Focus Issue Review

Wurtzite-derived ternary I–III–O₂ semiconductors

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Abstract

Ternary zincblende-derived I–III–VI₂ chalcogenide and II–IV–V₂ pnictide semiconductors have been widely studied and some have been put to practical use. In contrast to the extensive research on these semiconductors, previous studies into ternary I–III–O₂ oxide semiconductors with a wurtzite-derived β-NaFeO₂ structure are limited. Wurtzite-derived β-LiGaO₂ and β-AgGaO₂ form alloys with ZnO and the band gap of ZnO can be controlled to include the visible and ultraviolet regions. β-CuGaO₂, which has a direct band gap of 1.47 eV, has been proposed for use as a light absorber in thin film solar cells. These ternary oxides may thus allow new applications for oxide semiconductors. However, information about wurtzite-derived ternary I–III–O₂ semiconductors is still limited. In this paper we review previous studies on β-LiGaO₂, β-AgGaO₂ and β-CuGaO₂ to determine guiding principles for the development of wurtzite-derived I–III–O₂ semiconductors.

Keywords: II–VI semiconductor, I–III–VI₂ semiconductor, oxide semiconductor

1. Introduction

Oxide semiconductors have advanced much over the last two decades and currently play an important role in inorganic functional materials. They are used in optoelectronic devices; for example, indium tin oxide, tin oxide and zinc oxide are used as transparent electrodes [1–3] and amorphous indium–gallium–zinc oxide is used in transparent thin-film transistors [4]. Their transparency for visible light is a relatively passive optoelectronic function that comes from their wide band gap and this is used in their applications. Among the oxide semiconductors, ZnO is a II–VI semiconductor with a wurtzite structure [5, 6] and it is an attractive material for use in active optoelectronic devices such as light emitting diodes (LEDs), lasers and photovoltaics because of the nature of its direct band gap [7]. However, the binary oxide semiconductors that possess the wurtzite structure are limited to ZnO and the carcinogenic BeO [8]. Therefore, the band gap engineering of ZnO over a wide energy range is difficult compared to II–VI chalcogenide and III–V pnictide semiconductors. The band gap (Eg) of ZnO is usually controlled by alloying with rock-salt-type MgO [9–11]. The adjustable energy range of these alloys is limited to the range from 3.4 to 4.0 eV because the alloying range is small and x < 0.4 in xMgO–(1−x)ZnO due to structural differences between MgO and ZnO [9, 10]. Consequently, the usable wavelength region of devices using ZnO is limited to the near-ultraviolet region.

For chalcogenide semiconductors, ternary I–III–VI₂ chalcopyrite semiconductors such as CuInS₂ and CuGaSe₂ have been extensively studied [12–14]. The band gap...
engineering of II–VI zincblende chalcogenides alloyed with I–III–VI$_2$ chalcopyrite chalcogenides has also been studied [15–21]. The chalcopyrite structure is a binary zincblende superstructure [22] where two divalent cations in a II–VI zincblende material are replaced by a monovalent and a trivalent cation. A similar superstructure with a specific relationship between the zincblende and chalcopyrite structures is found in the wurtzite structure of wurtzite-derived $\beta$-NaFeO$_2$ structure [23]. Here, monovalent and trivalent cations occupy the divalent cation site in the wurtzite structure, and both cations have a four-fold tetrahedral coordination to oxygen atoms in addition to an ordered arrangement, as schematically shown in figure 1. Based on the structural similarity between $\beta$-NaFeO$_2$ and the wurtzite structure, the alloying of ZnO with ternary oxides possessing the $\beta$-NaFeO$_2$ structure is expected to occur over a wide composition range. This is preferred over alloying with binary oxides that possess a rocksalt structure such as MgO and CdO. The possible energy range of the band gap engineering of ZnO is expected to increase upon alloying with the ternary oxides. Whereas research into the chalcogenide I–III–VI$_2$ chalcopyrite semiconductors has been much active, and even ternary II–IV–N$_2$ nitrides such as ZnGeN$_2$ and ZnSnN$_2$ have recently been studied extensively [24–26], ternary I–III–O$_2$ semiconductors with a wurtzite-derived $\beta$-NaFeO$_2$ structure have received little attention.

