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Metal Oxide Semiconductors: State-of-the-Art and New Challenges

1.1 Introduction

Metal oxide semiconductors (MOS) are abundant materials found in the Earth's crust and are commonly used in traditional ceramics. However, they differ significantly from conventional inorganic counterparts like silicon and III-V compounds in various aspects. These distinctions encompass materials design concepts, electronic structure, charge transport mechanisms, defect states, thin-film processing, and optoelectronic properties. As a result, oxide semiconductors enable the realization of both established and innovative functionalities [1].

In comparison to inorganic semiconductors, oxide semiconductors possess unique characteristics. These include exceptional carrier mobilities even in the amorphous state, resilience against mechanical stress, compatibility with organic dielectric and photoactive materials, and high optical transparency. These properties make oxide semiconductors particularly appealing for various applications.

In recent decades, MOS have garnered significant attention in various research fields, including optoelectronics, thin-film transistors (TFTs), photocatalysts, gas sensors, solar cells, and memristors [1–14], as shown in Figure 1.1. MOS can be categorized into two types based on their conductivity: *n*-type, where electrons are the majority carriers, and *p*-type, where holes are the majority carriers. These semiconducting properties arise from factors such as doped aliovalent cations or oxygen nonstoichiometry [15, 16]. Among the *n*-type MOS, ZnO, SnO₂, TiO₂, In₂O₃, and Ga₂O₃ are widely studied concerning synthesis, characterization, and applications [17–21]. As for the *p*-type MOS, research efforts primarily focus on Cu_xO (CuO and Cu₂O), SnO, and NiO_x [22–24].

1.2 *n*-Type Metal Oxide Semiconductors

1.2.1 ZnO

Zinc oxide (ZnO), as an *n*-type semiconductor, has sparked significant research interest due to its distinctive physical and chemical properties [25–27]. In the field of materials science, ZnO is classified as a II–VI compound semiconductor, possessing

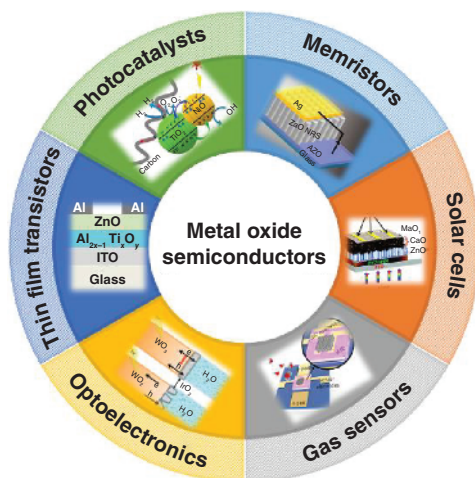


Figure 1.1 Applications of metal oxide semiconductors. Source: Reprinted with permission from Refs. [9–14]. Copyright 2015 American Chemical Society, 2016 American Chemical Society, 2020 American Chemical Society, 2020 The Royal Society of Chemistry.

a covalence level between ionic and covalent semiconductors. Its attributes, such as a direct wide bandgap ($E_g \sim 3.3$ eV at 300 K), large free exciton binding energy (60 meV), and high thermal and mechanical stability at room temperature, make ZnO a promising candidate for various applications in electronic devices, optoelectronics, gas sensors, and laser technology [28, 29]. Additionally, ZnO can be utilized as an energy collector due to its piezo- and pyroelectric properties, as well as a photocatalyst for hydrogen production [30–32].

The crystal structure of ZnO can be classified into three types: wurtzite (B4), zinc blende (B3), and rocksalt (B1), as shown in Figure 1.2. Thereinto, wurtzite ZnO possesses a hexagonal structure (space group $C6mc$) with lattice parameters $a = 0.3296$ nm and $c = 0.52065$ nm. The structure of ZnO can be simply described as a number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions, stacked alternately along the c -axis. The tetrahedral coordination in ZnO results in noncentral symmetric structures and consequently piezoelectricity and pyroelectricity [33].

