Diameter Dependent Polarization in ZnO/MgO Disk-in-Wire Emitters: Multiscale Modeling of Optical Quantum Efficiency

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Abstract—A multiscale computational study is performed to investigate how electronic structure, optical transitions, and terminal characteristics of nanostructured ZnO/MgO disk-in-wire emitters are governed by an intricate coupling of size-quantization, atomicity, and built-in structural and polarization fields. As for the models, an 8-band sp^3 (with spin) atomistic tight-binding basis set was used to construct the Hamiltonian of the device in wurtzite crystal symmetry. Strain and the associated distortions of bond directions and bond lengths were modeled via the valence force-field (VFF) molecular mechanics framework. Specifically, in this work, a recently proposed *ab initio* based *diameter-dependent* model for the piezoelectric fields was implemented, which, as compared to the conventional diameter-independent model, was found to curb the influence of spontaneous (pyroelectric) polarization significantly. This particular finding is further illustrated through the calculation of electronic bandgap and localization of wavefunctions, optical emission characteristics, and the internal quantum efficiency of the device.

Index Terms—ZnO nanostructures, valence force-field, tight-binding, polarization, electronic structure, optical transitions, internal quantum efficiency

I. INTRODUCTION

Recently, ZnO/MgO material system has attracted considerable attention for applications in optoelectronic as well as spintronic devices. ZnO based optical emitters offer several advantages over the conventional GaN based counterparts [1][2][3], such as—(1) Direct bandgap of 3.37 eV, which indicates the operability in blue and ultra-violet emission frequencies; (2) High exciton binding energy of about 60 meV (compared with ~25 meV for GaN); (3) Availability of native ZnO substrates as well as wurtzite MgZnO and/or CdZnO alloys with a bandgap ranging from 2 eV to 4 eV allowing growth of low-defect materials necessary for LEDs; (4) Availability of low-temperature epitaxial and wet etching processing; and (5) High radiation hardness. Furthermore, ZnO has large non-linear optical coefficients, growth temperature nearly 500 °C, is inexpensive, relatively abundant, chemically stable, and nontoxic. The potential for ZnO as an excellent candidate for room-temperature lasers was studied in Ref. [2] and later experimentally demonstrated [4].

Undoped ZnO is unintentionally *n*-type. Lack of a feasible *p*-doping methodology has been the main factor behind the slow development of ZnO-based light emitters [5]. While some progresses have been made along this line, in the recent years, several hybrid single-heterostructure and double-heterostructure LEDs have been reported using *n*-type ZnO deposited on *p*-type materials of GaN [6][7], AlGaIn [8], MgZnO [9], CdZnO [10], Si [11][12][13], and other conducting oxides [14]. *LEDs with ZnO Nanostructures*—An important step in order to design ZnO-based LEDs is the realization of *efficient* active layers through appropriate bandgap engineering. Optical devices using ZnO *nanostructures* have attracted much attention due to their superior optical properties arising from quantum confinement such as enhanced radiative recombination of carriers. Most ZnO nanostructures have been realized from 1-D nanowires/nanorods, and some from 0-D quantum dots [15] of different materials, such as GaN [16][17][18], Si [19], NiO [20], and *p*-type polymers [21][22]. With a greater relaxation of strain at the free surfaces, nanostructures, as compared to bulk and thin-film quantum well heterostructures, offer the integration of a broader range of lattice mismatch leading to devices with minimal dislocation defects and a wider emission spectrum.

Nevertheless, recently reports in this area (e.g. on nitride material systems) demonstrate that the efficiency of these quantum emitters is significantly degraded due mainly to symmetry breaking in the underlying materials originating from fundamental *atomicity* of the lattice, atomistic strain relaxation in the active region and associated polarization fields [23][24][25][26][27]. Note that both piezoelectric and spontaneous polarization coefficients are large in ZnO, which could significantly influence the electronic and optical properties of devices made from this material system. Specifically, for nanostructured devices, it has been reported that the piezoelectric polarization coefficient is a strong function of the nanowire

diameter and increases significantly as diameter is reduced below 10 nm [28]. This, in effect, enhances the *degrees-of-freedom* for device design and creates routes to *fine-tune* the energy bandgap as well as the emission characteristics in an optical emitter. Motivated by these recent developments, in this paper, our objective is to carry out a multiscale computational study employing a *diameter-dependent* model for the piezoelectric fields and investigate how electronic structure, optical transitions, and terminal characteristics of a *model* nanostructured ZnO/MgO disk-in-wire emitter are governed by an intricate coupling of size-quantization, atomicity, and built-in structural and polarization fields.

