Spatially-Resolved Cathodoluminescence Spectroscopy of ZnO Defects

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Abstract

Spatially-resolved cathodoluminescence spectroscopy has contributed significant new information to our understanding of native point defects in ZnO micro- and nanoscale structures. This paper aims to review representative examples of this work and the new perspectives gained from spatially resolving these defects both laterally and depth-wise. Results obtained from many groups worldwide include studies of Schottky diodes, polycrystalline ceramics, nanostructures, and microwires. The nature and spatial distribution of native point defects in these materials together with their strong dependence on growth and processing suggest new avenues for their control in transport and optoelectronic device structures.

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I. Introduction

A key aspect of ZnO-based materials and applications, the topic of this special issue, is the nature, spatial distribution, and electronic impact of native point defects. These features are particularly important at the micro- and nanoscale, where their physical properties can dominate charge carrier transport and electronic contacts. Starting from the optical identification of specific defects already discussed in the literature, this work focuses on the new defect information provided by spatially-localized cathodoluminescence spectroscopy (CLS). This technique has unique advantages in measuring the nature, spatial distribution, and electronic impact of defects in ZnO micro- and nanostructures. Spatially-resolved CLS has now shown that: (1) native point defects: are present inside these structures and not just on their surfaces, (2) their nature and distribution depend on the specific growth method used to create them, and (3) they can strongly affect nanoscale transport and device properties. Defects in micro- and nanostructures of other semiconductors can exhibit similar effects. However, space requirements limit our focus to ZnO and to the unique information that the spatially-localized CLS technique provides. Nevertheless, we provide a range of general references to the CLS technique and to its application in nanoscale studies of other semiconductors.

Cathodoluminescence spectroscopy (CLS) has emerged rapidly as a technique for characterizing the physical properties of electronic materials and devices. CLS involves incident electron beams focused on solids to generate light emission characteristic of the solid's electronic and structural properties—its band gap, defect states within the band gap, as well as the presence of new material phases. CLS is contactless, highly sensitive to relatively low concentrations of defects, and a direct measure of carrier recombination pathways that involve those defects. CLS has been used to study a wide variety of electronic materials, resulting in many thousands of archival publications. For a general CLS reference, see Yacobi and Holt's *Cathodoluminescence Microscopy of Inorganic Solids*.¹ More recent reviews focus on laterally-localized^{2,3} and depth-resolved⁴ CLS applications.

Scanning electron microscope (SEM) – based CLS provides material properties with lateral resolution down to the nanometer scale and has focused on a variety of nano- and quantum-scale structures. Faster recombination velocity at defects limits minority carrier diffusion, contributing to this nanoscale resolution.⁵ Nanostructure studies have included the

growth,^{6,7,8,9,10,11,12,13,14,15,16,17} processing,¹⁸ and electronic properties of nanowires,^{19,20,21, 22} nanobelts,²³ nanotubes,²⁴ nanoparticles,²⁵ homo- and heterojunctions,^{26,27,28,29} as well as their strain effects^{30,31,32,33} and defects.^{34,35} Quantum structure studies have included wells,^{36,37,38,39} disks,^{40,41} and dots.^{42,43,44,45,46,47,48} CLS has been used to track the spatial/strain dependence of near-gap luminescence (D^0 ,X) in ZnO nanowires, from which deformation potentials could be derived.⁴⁹ Likewise, time-resolved CLS has described the dynamics of exciton transport in ZnO microwires under elastic bending deformation.⁵⁰ Studies have also included correlations of optical emissions to nanoscale features and the physical mechanisms involved,^{51,52} particularly following the development of what is now termed hyperspectral imaging (HSI), *i.e.*, single wavelength intensity maps extracted from full spectra acquired pixel-by-pixel across extended areas.⁵³

CLS has also proven useful in studying electronic device properties. Even without nanoscale depth or submicron lateral resolution, CLS can provide information relevant to device degradation in transistors, including dopant diffusion,⁵⁴ thermal stress,⁵⁵ electric field stress,⁵⁶ and defect formation.^{57,58} Similar degradation studies have centered on light emitting and laser diodes.^{59,60,61,62} Other device structures measured using CLS include solar cells,⁶³ antennas,⁶⁴ resonators,^{65,66} and dielectric layers.^{67,68} Combining nanoscale scanning electron microscopy with depth-resolved CLS, *i.e.*, tuning the electron beam's interaction depth by changing incident beam energy, enables one to probe selectively in three dimensions. This added spatial constraint expands the capability for analyzing electronic device structures, in particular, their interfaces, whose features can dominate micro- and optoelectronic properties at the macroscale.

There is now a considerable body of CLS research on ZnO, motivated by its potential for optoelectronic and microelectronic applications⁶⁹ and based on a number of factors: its 60 meV exciton binding energy for efficient light emitters, high mobility transport,⁷⁰ ease of large area growth,⁷¹ wet chemical processing, resistance to space radiation, and environmental compatibility. For a general review of ZnO materials and devices, see Özgür *et al.*⁷² Extended to the nanoscale, CLS can describe how ZnO properties vary within interfaces, micro- and nanostructures together with how they can depend on growth and processing.^{73,74} Several comprehensive reviews of CLS applied to ZnO nanostructures are now available.^{75,76,77, 78,79}

This chapter focuses on a very specific aspect of ZnO, *i.e.*, the nature and spatially-resolved distribution of defects at their interfaces and in particular inside their micro- and nanostructures. In general, defects in semiconductors have negative effects: they introduce states that can trap charge, increase non-radiative recombination, alter Schottky barriers and ohmic contacts. However, they may also decrease absorption thresholds and induce ferromagnetism.⁸⁰ Spatially-resolved CLS can now address several key questions about defects in ZnO: As with bulk ZnO single crystals, what is the nature of defects inside spatially confined ZnO and how are they distributed spatially? How do chemical processing, mechanical strain, and electrical forces affect these defect distributions? How does the nature and spatial distribution of these defects affect device transport and optoelectronic properties? And can these features be controlled?