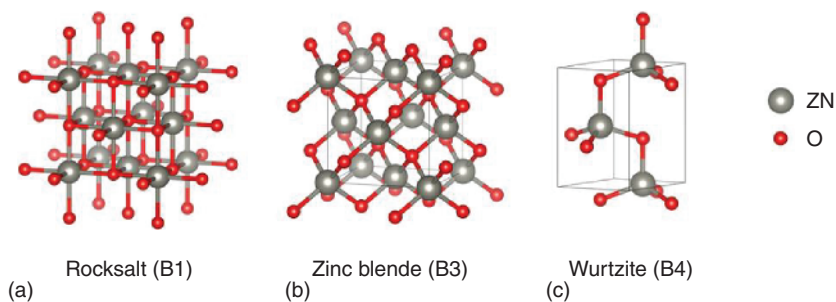


Figure 1.2 Stick and ball representation of ZnO crystal structures: (a) cubic rocksalt (B1), (b) cubic zinc blende (B3), and (c) hexagonal wurtzite (B4). The gray and red spheres denote Zn and O atoms, respectively.

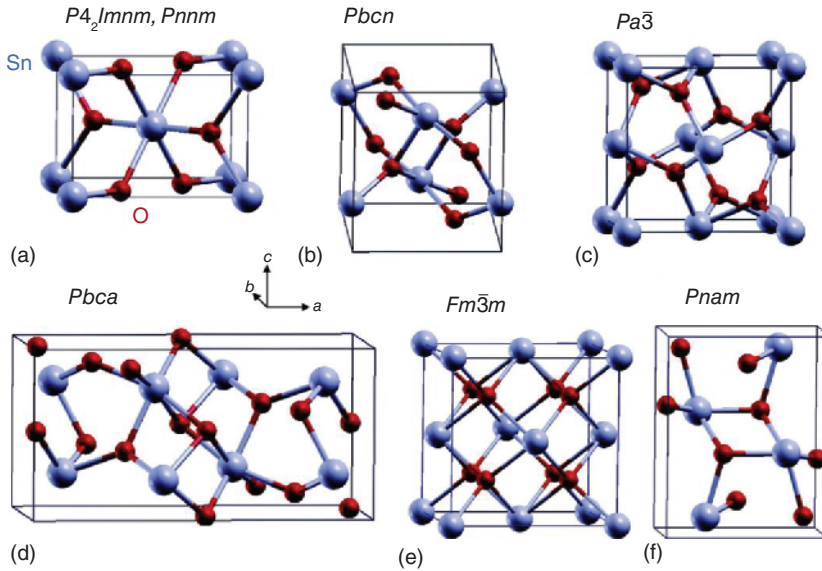


Figure 1.3 Bulk structures of SnO₂ polymorphs (gray and red colors represent Sn and O atoms, respectively). (a) Rutile ($P4_2/mnm$) and CaCl₂-type ($Pnnm$), (b) R-PbO₂-type ($Pbcn$), (c) pyrite-type ($Pa\bar{3}$), (d) ZrO₂-type ($Pbca$), (e) fluorite-type ($Fm\bar{3}m$), and (f) cotunnite-type ($Pnam$). Source: Reproduced from Gracia et al. [40]/with permission of American Chemical Society.

1.2.2 SnO₂

SnO₂ is also a wide-bandgap (~ 3.6 eV) *n*-type semiconductor, belongs to the group-IV compounds, and exhibits remarkable transparency and conductivity simultaneously [20, 34, 35]. The unique chemical, electronic, and optical properties of SnO₂ have led to extensive research on its applications in various devices, including solar cells [36], catalytic materials [37], and gas sensors [38]. Additionally, SnO₂ serves as a distinctive transparent metal oxide and finds wide-ranging applications as transparent conducting oxide electrodes in optoelectronic devices. This is due to its excellent chemical and thermal stabilities in atmospheric environments, as well as its high optical transmission properties [39].