II. SIMULATION MODEL

A detail description of the *atomistic* simulation platform used in this study can be found in Refs. [25][26][27][29]. Here, we present only a synopsis of the models, parameters, and methodologies used in regard to an accurate treatment of the internal fields. The overall numerical model is based on a combination of valence force-field molecular mechanics (VFF-MM), 8-band sp^3 atomistic tight-binding (TB), and a quantum-corrected drift-diffusion transport toolkit as integrated in our in-house QuADS 3-D (quantum atomistic device simulation in three dimensions) simulator [30][31]. After creating the entire structure from a basis set, the atom positions are relaxed and the resulting strain fields are calculated via the valence force-field (VFF) method using the Keating potentials. The effect of thermal strain is small and neglected in this work. The spontaneous (pyroelectric) polarization is strain-independent and arises from fundamental asymmetry of the crystal structure. In contrast, the piezoelectric polarization is calculated from diagonal and shear components of the *atomistic* strain fields. Here, to account for the diameter-dependence of piezoelectric polarization coefficient, derivative of a recently proposed model by Agrawal *et al.* [28] has been implemented in this work. In Ref. [28], authors carried out first principles-based density functional theory (DFT) calculations using the SIESTA toolkit to model zinc oxide nanowires having hexagonal geometrical symmetry. It was found that the piezoelectric coefficient along the growth direction (e_{33}) in a ZnO nanowire with diameter of 1 nm could rise to $\sim 25 \text{ C/m}^2$ as compared to $\sim 1.24 \text{ C/m}^2$ of its bulk counterpart! Such a huge increase in the polarization coefficient was attributed to local polarization originating from charge redistribution and reduction of unit cell volume in the vicinity of free surfaces of the nanowire. In the current work, the piezoelectric polarization coefficients were extracted and fitted for nanowires having diameter ranging from 5 nm to 10 nm and are listed in Table I. The polarization induced potential is obtained by solving the 3-D Poisson equation on an atomistic grid. Next, the single-particle eigenvalues, wave functions, and the interband optical transition rates are calculated using an empirical nearest-neighbor 8-band sp^3 tight-binding model as implemented in the open source NEMO 3-D simulator [34]. Finally, the microscopically determined optical transition pa-

rameters are incorporated in the Synopsys' *Sentaurus* TCAD toolkit to obtain the terminal characteristics of the LED and investigate how various internal fields affect the quantum efficiency of the device.

III. RESULTS AND DISCUSSION

As a model device, in this study, we considered an MgO/ZnO/MgO hexagonal disk-in-wire structure in the [0001] direction (c -axis) as depicted in Figure 1. The model nanowire has a diameter of 5 nm, height of 50 nm, and the thickness of the ZnO disk is 2 nm. For the wurtzite lattices underlying, we assumed $c/a = \sqrt{8/3}$. Initially, all atoms in the entire domain (including ZnO) are placed on an MgO lattice. However, while constructing the device Hamiltonian, strain dependence is ignored. By doing this, only the effect of quantum confinement can be studied (denoted as W/O in the Figures to follow). Nevertheless, in the next step, the structure is relaxed (using the VFF framework) and the atomistic strain distribution is obtained via minimization of the total elastic energy of the computational domain. In this step, the atoms at the bottom surface are fixed to MgO lattice constants and a closed boundary condition is employed.

