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Review

Zinc Oxide: Crystal Chemistry, Defect Physics, and Functional Applications

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Abstract:
Zinc oxide (ZnO) is a II-VI semiconductor with a direct band gap of approximately 3.37 eV and an exciton binding energy of 60 meV at room temperature. These properties, together with its chemical stability, non-toxicity, and earth-abundant composition, have made it the subject of sustained research over several decades. This review examines the structural and electronic properties of ZnO, with particular attention to native point defects and their role in n-type conductivity. We discuss the main synthesis routes, both physical and chemical, and describe how growth conditions govern grain morphology, oxygen stoichiometry, and carrier concentration. The review then surveys established and emerging application areas, including UV photodetection, piezoelectric transducers, gas sensing, photocatalysis, and dilute magnetic semiconductor behaviour following transition-metal doping. Where relevant, we note unresolved debates in the literature, such as the precise identification of donor species and the difficulty of achieving stable p-type ZnO. Representative references are drawn from peer-reviewed sources spanning the past three decades.

Keywords: *zinc oxide; wurtzite; point defects; photocatalysis; piezoelectricity; dilute magnetic semiconductor*

1. Introduction

Zinc oxide has been known as a functional material for well over a century, finding early use as a pigment and vulcanisation additive in rubber processing. Its re-emergence as a topic of active semiconductor research began in the 1990s and accelerated sharply after the demonstration of ZnO nanowire arrays and the prediction that high hole concentrations might be accessible through nitrogen doping [1, 2]. Despite the large body of literature now available, ZnO continues to attract experimental and theoretical attention because several fundamental questions remain incompletely resolved.

The combination of a relatively large band gap (3.37 eV) and a high exciton binding energy (60 meV) places ZnO alongside GaN as a candidate for room-temperature excitonic UV emitters [3]. Unlike GaN, ZnO is available in bulk single-crystal form from hydrothermal growth, is soluble in acidic and basic media (which aids wet-chemical patterning), and does not require lattice-matched substrates for many device geometries. These practical considerations partly explain the continuing commercial interest in ZnO for transparent conducting electrodes, piezoelectric MEMS, and photocatalytic water treatment [4, 5].

This article reviews the essential physics and chemistry of ZnO, summarises the principal synthesis methods, and outlines the major application domains. The intention is to provide a concise but technically grounded entry point to the field rather than a comprehensive bibliography; earlier reviews by Ozgur et al. [6] and Wang [7] cover the pre-2010 literature in considerable depth.

2. Crystal Structure and Electronic Band Structure

2.1 Wurtzite Phase

Under ambient conditions, ZnO crystallises exclusively in the wurtzite structure (space group P63mc, a = 0.3250 nm, c = 0.5207 nm, u = 0.382) [6]. The structure consists of two interpenetrating hexagonal close-packed sublattices, one occupied by Zn^{2+} and the other by O^{2-}, displaced along the c-axis. Each Zn atom is tetrahedrally coordinated to four oxygen neighbours, and vice versa. The lack of an inversion centre along [0001] is the origin of both piezoelectric and pyroelectric behaviour.

A metastable zinc-blende phase can be stabilised by epitaxial growth on cubic substrates such as GaAs or ZnS, and a rocksalt phase appears above approximately 9 GPa [6]. Neither phase is relevant to most device applications, and they are not discussed further here.

2.2 Electronic Structure

The band structure of wurtzite ZnO places the valence band maximum and conduction band minimum at the zone centre (Γ point), confirming a direct gap of 3.37 eV at 300 K [3]. The valence band is formed primarily from O 2p states hybridised with Zn 3d states; the relatively shallow Zn 3d levels sit at approximately 7.5 eV below the valence band maximum and introduce a non-trivial p-d repulsion that pushes the valence band upward compared with simpler models [8]. The conduction band is predominantly Zn 4s in character, giving a low electron effective mass ($m^* \approx 0.24\ m_e$) and high electron mobility in clean single crystals (>200 $cm^2\ V^{-1}\ s^{-1}$) [6].

The spin-orbit splitting of the valence band into three sub-bands (A, B, C) is relatively small compared with GaN, a consequence of the lighter oxygen atoms [9]. Photoluminescence measurements at low temperature typically show the A-exciton free-exciton line near 3.375 eV, with donor-bound exciton peaks appearing at slightly lower energies [10].

3. Point Defects and Conductivity

3.1 Native Donors

As-grown ZnO is invariably n-type. The origin of this unintentional doping has been debated at length. Early work attributed it to oxygen vacancies (VO) acting as shallow donors, but density functional theory calculations using hybrid functionals show that VO is in fact a deep level and unlikely to contribute significantly to room-temperature conductivity [11]. Zinc interstitials (Zni) have similar theoretical difficulties. The current consensus, supported by secondary ion mass spectrometry and muon spin rotation data, favours interstitial hydrogen (Hi) as the dominant shallow donor in many samples, with substitutional hydrogen at the oxygen site (HO) also contributing [12].