SnO₂ possesses several polymorphs including rutile-type ($P4_2/mnm$), CaCl₂-type ($Pnnm$), a-PbO₂-type ($Pbcn$), pyrite-type ($Pa\bar{3}$), ZrO₂-type orthorhombic phase I ($Pbca$), fluorite-type ($Fm\bar{3}m$), and cotunnite-type orthorhombic phase II ($Pnam$) with ninefold coordination, as shown in Figure 1.3. All these structures are sequentially obtained when the most commonly available and stable rutile phase is subjected to a high mechanical pressure [40].

1.2.3 In₂O₃

Another widely studied *n*-type semiconductor is indium oxide (In₂O₃), which has a bandgap ranging from 3.5 to 3.7 eV. It finds numerous applications in electronic

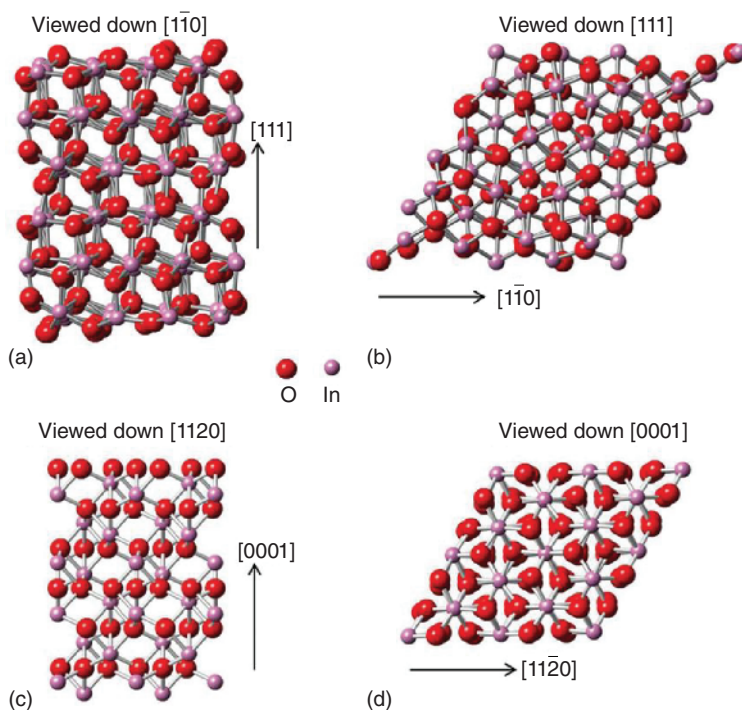


Figure 1.4 Ball and stick representations of crystal structures of *bcc*-In₂O₃ (a, b) and *rh*-In₂O₃ (c, d). In atoms are pale pink, and O atoms are dark red. The viewing directions and the in-plane orientation are indicated in the figure. Source: Reproduced from Zhang et al. [42]/with permission of American Chemical Society.

and optoelectronic fields such as solar cells, gas sensors based on TFTs, and Schottky contacts and diodes [21, 41]. In₂O₃ can exist in two well-established crystal structures: body-centered cubic (*bcc*) and rhombohedral (*rh*), as depicted in Figure 1.4 [42]. The phase of In₂O₃ thermodynamically stable under ambient conditions adopts the body-centered cubic bixbyite structure, with the space group $Ia\bar{3}$ (#206) and a lattice constant of 10.118 Å. The rhombohedral structure is stabilized under high-pressure conditions. The rhombohedral cell belongs to the $R\bar{3}c$ space group with lattice constants $a = 5.478$ Å and $c = 14.51$ Å. There are six formula units per hexagonal cell, and the volume per formula of 62.85 Å³ for the *rh* phase is much smaller than the value of 64.72 Å³ for the ambient *bcc* phase.

1.2.4 TiO₂

As a member of transition metal oxides, TiO₂ is a well-known *n*-type semiconductor [43–46]. It exhibits excellent electronic and optical properties, making it highly suitable for various applications in the fields of gas sensors [47], solar cells [48], and photocatalysis [49]. In its natural form, TiO₂ exists in three different