Figure 2 shows the diagonal and the off-diagonal strain distributions in the growth direction. Both the biaxial and the hydrostatic strain were found to be *tensile* within the disk region and *compressive* in the substrate and cap layers. The off-diagonal strain component ε_{xy} is negligible; however, the same in the other two planes (x - z and y - z) are significantly large. The strain induced piezoelectric (PZ) and the (spontaneous) pyroelectric (PY) potential distributions are shown in Figure 3. Here, for comparison, we have considered and plotted both the diameter-independent (bulk, denoted as D/IND) and diameter-dependent (denoted as D/DEP) piezoelectric potential for a nominal device having a diameter of 5 nm. Two salient features were observed in the analysis: a) The peak piezoelectric potential as obtained using the D/DEP model (~ 120 mV) is almost $3\times$ higher than its D/IND counterpart (~ 40 mV); and b) Pyroelectric potential is significantly large and well-spread in these structures (peak being ~ 100 mV); However, with the D/DEP piezoelectric model used, its effect is curbed and the net potential in the device's active region decreases significantly.

The quantum mechanical wavefunctions for the valence band (HOMO) and the conduction band (LUMO) in the confined region are shown in Figure 4 for four different cases, namely, *quantum confinement* (W/O), *atomistic strain*, *diameter-independent*, and *diameter-dependent* polarization models. The bottom row in this Figure lists the single-particle energy bandgap, which is also plotted in Figure 5 for clarity. Note the large red-shift as seen in the diameter-independent model; whereas, the use of a more accurate diameter-dependent model leads to an insignificant modification in the bandgap (as compared to the

strain case). Next, the variation of the energy bandgap is plotted against the nanowire diameter ranging from 5 nm to 10 nm (Figure 6). Here, as depicted on the secondary y-axis, given that the percentage change in bandgap is nearly identical for both the two models, the gradual increase in the energy bandgap with a reduction in diameter is due mainly to quantum mechanical size quantization effect.

The interband optical transition rates between the HOMO (valence band maxima) and the LUMO (conduction band minima) states are plotted in Figure 7. As expected, the D/IND model, because of a larger internal potential, underestimates the magnitude as well as isotropy in the optical transition for all the nanowires. Nevertheless, the difference in the transition rates as calculated from the two models gradually diminishes as the wire diameter increases. Finally, a TCAD toolkit as available from Synopsys' Sentaurus package is used to obtain the terminal optical characteristics of an LED that employs the model (nominal) disk-in-wire structure with a diameter of 5 nm as its core active region. Here, the effect of polarization fields is modeled via a *scaling factor* (k_{sp}), which is obtained from averaging the transition rates over the angle of emission. Figure 8 shows the spontaneous emission rate (a) and the variation of internal quantum efficiency (IQE) as a function of injected current for the two different models used in the calculation. Here, we have taken into account the effects of Auger and Shockley-Read-Hall (SRH) non-radiative recombination processes. Note that, under these circumstances, the rollover in the efficiency characteristic, which is known as *droop* in the optoelectronics and photonics community, is attributed due mainly to carrier (electron) loss from within the confined disk region.

IV. CONCLUSION

Internal fields originating primarily from strain and material discontinuity play an important role in the determination of electronic structure and emission characteristics of emerging optoelectronic devices. However, the polarization coefficients exhibit a strong size-dependence, which, to avoid any artifacts, must be taken into account while modeling these devices. It is found that in thin disk-in-wire structures, having a large pyroelectric potential, the use of diameter-independent model for the piezoelectric polarization overestimates the net potential within the device active region. On the other hand, the diameter-dependent piezoelectric model results in a large piezoelectric potential that tends to *oppose* the pyroelectric counterpart resulting in a much smaller net internal potential and improved efficiency and optical emission characteristics.