To address several of these questions, we first discuss in Sec. II the various types of defects whose electronic energies and thermodynamic stabilities have been calculated and that have been suggested to account for ZnO optical and electrical measurements as well as complementary atomic-scale properties reported by other experimental techniques. We then present representative results using laterally and depth-resolved CLS to identify native defects at metal-bulk ZnO interfaces, illustrating the importance of defect segregation to surfaces and interfaces (Sec. III); laterally-resolved defect distributions that redistribute on a microscale as a result of electric and thermal stress (Sec. IV); spatially-resolved defects in micro- and nanostructures that depend on growth method and geometry as well as diffusion from neighboring growth substrates (Sec. V), and finally the impact of these defects on electrical device properties as well as new directions to study and control them (Sec. IV). Due to space constraints, the spatially-resolved results presented here are by no means inclusive but are intended to be representative of many related results on these topics.

II. Native Point Defects in ZnO

Native point defects in ZnO have been studied extensively by a number of theoretical and experimental techniques over the past few decades. To determine defect energetics and electronic structure in ZnO, recent theoretical techniques have included first-principles calculations based on density functional theory within the local density approximation and refinements to closely match the band gap^{81,82,83} as well as hybrid Hartree-Fock density

functionals⁸⁴ Figure 1 summarizes the most common types of defects expected, their energy level positions within the band gap (a) and their thermodynamic stability (b). Both approaches

Fig. 1. (a) Defect transition levels in the ZnO band gap for various native point defects.⁸⁴ (b) Formation energies versus Fermi level position for various native point defects.⁸¹ Reprinted with permission from [84], © 2008 and [81], © 2007 American Physical Society.

yield similar transition energy levels, particularly for the oxygen vacancy (V_O) and the zinc vacancy (V_{Zn}), the two most energetically favorable defects for Zn-rich growth. Figure 1(a) shows that V_O and V_{Zn} both have states deep within the band gap, unlike all other defects except Zn_O antisites, which are much less favorable energetically. Electronic transitions between gap states and the band edges can emit or absorb light at characteristic energies that can be detected spectroscopically and used to identify their physical nature.

Besides CLS, leading characterization techniques have included photoluminescence spectroscopy (PL), electron paramagnetic resonance (EPR), optically detected magnetic resonance (ODMR), positron annihilation spectroscopy (PAS), Hall effect and transport methods. PL is limited in depth resolution by the absorption length of light, typically tens of nm or more, and diffraction-limited in lateral resolution to the wavelength of incident light, typically a fraction of a micron or higher. EPR and ODMR can provide quantitative information on the density of unpaired spins associated with particular defects, but they are typically limited to detection limits of $\sim 10^{11}$ spins overall. PAS also provides quantitative density information of both isolated and clustered defects but without their energy levels.⁸⁵ Depth-resolved CLS (DRCLS)⁸⁶ and PAS can be directly correlated to identify defect types associated with specific

optical emissions. Hall effect and current transport can provide the nature, density, and mobility of charge carriers but require advanced analytic techniques to identify specific transport pathways inside multilayer conducting films.⁸⁷ Both PL and CLS provide luminescence energies but do not identify the nature of the gap state transition. However, they can be correlated with optically stimulated charge state filling and unfilling transitions that result in changes of surface band bending or conductivity by surface photovoltage spectroscopy (SPS)⁸⁸ or surface conductivity measurements, respectively, to identify the conduction or valence band associated with the luminescence transition.

Combined DRCLS and PAS measurements have identified luminescence from 1.6 to ~ 2 eV with isolated and clustered V_{Zn} , increasing in energy with cluster size.⁸⁹ Subsequent combined PL, PAS and Hall effect⁹⁰ and ODMR⁹¹ measurements are consistent with this result, with the latter and SPS determining energies in the band gap consistent with V_{Zn} energy levels predicted by theory. In contrast, optical identification of V_O defects has been the subject of considerable debate. Correlated PL, absorption, and EPR measurements under oxidation and annealing conditions initially suggested that V_O is associated with emission at 510 nm (2.43 eV).⁹² Debate focused on the value of the magnetic moment g -factor associated with this assignment, particularly due to the proximity of a 2.35 eV emission associated with Cu impurities on Zn sites.⁹³ Nevertheless, more recent EPR, optically detected magnetic resonance (ODMR), and PL measurements show that these two emissions are of different origin and that the 2.45 eV emission is due to V_O defects in ZnO.^{94, 95, 96, 97} There is no unambiguous identification of other native point defects in ZnO except for shallow dopant levels due to impurities such as Al, Ga, In, and H. Comparative studies of ZnO defects in microwires, thin films, and bulk crystals reveals shallow defects common to all three.⁹⁸ See review of bound exciton and donor-acceptor pair recombination features in ZnO by Meyer *et al.*⁹⁹ Table I lists calculated energy levels of the most thermodynamically stable and commonly discussed deep levels in Zn-rich ZnO compared with values measured by a variety of experimental processing and measurement techniques.

