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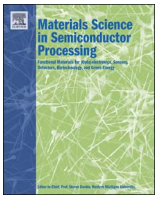

Review

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.

1. 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-resolved [4] 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, [6–17] processing, [18] and electronic properties of nanowires, [19–22] nanobelts, [23] nanotubes, [24] nanoparticles, [25] homo- and heterojunctions, [26–29] as well as their strain effects [30–33] and defects [34,35]. Quantum structure studies have included wells, [36–39] disks, [40,41] and dots [42–48]. CLS has been used to track the spatial/strain dependence of near-gap luminescence (D°,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

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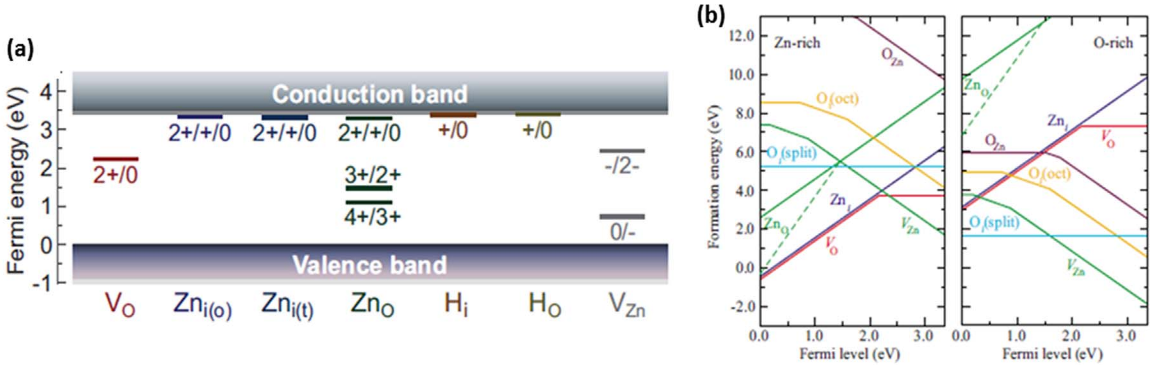

Fig. 1. (a) Defect transition levels in the ZnO band gap for various native point defects [84]. (b) Formation energies versus Fermi level position for various native point defects [81]. Reprinted with permission from [84], © 2008 and [81], © 2007 American Physical Society.

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 [59–62]. 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 applications [69] 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 [75–79].

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 Section 2 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 (Section 3); laterally-resolved defect distributions that redistribute on a microscale as a result of electric and thermal stress (Section 4); spatially-resolved defects in micro- and nanostructures that depend on growth method and geometry as well as diffusion from neighboring growth substrates (Section 5), and finally the impact of these defects on electrical device properties as well as new directions to study and control them (Section 4). 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.

2. 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 [81–83] as well as hybrid Hartree-Fock density functionals [84] Fig. 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 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. Fig. 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 ~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