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REFERENCES

- [1] Yong-Seok Choi, Jang-Won Kang, Dae-Kue Hwang, and Seong-Ju Park, "Recent Advances in ZnO-Based Light-Emitting Diodes," *IEEE Transactions on Electron Devices*, vol. 57, no. 1, pp. 26–41, 2010.
- [2] Marian Zamfirescu, Alexey Kavokin, Bernard Gil, Guillaume Malpuech, and Mikhail Kaliteevski, "ZnO as a material mostly adapted for the realization of room-temperature polariton lasers," *Phys. Rev. B* 65, 161205(R), 15 April 2002.
- [3] A. Janotti and C. G. Van de Walle, "Fundamentals of zinc oxide as a semiconductor," *Rep. Prog. Phys.*, vol. 72, pp. 126501, 2009.
- [4] Ying-Yu Lai, Yu-Pin Lan and Tien-Chang Lu, "High-Temperature Polariton Lasing in a Strongly Coupled ZnO Microcavity," *Applied Physics Express*, vol. 5, no. 8, 2012.
- [5] K. A. Bulashevich, I. Yu. Evstratov, and S. Yu. Karpov, "Hybrid ZnO/III-nitride light-emitting diodes: modelling analysis of operation," *Phys. Stat. Sol. (a)* 204, no. 1, pp. 241–245, 2007.
- [6] D. J. Rogers, F. Hosseini Teherani, A. Yasan, K. Minder, P. Kung, and M. Razeghi, "Electroluminescence at 375 nm from a ZnO/GaN:Mg/c-Al₂O₃ heterojunction light emitting diode," *Appl. Phys. Lett.*, vol. 88, no. 14, p. 141 918, April 2006.
- [7] T. P. Yang, H. C. Zhu, J. M. Bian, J. C. Sun, X. Dong, B. L. Zhang, H. W. Liang, X. P. Li, Y. G. Cui, and G. T. Du, "Room temperature electroluminescence from the n-ZnO/p-GaN heterojunction device grown by MOCVD," *Mater. Res. Bull.*, vol. 43, no. 12, pp. 3614–3620, Dec. 2008.
- [8] Y. I. Alivov, E. V. Kalinina, A. E. Cherenkov, D. C. Look, B. M. Ataev, A. K. Omaev, M. V. Chukichev, and D. M. Bagnall, "Fabrication and characterization of n-ZnO/p-AlGaIn heterojunction light-emitting diodes on 6H-SiC substrates," *Appl. Phys. Lett.*, vol. 83, no. 23, pp. 4719–4721, Dec. 2003.
- [9] T. Ohashi, K. Yamamoto, A. Nakamura, and J. Temmyo, "Red emission from ZnO-based double heterojunction diode," *Jpn. J. Appl. Phys.*, vol. 47, no. 4, pp. 2961–2964, April 2008.
- [10] J. W. Mares, M. Falanga, A. V. Thompson, A. Osinsky, J. Q. Xie, B. Hertog, A. Dabiran, P. P. Chow, S. Karpov, and W. V. Schoenfeld, "Hybrid CdZnO/GaN quantum-well light emitting diodes," *J. Appl. Phys.*, vol. 104, no. 9, p. 093 107, November 2008.
- [11] J. D. Ye, S. L. Gu, S. M. Zhu, W. Liu, S. M. Liu, R. Zhang, Y. Shi, and Y. D. Zheng, "Electroluminescent and transport mechanisms of n-ZnO/p-Si heterojunctions," *Appl. Phys. Lett.*, vol. 88, no. 18, 182112, May 2006.
- [12] M. K. Choi, W. S. Han, Y. Y. Kim, B. H. Kong, H. K. Cho, J. H. Kim, H. S. Seo, K. P. Kim, and J. H. Lee, "n-ZnO : Ga/i-ZnO/p-Si heterojunction light emitting diodes fabricated on patterned Si substrates," *J. Mater. Sci., Mater. Electron.*, vol. 20, no. 12, pp. 1214–1218, December 2009.
- [13] E. Placzek-Popko, K. Paradowska, M. Pietrzyk, Z. Gumienny, P. Biegański and A. Kozanecki, "Deep traps and photo-electric properties of p-Si/MgO/n-Zn_{1-x}Mg_xO heterojunction", *J. Appl. Phys.*, vol. 118, no. 7, p. 074501, 2015.
- [14] H. Ohta, K.-I. Kawamura, M. Orita, M. Hirano, N. Sarukura, and H. Hosono, "Current injection emission from a transparent p-n junction composed of p-SrCu₂O₂/n-ZnO," *Appl. Phys. Lett.*, vol. 77, no. 4, p. 475, May 2000.
- [15] T. Omata, Y. Tani, S. Kobayashi, K. Takahashi, A. Miyanaga, Y. Maeda and S. Otsuka-Yao-Matsuo, "Ultraviolet electroluminescence from colloidal ZnO quantum dots in an all-inorganic multilayer light-emitting device," *Appl. Phys. Lett.*, vol. 100, no. 6, p. 061104, 2012.