Table I. Theoretically calculated and experimentally confirmed deep energy levels of commonly discussed native point defects in Zn-rich ZnO. Energies are referenced to the valence band maximum.

Native defect Assignment	Energy level (eV): Theory	References	Energy level (eV): Experiment	References / Techniques
V_{Zn}	0.87	81	1.36-1.76 (E_C -1.6~2, increasing with cluster size) 1.36-1.56 (E_C -1.8~2) 1.58 (E_C -1.78)	89 (DRCLS, PAS, SIMS); 90 (PL, PAS, HE); 100 (DRCLS, HE); 101 (SPS) 101 (IC, DRCLS) 97 (CL, PL, EPR) 91 (ODMR, PL)
	2.16	84	1.6	
Cu_{Zn}			2.42 (5K)	93 (EPR, PL), 102 (EPR, PL)
V_O	2.51 - 2.7	81, 103	2.43 -2.5 2.45 2.48 2.6 2.5 2.48-2.38	92 (A, EPR, PL) 94,95,96 (EPR,ODMR, PL) 104 (ODEPR) 91 (ODMR, PL) 105 (IC, DRCLS) 114 (IC, CL)
Zn_I	3.25, 3.3	84	2.81 3.03	106 (IC, PL) 107 (IC, A, EPR)
O_I	1.59*	81	-	-

A - absorption; DRCLS; IC – interface chemistry; EPR – electron paramagnetic resonance; HE- Hall effect; ODEPR – optically detected electron paramagnetic resonance; ODMR – optically detected magnetic resonance; PAS – positron annihilation spectroscopy; PL – photoluminescence spectroscopy; SIMS – secondary ion mass spectrometry; SPS – surface photovoltage spectroscopy.

* Thermodynamically unstable.

III. Depth-Resolved Defects at ZnO-Metal Interfaces

SEM-based DRCLS permits detection of defect formation in three dimensions – laterally localized within metal diodes and depth-resolved to within nm's of the metal-ZnO interface. Here the electron beam can be directed through a 500 nm diameter metal diode film or into the bare surface contiguous with the diode in order to measure light emitted back through the metal from new defects created by the metal deposition. These features can then be compared with those of the bare ZnO within nm's of the diode in order to identify metal-induced features unambiguously. Because of the high lateral and depth resolution required, these measurements would be difficult for other techniques to achieve. These DRCLS measurements reveal the role of near-room temperature chemical interactions in forming localized electronic states within the ZnO band gap.^{108,109} Figure 2(a) shows a CL spectra taken through a 30 nm Pd on ZnO(0001) with the 3.35 eV band gap and 2.45 eV deep level emission obtained for several different

incident beam energies E_B . All Fig.2 spectra were acquired at 10 K with constant beam power $P_b = 2 \mu\text{W}$ over 50 nm spot size, beam power typical for many of our examples presented here. The inset shows Monte Carlo simulations¹¹⁰ of electron-hole ($e-h$)

Fig. 2. (a) DRCLS of 30 nm Pd on ZnO(0001) showing increasing V_O -related emission within < 20 nm of the diode interface.¹⁰⁸ (b) Increased V_O -related defects within tens of nm of the Al-ZnO interface. (c) V_{Zn} at the Au-ZnO interface annealing above the Au-Zn eutectic temperature.¹⁰⁹ Reprinted with permission from [108], © 2008 and [109], © 2007 AIP Publishing.

pair creation rate that extend < 20 nm past the interface for $E_B = 3$ keV, increasing in depth with increasing E_B . These distributions account for backscattering and the energy-dependent electron scattering cross section, with inputs of 50 eV minimum electron energy, 45° incident angle, 300 μm spot size, and 10^6 incident electrons. Deep level emission increases strongly as excitation occurs closer to the Pd-ZnO interface, indicating defect formation tens of nm inside the ZnO.

Figure 2(b) illustrates CL spectra with $E_B = 5$ keV for 30 nm Al on ZnO compared with 2 keV spectra at a comparable ZnO depth from the neighboring bare ZnO. The inset illustrates the experimental geometry for excitation through versus next to the metal diode. Here Al deposition causes an increase in V_O -related defects, consistent with Al-O reactions on a scale of tens of nm or less. Figure 2(c) illustrates the analogous CL spectra for 30 nm Au on ZnO with annealed at the temperatures shown. For annealing temperatures up to 550°C, little or no change is evident, consistent with the noble metal character of Au. However at temperatures above the 642°C Au-Zn eutectic,¹¹¹ new defect emission appears at ~ 1.9 eV that corresponds to V_{Zn} formation.