We have recently focused on ternary I–III–O$_2$ semiconductors with a wurtzite-derived $\beta$-NaFeO$_2$ structure and their alloys with ZnO in these circumstances. In particular, the band gap engineering of ZnO in the UV and visible regions has been demonstrated by alloying with $\beta$-LiGaO$_2$ ($E_g = 5.6$ eV) [27] and $\beta$-AgGaO$_2$ ($E_g = 2.2$ eV) [28], respectively. We found that $\beta$-CuGaO$_2$, which is a p-type semiconductor with a direct band gap of 1.47 eV, is a new ternary wurtzite oxide semiconductor material [29]. In this paper, we briefly review recent advances in ternary I–III–O$_2$ semiconductors with a $\beta$-NaFeO$_2$ structure with a focus on our previous studies.

![Figure 1. Schematic of (a) $\beta$-NaFeO$_2$ and (b) wurtzite structures.](image)

![Figure 2. Phase variation in the $(1-x)$ZnO–$(x$LiGaO$_2$)$_{1/2}$ pseudo-binary system together with the selected area electron diffraction (SAED) of ZnO, Zn$_2$LiGaO$_4$ and $\beta$-LiGaO$_2$. The SAED patterns were recorded for the $(111)$ zone axis of the hexagonal wurtzite structure for ZnO and Zn$_2$LiGaO$_4$ and the $(101)$ zone axis of orthorhombic $\beta$-LiGaO$_2$. The arrows in the SAED of Zn$_2$LiGaO$_4$ indicate superlattice diffractions.](image)

2. $\beta$-LiGaO$_2$ and its alloys with ZnO

$\beta$-LiGaO$_2$, which possesses a band gap of 5.6 eV, is the best-known wurtzite-derived ternary oxide semiconductor. High purity single crystals several inches long can be grown by the Czochralski method and they can be cleaved to form faces that are lattice-matched to ZnO and GaN [30–32]. It has been studied as a substrate material for ZnO and GaN and as an insulating layer for epitaxially grown ZnO-based multilayers [33]. $\beta$-LiGaO$_2$ has also been studied as a material for use in nonlinear optics [34–36]. We reported on the band gap engineering of ZnO, which included the UV region, upon alloying with $\beta$-LiGaO$_2$ [37, 38]. Figure 2 shows the phase variation in the pseudo-binary alloy system of $x$(LiGaO$_2$)$_{1/2}$–(1−$x$)ZnO. This was determined by the solid state reaction between ZnO and $\beta$-LiGaO$_2$ at 1100 °C. $\beta$-LiGaO$_2$ dissolves in ZnO to form wurtzite-related alloys up to $x \approx 0.5$. This alloy formation range is much wider than that of the MgO–ZnO system, where the equilibrium solubility limit of MgO in ZnO at 550°–1200 °C is $x \sim 0.15$ in $x$MgO–(1−$x$)ZnO [10, 11]. Detailed characterization of the phases revealed that a quaternary wurtzite-derived Zn$_2$LiGaO$_4$ phase is present at $x=0.5$ [39]. The Zn$_2$LiGaO$_4$ is clearly distinguished from the wurtzite phase (the space group of P6$_3$mc) and the $\beta$-LiGaO$_2$ phase (the space group of Pna2$_1$) because clear superlattice diffractions appear in its powder x-ray diffraction (XRD) and
selected area electron diffraction (SAED; figure 2). Its Raman spectrum was also completely different from that of wurtzite and β-LiGaO₂ phases. The cations of Zn²⁺, Li⁺ and Ga³⁺ in Zn₂LiGaO₄ may have an ordered arrangement similar to the Li₂BeSiO₄ crystal (the space group P1n1) [40]; however, the crystal structure has not been determined yet because of its incommensurate nature. Powder XRD, SAED and Raman spectra also elucidated that the phase that appeared in the x (LiGaO₂)₁/₂-(1-x)ZnO pseudo-binary system varied upon increasing the alloying level as the wurtzite-type phase for 0≤x<0.2, the Zn₂LiGaO₄-type phase for 0.2≤x≤0.5 and the β-LiGaO₂-type phase for 0.8≤x<1. The intermediate composition of 0.5<x<0.8 is a mixture of the Zn₂LiGaO₄ and β-LiGaO₂ phases.

The band gap of ZnO increases to 4.04 eV upon alloying with β-LiGaO₂ as shown in Figure 3 [37, 38]. The largest band gap of the β-LiGaO₂-ZnO alloy system is comparable with that of MgO–ZnO alloy films (~4.0 eV) that are fabricated under non-equilibrium conditions [9, 10]. The band gap is significantly larger than that of MgO–ZnO alloys fabricated under equilibrium conditions (~3.5 eV) [10, 11]. β-LiGaO₂ enables a widening of the band gap of ZnO to ~4 eV under equilibrium conditions because of its high solubility in ZnO, which arises from their structural similarity. Although the change in band gap depending on the alloying level exhibits bowing as observed in figure 3, the extent of the bowing is very small [38]. This also comes from the small lattice mismatch and the chemical mismatch, i.e., the band offset between β-LiGaO₂ and ZnO.