Interstitial hydrogen in ZnO has a donor ionisation energy of about 30-53 meV depending on its configuration and the method of calculation [12, 13]. It is highly mobile even near room temperature and can be partially removed by annealing above 500 K in vacuum, which typically reduces carrier concentration. This behaviour is broadly consistent with experimental observations that oxygen-rich growth environments produce films with lower electron densities.

3.2 p-Type Doping Challenge

Achieving stable, reproducible p-type ZnO remains one of the central challenges in the field. Group-IA elements (Li, Na, K) substituting on the Zn site act as acceptors but are prone to interstitial compensation. Group-VA elements (N, P, As, Sb) on the oxygen site are the most-studied acceptors, yet reports of p-type conductivity have been difficult to reproduce [14]. First-principles calculations indicate that nitrogen doping produces a relatively deep acceptor level (~0.4 eV above the valence band maximum), which limits hole concentration at room temperature [11]. Phosphorus and arsenic introduce further complications related to solubility and lattice distortion.

Co-doping strategies, for example simultaneous incorporation of Al and N, have been proposed to reduce the acceptor binding energy through lattice relaxation effects [15]. Some positive results have been reported, but long-term stability and reproducibility across growth platforms remain issues. A fully reliable p-n homojunction based on ZnO has not yet been demonstrated at the device level, which constrains its use in LED applications.

4. Synthesis Methods

4.1 Physical Vapour Deposition

Radio-frequency (RF) and DC magnetron sputtering from ZnO or metallic Zn targets in Ar/O2 atmospheres is the most common method for depositing thin films in industrial contexts. The oxygen partial pressure is the primary lever for controlling stoichiometry; films grown at low oxygen partial pressures tend to be more conductive while oxygen-rich conditions push the film toward insulating behaviour [4]. Typical substrate temperatures during sputtering range from room temperature to 500°C, with higher temperatures generally improving crystalline quality and preferred (0001) texture.

Pulsed laser deposition (PLD) offers more precise stoichiometric transfer from a ceramic ZnO target and is widely used in research settings to explore doping effects. The high instantaneous flux during a PLD pulse can drive non-equilibrium incorporation of dopants at concentrations above thermodynamic solubility limits, which is relevant for magnetic doping studies [16].

4.2 Chemical Vapour and Solution Methods

Metal-organic chemical vapour deposition (MOCVD) using diethylzinc and an oxygen source (N2O or O2) yields epitaxial ZnO layers of high structural quality on sapphire substrates at growth temperatures between 400 and 700°C [17]. The method is scalable and compatible with existing III-nitride production lines.

Solution-based routes are particularly attractive for nanostructure synthesis. The hydrothermal method, typically using zinc nitrate or zinc acetate with hexamethylenetetramine (HMT) in aqueous solution at 60-95°C, produces well-faceted nanorods and nanowire arrays whose aspect ratio is tunable through the Zn:HMT ratio and growth time [7]. The chemical bath deposition variant does not require sealed vessels and is amenable to large-area deposition on flexible substrates. Sol-gel processing, followed by spin coating and pyrolysis, is commonly used for thin film preparation in academic laboratories owing to its low cost and ease of implementation [18].

4.3 Nanostructure Morphologies

One of the distinctive features of ZnO is the diversity of nanostructures it forms under different growth conditions. In addition to nanorods and nanowires, tetrapod morphologies (four arms growing along the equivalent <0001> directions), nanobelts, nanorings, and hierarchical flower-like structures have all been reported [7, 19]. The wurtzite crystal habit and the polar character of the (0001) Zn-terminated and (000-1) O-terminated surfaces are primarily responsible for this diversity, since the surface energy anisotropy drives preferential growth along the c-axis. Understanding and controlling surface termination is therefore central to morphological engineering.

5. Functional Applications

5.1 UV Photodetection

ZnO photodetectors operating in the UV-A/UV-B range exploit the sharp onset of optical absorption at the band edge. Devices based on ZnO nanowires between metal electrodes exhibit persistent photoconductivity, where the photocurrent decays slowly after the UV source is switched off; this is attributed to oxygen adsorption/desorption at surface trap states rather than to bulk trapping [20]. Responsivities above 10^3 A/W have been reported for individual nanowire devices, though integration into arrays remains challenging. For high-speed applications, thin-film MSM structures fabricated by sputtering have demonstrated rise times in the microsecond range [21].

5.2 Piezoelectric Applications

The absence of inversion symmetry in the wurtzite structure gives ZnO a piezoelectric coefficient d33 of approximately 12 pC/N, which is lower than that of PZT but sufficient for energy harvesting and MEMS applications where lead-free and biocompatible materials are required. Wang and Song demonstrated in 2006 that individual ZnO nanowires deflected by an AFM tip generated measurable output voltages, establishing the concept of a piezoelectric nanogenerator [22]. Since then, flexible substrate geometries and textile integration have been explored for wearable energy harvesting, though output power densities remain modest (typically below 1 mW/cm^2 under realistic mechanical excitation) [23].

