K. A model for acceptor doping in ZnO based on nitrogen pair formation. *Phys. Status Solidi* **2011**, *248*, 1217−1221.

(11) Rodnyi, P. A.; Khodyuk, I. V. Optical and luminescence properties of zinc oxide. *Opt. Spectrosc.* **2011**, *11*, 776−785.

(12) Nakagawa, A.; et al. Photoluminescence properties of nitrogen-doped ZnO films deposited on ZnO single crystal substrates by the plasma-assisted reactive evaporation method. *Appl. Surf. Sci.* **2007**, *254*, 164−166.

(13) Meyer, B. K.; et al. Bound exciton and donor−acceptor pair recombinations in ZnO. *Phys. Status Solidi B* **2004**, *241*, 231−260.

(14) Norton, D. P.; Heo, Y. W.; Ivill, M. P.; Ip, K.; Pearton, S. J.; Chisholm, M. F.; Steiner, T. ZnO: growth, doping & processing. *Mater. Today* **2004**, *7*, 34−40.

(15) Iwata, K.; Fons, P.; Yamada, A.; Matsubara, K.; Niki, S. Nitrogen-induced defects in ZnO: N grown on sapphire substrate by gas source MBE. *J. Cryst. Growth* **2000**, *209*, 526−531.

(16) Look, D. C.; Reynolds, D. C.; Litton, C. W.; Jones, R. L.; Eason, D. B.; Cantwell, G. Characterization of homoepitaxial p-type ZnO grown by molecular beam epitaxy. *Appl. Phys. Lett.* **2002**, *81*, 1830 1−3.

(17) Liu, L.; Xu, J.; Wang, D.; Jiang, M.; Wang, S.; Li, B.; Zhang, Z.; Zhao, D.; Shan, C.-X.; Yao, B.; Shen, D. Z. p-Type Conductivity in N-Doped ZnO: The Role of the N_{Zn}-V_O Complex. *Phys. Rev. Lett.* **2012**, *108*, 215501-1−4.

(18) Varley, J. B.; Janotti, A.; Franchini, C.; Van de Walle, C. G. Role of self-trapping in luminescence and p-type conductivity of wide-band-gap oxides. *Phys. Rev. B* **2012**, *85*, 081109-1−4.

(19) Lyons, J. L.; Janotti, A.; Van de Walle, C. G. Why nitrogen cannot lead to p-type conductivity in ZnO. *Appl. Phys. Lett.* **2009**, *95*, 252105-1−3.

(20) Tarun, M. C.; Zafar Iqbal, M.; McCluskey, M. D. Nitrogen is a deep acceptor in ZnO. *AIP Adv.* **2011**, *1*, 022105-1−7.

(21) Nilius, N.; Cörper, A.; Bozdech, G.; Ernst, N.; Freund, H.-J. Experiments on Individual Alumina-supported adatoms and Clusters. *Prog. Surf. Sci.* **2001**, *67*, 99−121.

(22) Stavale, F.; Pascua, L.; Nilius, N.; Freund, H.-J. Morphology and Luminescence of ZnO Films Grown on a Au(111) support. *J. Phys. Chem. C* **2013**, *117*, 10552−10557.

(23) Yin, X. L.; Birkner, A.; Hanel, K.; Lober, T.; Kohler, U.; Wöll, C. Adsorption of atomic hydrogen on ZnO(1010): STM study. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1477−1481.

(24) Lauritsen, J. V.; et al. Stabilization principles for polar surfaces of ZnO. *ACS Nano* **2011**, *5*, 5987−5994.

(25) Torbrügge, S.; Ostendorf, F.; Reichling, M. Stabilization of Zinc-Terminated ZnO(0001) by a Modified Surface Stoichiometry. *J. Phys. Chem. C* **2009**, *113*, 4909−4914.

(26) Stavale, F.; Nilius, N.; Freund, H.-J. STM Luminescence Spectroscopy of Intrinsic Defects in ZnO(0001) Thin Films. *J. Chem. Phys. Lett.* **2013**, *4*, 3972−3976.

(27) Janotti, A.; Van de Walle, C. G. Native point defects in ZnO. *Phys. Rev. B* **2007**, *76*, 165202-1−22.

(28) Lautenschlaeger, S.; et al. Optical signatures of nitrogen acceptors in ZnO. *Phys. Rev. B* **2012**, *85*, 235204-1−7.

(29) Lee, E. C.; Kim, Y. S.; Jin, Y. G.; Chang, K. J. Compensation mechanism for N acceptors in ZnO. *Phys. Rev. B* **2001**, *64*, 085120-1−5.

(30) Myrach, P.; et al. Temperature-dependent morphology, magnetic and optical properties of Li-doped MgO. *ChemCatChem.* **2010**, *2*, 854−862.

(31) Ye, Z. Z.; Chen, L. L.; Zhao, B. H.; He, H. P. Photoluminescence in heavily doped ZnO:N:In films. *Appl. Phys. Lett.* **2008**, *92*, 231913-1−3.