Some theoretical studies about the electronic structure of β-LiGaO₂ have been reported [41–44]. They indicate that β-LiGaO₂ is a direct band gap semiconductor and its valence band (VB) and conduction-band consist mainly of O 2p and Ga 4s states, respectively. This is similar to other oxide semiconductors containing cations with a (n−1)dⁿ⁻¹σⁿ⁻⁰ electronic configuration. Recently, first principle calculations of the electronic structure of x(LiGaO₂)₁/₂-(1−x)ZnO alloys were reported by Li and Kuo [45]. They found that the band gaps for all the alloy compositions are direct and a slight band gap bowing between x=0 and 0.5 was evident, which is consistent with experimental observations. The direct band gap nature of these alloys allows their use in optoelectronic applications such as LEDs.

The n-type electrical conduction of ZnO is retained in the x(LiGaO₂)₁/₂-(1−x)ZnO alloys up to at least x≤0.5. The alloy ceramics sintered under atmospheric conditions are white and they are electrically insulating. When the ceramics are annealed in a hydrogen atmosphere, the color changes to grayish blue because of the plasma oscillation of the conduction electrons, and significant electrical conductivity results. For the 0.38(LiGaO₂)₁/₂-0.62ZnO alloy ceramic, the electrical conductivity after annealing at 600 °C for 5 h under hydrogen atmosphere was 8.2 Scm⁻¹ at room temperature [37]. The fabrication of alloyed thin films of x(LiGaO₂)₁/₂-(1−x)ZnO have also been studied by rf-magnetron sputtering using mixed powders of ZnO and β-LiGaO₂ in an appropriate molar ratio as sputtering target materials [46]. The alloying range and changes in the band gap of the alloy films were almost identical to those observed in alloy ceramics as shown in figure 3. In the optical transmission spectrum of the as-deposited 0.49(LiGaO₂)₁/₂-0.51ZnO film, a broad absorption in the near-infrared region that is attributable to the plasma oscillation of the conduction electrons was clearly observed. This indicates that the film has significant electrical conduction despite its wide band gap of ~4.0 eV.

3. β-AgGaO₂ and its alloys with ZnO

At the AgGaO₂ composition, the α-AgGaO₂ with a delafossite structure (the space group P6₃/mmc) [47], where the monovalent silver ions are two-fold linearly coordinated to oxygen ions, and the trivalent gallium ions are six-fold octahedrally coordinated to oxygen ions, is a well-known p-type and transparent oxide conductor [48]. β-AgGaO₂ with a wurtzite-derived β-NaFeO₂ structure (the space group Pna2₁) is probably a metastable phase that can be synthesized by ion-exchange with the precursor β-NaGaO₂ [28, 49]. Previous studies on β-AgGaO₂ have focused on the visible light-driven photocatalytic activity of this material as well as the isostructural β-AgAlO₂ [28, 49–51], because the band gaps of β-AgGaO₂ and β-AgAlO₂ are 2.2 and 2.8 eV, respectively, and the gap is adjustable in the visible region by the alloying of these two materials, i.e., the β-Ag(Ga,Al)O₂ alloy system [52]. The band gap of ZnO has been previously reduced by alloying with toxic CdO; therefore, ZnO cannot be used practically for visible region applications. The band gap of 2.2 eV in less-toxic β-AgGaO₂ [28, 53] is very attractive in terms of the band gap engineering of ZnO into the visible region.

Unlike the x(LiGaO₂)₁/₂-(1−x)ZnO alloys, the x(AgGaO₂)₁/₂-(1−x)ZnO alloys cannot be fabricated by a conventional solid state reaction between ZnO and