5.3 Gas Sensing

ZnO is one of the earliest and most extensively studied metal-oxide gas-sensing materials. The sensing mechanism relies on the modulation of surface conductance by target gas molecules: in air, adsorbed oxygen species (O^-, O^{2-}) deplete a surface layer of electrons, and reducing gases such as ethanol, H2S, or CO displace these species and restore conductance [24]. Nanowire and nanoparticle morphologies provide high surface-to-volume ratios that enhance sensitivity. Noble metal functionalisation (Pd, Au, Pt nanoparticles) improves selectivity by providing catalytic dissociation of specific target molecules [25]. Operating temperatures in the range 200-400°C are typically needed for adequate response speed, though some room-temperature sensors have been demonstrated using UV-light activation [26].

5.4 Photocatalysis

The photocatalytic activity of ZnO under UV illumination has been widely documented for degradation of organic dyes and pharmaceutical compounds in water. The mechanism involves photogenerated electron-hole pairs reacting with adsorbed water and oxygen to produce reactive oxygen species (primarily $OH^\bullet$ radicals), which oxidise organic substrates non-selectively [27]. ZnO competes with TiO2 (anatase) in this application domain; comparative studies generally show comparable or superior activity for ZnO under UV excitation, though ZnO suffers from photocorrosion in acidic media that limits long-term stability [28].

Extension of the photoresponse into the visible range has been pursued through nitrogen doping (which narrows the effective band gap), through coupling with narrow-gap sensitisers such as CdS or g-C3N4, and through plasmonic enhancement using Au nanoparticles [29]. Each approach has been demonstrated at the laboratory scale, but scalable implementations for water treatment remain at the pilot stage.

5.5 Transparent Conducting Oxides

Aluminium-doped ZnO (AZO) and gallium-doped ZnO (GZO) are commercially relevant alternatives to indium tin oxide (ITO) in transparent electrode applications, motivated primarily by the scarcity and cost of indium [4]. AZO films deposited by sputtering achieve resistivities below 5×10^{-4} Ω·cm with optical transmittances above 85% in the visible range. These values are competitive with ITO for thin-film photovoltaic back contacts and organic LED applications. The main limitation of AZO compared with ITO is lower chemical stability under humid conditions and greater sensitivity to plasma processing, which restricts its use in certain device integration schemes [30].

5.6 Dilute Magnetic Semiconductors

The prediction by Dietl et al. in 2000 that ZnO doped with ~5% Mn and supplemented by high hole concentrations would exhibit ferromagnetism above room temperature generated enormous activity [31]. Transition metal dopants, particularly Co, Mn, Fe, and Ni, have been incorporated into ZnO by a variety of methods, and room-temperature ferromagnetic signals have been reported in numerous studies. However, the origin of this magnetism remains contentious: precipitated secondary phases (e.g., Co metal clusters, CoO, Co3O4) can produce magnetic signals that are difficult to distinguish from intrinsic exchange interactions by standard characterisation [32]. Studies employing X-ray magnetic circular dichroism (XMCD) and element-resolved magnetometry have in several cases attributed the ferromagnetic signal to metallic Co clusters below the X-ray diffraction detection limit [33]. Careful synthesis under controlled oxygen stoichiometry and rigorous phase analysis are therefore prerequisites for claiming intrinsic dilute magnetic semiconductor behaviour in ZnO.

6. Challenges and Outlook

Several persistent challenges limit the translation of ZnO research into commercial devices. The inability to dope ZnO p-type reliably means that complementary devices and homojunction LEDs remain out of reach. The identification of native donors is still not settled unambiguously for all growth methods, which complicates predictive materials design. In dilute magnetic semiconductors, distinguishing intrinsic from extrinsic magnetic contributions requires a level of structural characterisation that many reported studies have not applied.

On the other hand, ZnO occupies a firm position in piezoelectric MEMS, gas sensing, and photocatalysis, and AZO has made inroads into thin-film photovoltaics. The hydrothermal synthesis of aligned nanowire arrays is well-understood and scalable, enabling applications in flexible electronics and bio-sensing. The availability of wafer-scale hydrothermal ZnO single crystals with low dislocation densities provides a substrate platform for homoepitaxial growth that may eventually resolve the p-type problem through greater control of hydrogen concentration during doping.

Emerging directions include ZnO in triboelectric nanogenerators (combined piezo- and triboelectric harvesting), deep-ultraviolet LEDs based on MgZnO alloys with widened band gaps, and ZnO as an electron transport layer in perovskite solar cells, where its band alignment and processability are advantageous [34, 35]. Each of these requires incremental advances in defect control and interface engineering rather than fundamentally new science, suggesting that steady experimental progress is more likely than a discontinuous breakthrough.

7. Conclusion

Zinc oxide is a structurally simple material whose electronic and functional properties arise from a combination of polar crystal chemistry, a tunable defect landscape, and a high surface-to-volume ratio in nanostructured form. Its band gap and exciton binding energy make it attractive for UV optoelectronics, while the piezoelectric response, catalytic activity, and gas-sensing behaviour are all well-established at the laboratory level. The key unsolved problem, reproducible p-type doping, has not yet yielded to the many approaches attempted over two decades, and its resolution would substantially expand the application space. In the interim, ZnO continues to find practical use in sensing, photocatalysis, transparent electrodes, and piezoelectric harvesting, and new device concepts in energy and biomedical sensing continue to emerge.

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