- [16] M. C. Jeong, B. Y. Oh, M. H. Ham, S. W. Lee, and J. M. Myoung, "ZnO-nanowire-inserted GaN/ZnO heterojunction light-emitting diodes," *Small*, vol. 3, no. 4, pp. 568–572, April 2007.
- [17] S. H. Park, S. H. Kim, and S. W. Han, "Growth of homoepitaxial ZnO film on ZnO nanorods and light emitting diode applications," *Nanotechnology*, vol. 18, no. 5, p. 055 608, January 2007.
- [18] R. Guo, J. Nishimura, M. Matsumoto, M. Higshihata, D. Nakamura, and T. Okada, "Electroluminescence from ZnO nanowirebased p-GaN/n-ZnO heterojunction light-emitting diodes," *Appl. Phys. B, Photophys. Laser Chem.*, vol. 94, no. 1, pp. 33–38, January 2009.
- [19] H. Sun, Q. F. Zhang, and J. L. Wu, "Electroluminescence from ZnO nanorods with an n-ZnO/p-Si heterojunction structure," *Nanotechnology*, vol. 17, no. 9, pp. 2271–2274, April 2006.
- [20] Y. Y. Xi, Y. F. Hsu, A. B. Djuricic, A. M. C. Ng, W. K. Chan, H. L. Tam, and K. W. Cheah, "NiO/ZnO light emitting diodes by solution-based growth," *Appl. Phys. Lett.*, vol. 92, no. 11, p. 113 505, March 2008.
- [21] X. W. Sun, J. Z. Huang, J. X. Wang, and Z. Xu, "A ZnO nanorod inorganic/organic heterostructure light-emitting diode emitting at 342 nm," *Nano Lett.*, vol. 8, no. 4, pp. 1219–1223, March 2008.
- [22] A. Nadarajah, R. C. Word, J. Meiss, and R. Konenkamp, "Flexible inorganic nanowire light-emitting diode," *Nano Lett.*, vol. 8, no. 2, pp. 534–537, January 2008.
- [23] *III-Nitride Semiconductors and Their Modern Devices*, edited by Bernerd Gil, Oxford University Press 2013.
- [24] S. Sundaresan, V. Gaddipati, and S. Ahmed, "Effects of Spontaneous and Piezoelectric Polarization Fields on the Electronic and Optical Properties in GaN/AlN Quantum Dots: Multimillion-Atom $sp^3d^5s^*$ Tight-Binding Simulations," *Int. J. Numer. Model.*, vol. 28, pp. 321–334, 2015.
- [25] V. Chimalgi, Md. R. K. Nishat, and S. Ahmed, "Nonlinear Piezoelectricity and Efficiency Droop in Hexagonal In(Ga)N/GaN Disk-in-Wire LEDs," *Superlattices and Microstructures*, vol. 84, pp. 91–98, 2015.
- [26] K. Yalavarthi, V. Gaddipati, and S. Ahmed, "Internal Fields in InN/GaN Quantum Dots: Geometry Dependence and Competing Effects on the Electronic Structure," *Physica E: Low-Dimensional Systems and Nanostructures*, vol. 43, pp. 1235–1239, 2011.
- [27] S. Ahmed, S. Islam, and S. Mohammed, "Electronic Structure of InN/GaN Quantum Dots: Multimillion Atom Tight-Binding Simulations," *IEEE Trans. Electron Devices*, vol. 57, no. 1, pp. 164–173, 2010.
- [28] R. Agrawal and H. Espinosa, "Giant Piezoelectric Size Effects in Zinc Oxide and Gallium Nitride Nanowires. A First Principles Investigation," *Nano Letters*, vol. 11, no. 2, pp. 786–790, 2011.
- [29] S. Ahmed, N. Kharche, R. Rahman, M. Usman, S. Lee, H. Ryu, H. Bae, S. Clark, B. Haley, M. Naumov, F. Saied, M. Korkusinski, R. Kennel, M. McLennan, T. B. Boykin, and G. Klimeck, "Multimillion Atom Simulations with NEMO 3-D," *Encyclopedia of Complexity and Systems Science*, vol. 6, pp. 5745–5783, Springer New York, 2009.
- [30] S. Ahmed, K. Yalavarthi, V. Gaddipati, A. Muntahi, S. Sundaresan, S. Mohammed, S. Islam, R. Hindupur, D. John, and J. Ogden, "Quantum Atomistic Simulations of Nanoelectronic Devices using QuADS," In *Nano-Electronic Devices: Semiclassical and Quantum Transport Modeling*, Springer, Edited by D. Vasileska and S. M. Goodnick, pp. 405–441, 2011.