Eutectic formation above this temperature promotes Zn extraction from the nearby ZnO lattice,

leaving behind V_{Zn} -related defects near the interface. Both the contrast between nanoscale DRCLS through the diodes versus at their periphery plus the appearance of new defects with annealing of the same diode provide evidence for the chemical basis of defect formation at metal-semiconductor interfaces. Furthermore, the formation of these defects has a direct impact on free carrier concentration within the surface space charge region of the metal-ZnO contacts. At Au contacts to chemically-cleaned Zn-face ZnO, capacitance-voltage (C-V) – measured carrier concentration is nearly constant whereas the same surface treated with a remote oxygen plasma (ROP) to lower V_O and introduce V_{Zn} defects results in new emission at 2.1 eV and large ($>2x$) decreases in electron density within the depletion region.¹¹² These combined DRCLS – C-V measurements on the same Schottky barrier show how defect densities have a direct effect on free carrier densities near surfaces. This defect segregation is common not only to many ZnO surfaces and interfaces but to other semiconductors as well.¹¹³

IV. Laterally-Resolved Defects inside ZnO Granular Composites

Spatially-resolved CLS can be used to measure the distribution of defects inside sub-micron polycrystalline grains of ZnO created by applied voltages that induce thermal runaway. Researchers have applied electric fields in the range of 10 – 100 V/cm to trigger rapid densification of ZnO powders and other oxides at relatively low temperatures.¹¹⁴ In turn, this *flash sintering* process is aimed at ultrafast consolidation and densification of ceramic specimens (in seconds) while simultaneously optimizing structural homogeneity of ceramics with higher heating efficiency. Here current flows directly through ceramic specimens, causing local heating and the formation of point defects that lower resistance to subsequent annealing. SEM-based CLS and secondary electron imaging provide unique information to distinguish between multiple mechanisms suggested for this thermal runaway and the subsequent flash sintering, including the “conventional” coupled thermal and electric runaway as a consequence of exponentially-increased conductivities with increasing temperature and those as a result of an abrupt change of the specimen conductivity due to the sudden occurrence of another (more exotic) physical phenomenon such as avalanche nucleation of Frenkel pairs driven by the applied field, selectively-heated or melted grain boundaries that increase contact area between grains, or occurrence of a first-order bulk phase (or interfacial phase-like) transition.

Fig. 3. SEI and 2 keV DRCL spectra at room temperature of individual grains between anode and cathode. V_O integrated area in Grain #1 (a) and (b)) and Grain #2 ((c) and (d)) is higher in the grain bulk than at the grain boundary. Both grains exhibit similar defect behavior despite their size difference. (e) Micron-scale SEI morphology and (f) HSI maps of $A(\sim 2.4 \text{ eV}/A(\text{NBE}))$ in cross sectional regions between anode and cathode. (e) and (f) show two isolated grains circled with higher ratio intensity centers.¹¹⁵ Reprinted with permission from [115], © 2016, AIP Publishing.

ZnO powder samples sandwiched between Pt electrodes were electrically stressed in ultrahigh vacuum (UHV) with increasing voltages. Flash sintering resulted in a conductivity increase of more than an order of magnitude, while the secondary electron image (SEI) morphology showed average grain size doubling. Cross sectional imaging, DRCLS, and HSI of the cleaved sandwiches enabled measurements of defect densities within individual grains and at their boundaries as well as on a larger scale to image ‘tracks’ of high defect density. Figures 3(a) and 3 (c) illustrate SEI images of the sintered ZnO cross section.¹¹⁵ Corresponding DRCL spectra obtained at grain boundaries (circles) versus grain centers (x’s) appear in Figs. 3(b) and 3(d), respectively. These show significant increases in 2.41 eV defect peak areas inside grains versus at their grain boundaries. Figures 3(e) and (f) show micron-scale SEI and HSI maps of the

same sintered grains between anode and cathode. The HSI maps are extracted from full spectra similar to 3(b) and (d), taken pixel by pixel across SEM scanned areas on a scale of hundreds of microns. The circled areas identify the same isolated grains in both maps. The patterns of increased defect density in Fig. 3(f) suggest ‘tracks’ of increased defect density between anode and cathode. Inside individual grains as well as across multiple grains, it appears that thermal runaway generates more V_O defects at grain centers than at grain boundaries. Since V_O -related defects are typically associated with donors and increased n-type conductivity, the correlation between connected grains and ‘tracks’ with higher V_O densities suggests that these are higher conductivity pathways or filaments for local heating and dielectric resistance breakdown to occur.

V. Spatially-Resolved Defects in Nanostructures

CLS is uniquely suited to probe electronic properties of ZnO nanostructures. Spatially-localized CLS studies of nano- and microwires in particular describe numerous unique properties. They reveal the presence of impurities and how they redistribute both radially and lengthwise relative to their growth substrate. The spatial distribution of native point defects within nanowires is found to depend on wire diameter. Both the radial wire dimensions and the defect distributions within the wires are found to have a strong effect on wire conductivity and contact rectification of nanoscale device structures. These results emphasize the importance of defects and impurities in ZnO nanostructures and their device applications.

Nobis *et al.* showed that impurity and defect incorporation in ZnO micropillars is strongly inhomogeneous, in turn affecting their optical properties.¹¹⁶ Shown in Fig. 4(a), microcrystals were grown on *a*-plane sapphire using high pressure pulsed laser deposition. Besides band edge emission at ~ 3.23 eV, defect emission is present at 2.35 eV. This defect emission increases toward the micropillar center such that the intensity ratio $I(3.23 \text{ eV})/I(2.35 \text{ eV})$ decreases from the outer regions marked B toward the core marked A (Fig. 4(b)). High resolution ($\Delta E = 0.9 \text{ meV}$) CL spectra of the near band edge (NBE) region displays sharp features marked I_6 and I_3 associated with Al and ionized donor bound excitons, respectively.¹¹⁶ Slightly red shifted from these features is a broader peak whose maximum intensity broadens and shifts lower in spectra from the core region.

Fig. 4. (a) Top-view SEI of micro-pillar structure. A and B indicate core and outer diameter. (b) Corresponding map of UV/defect emission intensity ratios. (c) Local CL spectra for positions A and B. Reprinted from [116] © 2004 with permission of American Chemical Society.

In relation to the SEI image in Fig. 5(a), Fig. 5(b) illustrates this spectral shift relative to I_6 with position inside the micropillar. The authors conclude that Al impurities have accumulated at the center of the ZnO pillars, which was confirmed by energy dispersive X-ray (EDX) analysis

Fig. 5. (a) Micropillar SEI with central region marked. (b) Spectral map of band edge intensities vs. photon energy and position. (c) Red shift plotted vs. position inside micropillar. Reprinted from [116] © 2004 with permission of American Chemical Society.

and which could have originated from the Al_2O_3 substrate on which the pillars were grown. Since Al impurities are n-type dopants, this result indicates that the selection of growth substrates is important in order to control conductivity in nanostructures. Similarly, correlation of specific NBE features with doping, transport and thermal activation measurements can distinguish dopant versus extended defect features.¹¹⁷

Figure 6 shows spatially localized, high spectral resolution CLS obtained along the length of nanopillars that complement the radial studies of these micropillar studies.²² Figure 6(a) presents an SEI image of an 80-100 nm wire measured at the five points indicated. At Spot 2, Fig.6(b) exhibits spectral features due to I_6 , I_8 (Ga on a Zn site, Ga_{Zn}) and I_{8a} (not yet determined) excitons. While Ga is a specified impurity in the source material for these wires, Al may be present by diffusion from the sapphire substrate, as suggested by the gradual decrease of I_6 with

Fig.6. (a) ZnO nanopillar, (b) CL spectra corresponding to locations denoted in (a), (c) spatial variation in I_8 , I_{8a} , and I_6 from base (Spot 1) to tip (Spot 5). Reprinted with permission from [22], © 2007 AIP Publishing.

increasing distance from the substrate. More generally, these high resolution, spatially- localized spectral features highlight the extent of electronic structure detail that can be extracted from low temperature, high spectral resolution CLS.

Solution-based growth of ZnO rod assemblies provides further evidence for impurity redistribution in nanostructures and the role of different reaction mechanisms during growth. Al-doped ZnO rod assemblies grown hydrothermally by reacting zinc acetate, aluminum nitrate, and sodium hydroxide in a water-ethanol solvent produces concentric assemblies of ZnO rods with

distinct Zn- and O-polar orientations.¹¹⁸ The rods in these assemblies can grow in both Zn- or O-polar orientations, which exhibit striking differences in morphology, defect density and spatial distribution. Figure 7(a) illustrates an SEI image of an O-polar assembly, Fig. 7(b) shows a map of the intensity variation of 390 nm (3.176 eV) NBE emission corresponding to Fig. 7(a), and Fig. 7(c) presents CL spectra with both 390 NBE and 600 nm (2.06 eV) defect features corresponding to the four labelled spots in Fig. 7(a). CL spectra for Zn-polar growth are very similar. The intensity ratio $I(3.176 \text{ eV})/I(2.35 \text{ eV})$ decreases dramatically from base to tip, consistent with the emission decrease near the tips shown in Fig. 7(b). Figure 7(d) shows smooth variations of UV and Vis intensities across similar O- polar assemblies from tip to base, again consistent with the high UV intensities at intermediate distances along the rods. Corresponding

Fig. 7. (a) SEI image of O-polar ZnO concentric assembly and (b) corresponding CL map at 390 nm (3.176 eV). (c) CL spectra of four spots labelled in (a). (d) Relative amplitudes of UV (390 nm) versus visible (Vis) (600 nm) emissions from tip (1) to base (10) in similar O-polar assemblies (not shown). $E_B = 10 \text{ keV}$. Reprinted from [118] © 2010 with permission of PNAS.

Zn-polar intensity and defect distributions (not shown) exhibit qualitatively different features – high defect and low UV intensities at intermediate distances. Significantly, the spatial variations in Fig. 7(b) extend fully from side to side rather than exhibiting a radial dependence as in Figs. 4

and 5. This shows that the defect formation occurs as a function of growth time, in turn showing that growth kinetics play a role. These O-polar features also differ from those of Zn-polar growth pillars, which exhibit more than an order of magnitude higher defect emission as well as sharper edge and point morphology. Gautam *et al.* interpret these differences in terms of the differences in sequential stacking and charge polarity of Zn- and O-atomic layers along the c-axis, the interaction of the growing crystal surface with the changing concentration of reactants in solution, and the possible presence of additional defects such as Zn interstitials,¹¹⁹ not withstanding their high formation energy but given the Zn-rich growth environment. These opposite polar assemblies may yield distinctly different optoelectronics properties, which may however be influenced by the different defect distributions that are characteristic of each.