- [31] Shaikh S. Ahmed; Vinay Uday Chimalgi; Katina Mattingly; Krishna Kumari Yalavarthi (2015), "Nanoscale Solid-State Lighting Device Simulator," <https://nanohub.org/resources/nanoss1>. (DOI: 10.4231/D3DR2P94F)
- [32] S. Jang and S. Chichibu, "Structural, elastic, and polarization parameters and band structures of wurtzite ZnO and MgO," *J. Appl. Phys.*, vol. 112, no. 7, p. 073503, 2012.
- [33] M. Stölzel, A. Müller, G. Benndorf, M. Lorenz, C. Patzig, T. Höche and M. Grundmann, "Determination of the spontaneous polarization of wurtzite (Mg,Zn)O," *Appl. Phys. Lett.*, vol. 104, no. 19, p. 192102, 2014.
- [34] G. Klimeck, S. Ahmed, N. Kharche, H. Bae, S. Clark, B. Haley, S. Lee, M. Naumov, H. Ryu, F. Saied, M. Prada, M. Korkusinski, and T. B. Boykin, "Atomistic Simulation of Realistically Sized Nanodevices Using NEMO 3-D: Part I—Models and Benchmarks," *IEEE Trans. Electron Devices*, vol. 54, no. 9, pp. 2079–89, 2007.

TABLE I. POLARIZATION CONSTANTS (IN C/M²) FOR ZNO AND MGO

	P _{PZ} (Bulk) [32]			P _{PZ} Diameter Dependent e_{33} (extrapolated from [28])						P _{SP} [33]
	e_{15}	e_{31}	e_{33}	5 nm	6 nm	7 nm	8 nm	9 nm	10 nm	
ZnO	-0.38	-0.55	1.24	10.78	10.11	9.58	9.14	8.77	8.45	-0.07
MgO	-0.36	-0.78	0.14	0.903	0.847	0.803	0.766	0.735	0.0708	-0.05

Figure. 1. The *schematic* of the device simulated (left panel) and the atomistic structure of the disk-in-wire MgO/ZnO/MgO heterostructure.

Figure 2. One dimensional (1-D) strain distributions along the growth direction.

Figure 3. Internal potential distributions along the c -axis.

Figure 4. HOMO and LUMO wavefunctions in the x - y plane for four different cases: without internal fields (only quantum confinement), with strained relaxation, and net polarization using diameter-independent and diameter-dependent models.

Figure 5. Bandgap variations as a function of device internal fields. Five cases have been considered: without internal fields (only quantum confinement), with strained relaxation, spontaneous (pyroelectric) polarization, and net polarization using diameter-independent and diameter-dependent models.

Figure 6. Energy bandgap and percentage change in energy bandgap as a function of wire diameter as obtained from D/IND and D/DEP models.

Figure 7. Polar plots of optical transition rates in the x - y plane for nanowires with different diameters as obtained from D/IND and D/DEP models.

Figure 8. Spontaneous emission rate (a) and the variation of internal quantum efficiency (IQE) as a function of injected current for the two different models.