Nanorods grown by a vapor transport technique¹²⁰ exhibit significant differences in defect distribution compared with those grown from solution in Fig. 7. Fabbri *et al.* compared CL spectra of nanorods and nanostructured thin films in order to correlate different surface orientations with specific native point defects.¹²¹ Figure 8(a) illustrates a 5 kV cross sectional

Fig. 8. (a) Cross sectional SEI image of ZnO nanorods, (b) a corresponding monochromatic NBE and (c) 2.5 eV defect emission map. (d) CL spectra and (e) intensities corresponding to the areas labelled in (a). $E_B = 5$ keV. Reprinted from [121] © 2014 with permission of Nature Publishing Group.

image of ZnO nanorods and corresponding (b) NBE (3.3 eV) and (c) “green luminescence (2.3 – 2.5 eV) monochromatic maps. CL spectra corresponding to the marked areas of a single nanorod in Fig. 8(a) appear in Fig. 8(d), showing a NBE peak at 3.3 eV and broader defect luminescence centered at 2.45 eV. The peak intensities for each of the areas shown in Fig. 8(a) are plotted in Fig. 8(e). Both the maps and the CL spectra show increasing defect intensity and decreasing NBE emission with increasing distance from the substrate (area 5). This trend is similar to that of

O-polar growth in solution shown in Fig. 7 but opposite to that of Zn-polar growth. Even more significantly, defect luminescence energies are completely different between Fig. 7(c) (1.8 – 2 eV) and 8(d) (2.3 – 2.6 eV). As with Fig. 7, there is no radial dependence to these emissions, suggesting bulk rather than surface emission especially since the 5 keV beam excites predominantly the bulk versus the surface. The difference in solution versus vapor phase growth may account for these clear differences in defect type and distribution.

Hydrothermally grown ZnO hexagonal rod arrays from an aqueous solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{C}_6\text{H}_{12}\text{N}_4$ on a pulsed laser-deposited (PLD) ZnO substrate layer display CLS defect emissions in Fig. 9(a) that are similar to those in Fig. 8(d), *i.e.*, a broad unresolved peak centered at 500 – 520 nm (2.48 – 2.38 eV).¹²² While Fabbri *et al.* interpreted this feature from theory in terms of V_{Zn} defects, Lee *et al.* ascribed it to V_{O} defects based in part on a strong reduction in its intensity after an oxygen atmosphere anneal. A lower energy feature appears in Fig. 9(a) at 1.9 eV, similar to a peak ascribed to V_{Zn} defects in Fig. 2(c). Significantly, the ratio of deep level emission (DLE) versus NBE intensities $I(\text{DLE})/I(\text{NBE})$ increases with increasing radius. As Lee *et al.* note, this trend is opposite to that expected for defects confined to the

Fig. 9. (a) SEI images of 250 nm, 500 nm, 1 μm, and 2.5 μm radius ZnO rods. Corresponding 15 keV CL spectra and intensity ratio $I(\text{DLE})/I(\text{NBE})$ versus radius. Reprinted from [122] © 2012 with permission of American Chemical Society.

nanorod surface since the surface-to-volume ratio decreases with increasing radius. For example, Shalish *et al.*¹²³ and Pan *et al.*¹²⁴ attributed decreasing $I(\text{DLE})/I(\text{NBE})$ ratios with increasing radius observed with photoluminescence and cathodoluminescence spectroscopies,

respectively, to defects localized near the surface. These conflicting results suggested additional studies to determine the relative importance of surface versus bulk defect contributions to CL spectra as well as their impact on carrier transport, optoelectronics, and other device applications.

In order to characterize defect distributions in nano- and microwires quantitatively and to determine the relative importance of surface vs. bulk defects, Ruane *et al.* studied the spatial distribution of defect-related deep band emission in ZnO nano- and microwires grown by PLD or vapor transport using SEM-based DRCLS in a HSI mode.¹²⁵ Data from wires ranging from 380 nm to 2.7 μm diameter were analyzed using a 3D DRCLS simulation and used to estimate the segregation depth and decay profile of the near surface defects across wire diameters. See Fig. 10(a). They observed different dominant defects from each growth process as well as a diameter-dependent defect segregation behavior with radial precision of tens of nanometer or less, taking into the account the wire's hexagonal morphology, the 3D generation of free *e-h* carriers that recombine to emit light, and the refraction of CL-generated light out of the wire. See Fig. 10(b). Wires grown by PLD with hexagonal diameters from 100 nm-10 μm and length > 100 μm exhibited green band emission centered at 2.35 eV with phonon structure attributed to Cu on Zn sites (Cu_{Zn}).⁹³ Shorter, needle-shaped but hexagonal wires grown by chemical vapor deposition (CVD) with diameters 400 nm-2 μm exhibited unstructured green band emission centered at ~ 2.45 eV, while wires grown by PLD using a target consisting of $\text{ZnO}:\text{Ga}_2\text{O}_3/99:1$ wt% with ~ 2 μm length and 200 nm diameter exhibited defect peak emission at ~ 1.8 eV, again attributed to V_{Zn} defects that compensate the degenerately doped ZnO.^{89,90}

Figure 10(c) illustrates the excitation across a hexagonal wire with a segregation region whose width and defect density are modeled as either constant, linearly decreasing, or exponentially decreasing into the bulk. A constant power (beam current $I_B * E_B$) depth profile of $I(\text{defect})/I(\text{NBE})$ using three incident beam energies in Fig. 10(c) yielded the same best fit parameters of segregation width, bulk defect concentration, and decay profile as the 5 keV HSI line scan fit in Fig. 10(d). The latter shows how the simulation reflects the asymmetries and slope changes of the experimental data. Line-scan plots for 1.7 μm , 2.2 μm and 380 nm wires yielded segregation widths of 36 ± 9 , 36 ± 5 , and 12 ± 6 nm, respectively with linear, linear, and constant defect profiles, respectively. For microwires, these results can account for the 30 nm

Fig. 10. (a) Illustration showing the line-scan measurement process and an SEM image of a ZnO wire. Red arrow in SEM image represents a typical line-scan path from which defects were measured. (b) Illustration of simulation for a scan point. (c) Single spot depth dependence of $I(\text{defect})/I(\text{NBE})$ at 80K on a ZnO wire's top face (d) Corresponding 5 keV line-scan fit for wire from (c) (blue dots represent best fit). Reprinted from [125] © 2016 with permission of Royal Society of Chemistry.

recombination layer of Shalish *et al.*¹²³ while the thinner wire results are thicker than the 5-6 nm CL shell measurements of Xue *et al.* for 140-200 nm diameter wires grown by vapor phase transport.¹²⁶ These profiles of $I(\text{defect})/I(\text{NBE})$ are inconsistent with a defect emission process in which minority carriers diffuse to the surface and recombine there. Instead, they show that defects are not confined to the surface. Rather, they are distributed inside ZnO nano- and microwires and segregate toward free surfaces.

VI. Spatially-Resolved Native Point Defects and Electronic Devices

Native point defects are known to act as donors and acceptors in bulk ZnO single crystals and thin films. For example, V_O defects are typically associated with increased n-type doping while V_{Zn} are known to be compensating acceptors in n-type ZnO.¹²⁷ Spatially-resolved CLS shows that these defects extend tens of nanometers into these structures with radial distributions that vary with wire diameter and which can alter recombination and surface space charge regions governing the efficiency of light emission and charge transport. The presence of charged defects inside rather than just on the surface of these nanostructures changes the band bending shape and depletion width conventionally assumed for charge resident on the surface alone. Figure 11(a) illustrates the band bending and depletion width (shaded) of a metal-semiconductor junction under reverse bias, which increases the depletion width otherwise induced by charges at the semiconductor surface.¹²⁸ Figure 11(b) shows a top and side view of this depletion zone inside a

Fig. 11. (a) Energy vs. position under reverse bias of band bending region extending away from metal-semiconductor interface. Schematic top and side view of band bending inside a (b) thick and thin (c) wire. Reprinted from [128] © 2013 with permission of Institute of Physics.

relatively thick nanowire in contact with the metal. Here only a portion of the wire volume is depleted of charge. In contrast, Fig. 11(c) shows the corresponding top and side views of a thin microwire in which the depletion is comparable or larger than the wire diameter. In this case, the entire volume of the wire is depleted of charge. The density and distribution of defects both at the surface and inside the nanowire will strongly affect this depletion width and its change under

electrical bias. The defect density and distribution, compared with the free carrier density and wire diameter, will then determine how much they affect charge transport through the wire.

Spatially-resolved CLS combined with nanoscale transport measurements provide direct evidence that native point defects have an impact on device characteristics. Figure 12(a) shows drain-source current response to forward and reverse bias of ZnO nanowires with diameters between 30 and 100 nm grown by thermal chemical vapor deposition.¹²⁹ A gate bias was applied with a highly doped Si substrate and insulating SiO₂ layer underlying the nanowire with Ti/Au ohmic contacts. Here the inset shows *on-off* rectification ratio of drain-source current I_{ds} between forward and reverse bias exceeding 10^6 . In contrast, Fig. 12(b) shows no rectification and only a factor of 2 reduction in current with reverse bias. A CL spectrum of the wire measured in Fig. 12(a) shows a spectrum with a ZnO NBE peak at 380 nm (3.26 eV) and lower energy features at

Fig. 12. I_{ds} vs. V_G curve of a nanowire device (a) without vs. (b) with 510 nm defect emission. (c) CL spectra of device shown in (a). (d) CL spectra of device shown in (b). Inset in (d) shows monochromatic 510 nm map vs. no 510 nm emission in (c).¹²⁹ Reprinted from [129] © 2007 with permission of American Chemical Society.

460 nm (2.69 eV) and 650 nm (1.91 eV) that were identified with the E' and non-bonding oxygen hole center (NBOHC) of the underlying SiO₂ rather than any ZnO defect.¹³⁰ A CL spectrum of the wire measured in Fig. 12(b) shows all these features in addition to a pronounced shoulder that yields a deconvolved peak at 510 nm (2.43 eV). As already discussed, researchers have identified this emission with multiple point defects and complexes, but it is often ascribed to a V_O-related donor defect.⁹² Supporting the donor character of this emission are studies with combined CLS, capacitance-voltage (C-V), and remote oxygen plasma processing that show how these defect emissions are associated with increased n-type carrier density.¹³¹

The presence of additional donors in these thin nanowires does in fact increase the carrier density as evidenced by the higher currents measured for the same applied voltages. However, the authors point out that this increase is only a factor of 2 whereas the rectification ratio is orders of magnitude higher. One of the possible mechanisms they propose to account for these electrical properties is the narrowing of the depletion region due to the increase in carrier density. For example, the depletion width W for a planar metal-ZnO Schottky barrier can be calculated as

$$W = [2\varepsilon \cdot (V_0 - V_{\text{applied}}) / q \cdot N]^{1/2} \quad (1)$$

where $\varepsilon = 7.8 \varepsilon_0$ is the dielectric permittivity of ZnO, V_0 is the band bending without applied bias, and N is the carrier density. For nominal values of $N = 10^{17} \text{ cm}^{-3}$ and $V_0 = 1 \text{ eV}$, $W = 93 \text{ nm}$, which is sufficient to pinch off conduction radially in a 100 nm diameter wire with $V_{\text{applied}} \ll 10 \text{ V}$. If N increases by just one order of magnitude to 10^{18} cm^{-3} , $W = 29 \text{ nm}$ so that V_{applied} must exceed 40 V in order to pinch off a 100 nm wire with the depletion region extending into a circular current-carrying region from one side. For $N = 10^{19} \text{ cm}^{-3}$, $W = 9 \text{ nm}$, preventing pinch-off for even very high V_{applied} . For a given V_{applied} applied to only one side of the nanowire, I_{ds} would increase proportional to the increase in undepleted volume as depletion width decreases as well as the increase in conductivity $\sigma = Ne\mu$ for mobility μ . The much lower I_{ds} increase suggests that the increased donor density may not be uniformly distributed inside the nanowires and that mobility is degraded due to the increased carrier scattering by the charged defects. A non-uniform donor distribution with fewer donors in the wire core would be consistent with distribution represented in Fig. 10. The results shown in Fig. 12 provide one example of spatially-resolved CLS providing a tool to understand and quantify device properties of ZnO nano- and microwires.

VII. New Directions

This review is intended to provide a representative overview of key results using spatially-resolved CLS to study defects in ZnO in its many forms. Numerous other studies could not be discussed due to the limited space available. With the advent of new ZnO growth, process techniques, and device structures, studies using spatially-resolved CLS can take many new directions. Understanding ohmic and Schottky barrier formation at metal-ZnO micro- and nanowire contacts will require depth-resolved studies of defects in close proximity to the buried interface. Chemical treatments¹³² or dopant implantation to form ohmic contacts^{133,134} introduces defects that DRCLS can characterize and monitor to optimize processing. Similarly, correlating charge transport through nano/microwires with defect spatial distributions can reveal effective conduction pathways. Studies of heterojunctions formed along the length of nanostructures will require spatial resolution sufficient to resolve features inside the depletion regions of the constituents. Similarly, studies of coaxial heterojunction wires will make use of probes that distinguish between inner cores, outer shells, and the interfaces between them. Spatially-localized CLS will be needed to take into account effects of wire inhomogeneity¹³⁵ and defect dependence on growth processes.¹³⁶ Yet another nanoscale CLS application will be in monitoring process techniques such as plasma processing and annealing to reduce or rearrange defects inside nanostructures. Certainly such spatially-resolved probes in all three dimensions will be needed to probe inside transistor structures with sub-micron dimensions. As new device structures develop, CLS at the nanoscale can provide insights into both their performance as well as their degradation under operational stress. The quantitative spatial precision of 3D CLS modeling¹²⁵ can be further refined, *e.g.*, by comparison with implanted impurity distributions monitored by secondary ion mass spectroscopy (SIMS). CLS combined with other defect characterization techniques such as PAS, EPR, ODMR, and micro-Hall effect measurements can help identify specific defects, especially enabled by ZnO nano- and microstructures that can be thermally or chemically processed to alter the complete volume of the structure. These studies suggest many new avenues to understand and control defects in ZnO. Progress in this arena may be of more general significance as spatially-resolved cathodoluminescence spectroscopy extends to other semiconductors and device structures.

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Table I.

Native defect Assignment	Energy level (eV): Theory	References	Energy level (eV): Experiment	References / Techniques
V_{Zn}	0.87	81	1.36-1.76 (E_C -1.6~2, increasing with cluster size) 1.36-1.56 (E_C - 1.8~2) 1.58 (E_C -1.78)	89 (DRCLS, PAS; SIMS); 90 (PL, PAS, HE); 100 (DRCLS, He); 101 (SPS) 101 (IC, DRCLS) 97 (CL, PL, EPR)
	2.16	84	1.6	91 (ODMR, PL)
Cu_{Zn}			2.42 (5K)	93 (EPR, PL), 102 (EPR, PL)
V_O	2.51 - 2.7	81,103	2.43 -2.5 2.45 2.48 2.6 2.5 2.48-2.38	92 (A, EPR, PL) 94,95,96 (EPR,ODMR,PL) 104 (ODEPR) 91 (ODMR, PL) 105 (IC, DRCLS) 114 (IC, CL)
Zn_I	3.25, 3.3	84	2.81 3.03	106 (IC, PL) 107 (IC, A, EPR)
O_I	1.59*	81	-	-

A - absorption; DRCLS; IC – interface chemistry; EPR – electron paramagnetic resonance; HE- Hall effect; ODEPR – optically detected electron paramagnetic resonance; ODMR – optically detected magnetic resonance; PAS – positron annihilation spectroscopy; PL – photoluminescence spectroscopy; SIMS – secondary ion mass spectrometry; SPS – surface photovoltage spectroscopy.

* - Thermodynamically unstable.