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**Figure 3.** Band gap variation as a function of x in the (1−x)ZnO-x(LiGaO₂)₁/₂ pseudo-binary system. The red dots and green dots indicate the band gaps determined for the ceramics and the films, respectively. The blue rectangle indicates a two phase region of Zn₂LiGaO₄ and β-LiGaO₂ solid solutions. Although the boundary of the wurtzite-type phase and Zn₂LiGaO₄-type phase is between x=0.1 and 0.2, all data are connected by one line, because both the phases are based on the wurtzite structure.
β-AgGaO$_2$, because Ag$^+$ ions are easily reduced to metallic silver at high temperature. The alloy films are fabricated by rf-magnetron sputtering using mixed ZnO and β-AgGaO$_2$ powders as target materials [54]. Wurtzite-type alloy films form when $x \leq 0.33$. This alloying range is wider than that of the $x$CdO–(1–$x$)ZnO system with $x<0.17$. This is expected from the structural similarity between ZnO and β-AgGaO$_2$. Nevertheless, the alloying range is slightly smaller than that of the β-LiGaO$_2$–ZnO system because of the lattice mismatch between ZnO and β-AgGaO$_2$ (4.6% in the ab-plane and 5.2% along the c-axis of the wurtzite structure) [54], which is larger than between ZnO and β-LiGaO$_2$ (3.0% in the ab-plane and 3.8% along the c-axis) [37]. Figure 4 shows the change in optical band gap of the $x$(AgGaO$_2$)$_{1/2}$–(1–$x$)ZnO alloys as a function of the alloying level, $x$, together with that reported for the $x$CdO–(1–$x$)ZnO alloys for comparison [55]. The band gap decreased with an increase in alloying level and was 2.55 eV for $x=0.33$. Compared with the CdO–ZnO system, the narrowest band gap was approximately the same. In figure 4, comparatively large reduction in the band gap is evident for the composition with a small AgGaO$_2$ concentration at $x \leq 0.1$. However, a near linear decrease occurs with an increase in alloying level. Therefore, band gap bowing in the β-AgGaO$_2$–ZnO alloys is much smaller than that in the CdO–ZnO system. The large reduction in the band gap during the early alloying stage can be explained by the introduction of the Ag 4d contribution around the valence band maximum (VBM), which mainly consists of the O 2p states in pure ZnO. The introduction of the Ag 4d contribution highly modulates the electronic configuration of the VB of ZnO because of the higher energy of the Ag 4d atomic orbitals compared with that of the O 2p atomic orbitals.

The electronic band structures of β-AgGaO$_2$ and β-AgAlO$_2$ were calculated using density functional theory and reported by Maruyama et al [49] and Ouyang et al [28, 51, 52]. Both materials are indirect band gap semiconductors whereas β-LiGaO$_2$ is a direct band gap semiconductor. The Ag 4d states significantly contribute to the VBM similarly to the delafossite α-AgGaO$_2$ and this is expected because of the energy of the Ag 4d atomic orbitals. However, the dispersion of the VB of β-AgGaO$_2$ is smaller than that of the delafossite α-AgGaO$_2$. The lower photocatalytic activity of β-AgGaO$_2$ compared with α-AgGaO$_2$ can be explained by this small dispersion of the VB, which indicates the heavy effective mass of the holes [49]. Although β-AgGaO$_2$ is an indirect band gap semiconductor, $x$(AgGaO$_2$)$_{1/2}$–(1–$x$)ZnO alloys where $x \leq 0.33$ are expected to be direct band gap semiconductors because no discontinuity is observed upon a change in band gap as shown in figure 4. The contribution of the Ag 4d states around the VBM may enable an easier realization of p-type electronic conduction for the β-AgGaO$_2$–ZnO alloys based on the p-type conduction of delafossite α-AgGaO$_2$ [48]. The electrical conduction of β-AgGaO$_2$ and its alloys with ZnO has not been reported. Future progress in this field is anticipated.

4. β-CuGaO$_2$: a direct and narrow band gap oxide semiconductor

For I–III–O$_2$ semiconductors with a delafossite structure, materials containing monovalent copper such as α-CuAlO$_2$, α-CuGaO$_2$, and α-CuInO$_2$ exist in addition to materials containing monovalent silver [56, 57]. However, wurtzite-derived I–III–O$_2$ materials with a β-NaFeO$_2$ structure that contain monovalent copper had not been reported before we began to study the synthesis of β-CuGaO$_2$. Figure 5 shows a schematic illustration of formation of the chemical bond between an oxide ion and a monovalent silver or copper ion with an ($n-1$)d$^{10}$ns$^0$ electronic configuration. The top of the VB is formed by the Ag 4d or Cu 3d states and the O 2p states. Both the O 2p and Ag 4d or Cu 3d orbitals are fully occupied by electron pairs assuming that the O$^{2-}$, Ag$^+$ or Cu$^+$ ions and the resulting antibonding level forms the highest occupied level, i.e., the Ag 4d or Cu 3d significantly contributes to the VBM of the materials [58]. Taking the higher energy of the Cu 3d atomic orbitals rather than the Ag 4d atomic orbitals into account [59], the VBM for the wurtzite-derived I–III–O$_2$ materials containing the monovalent copper should be higher than that of the materials that contain monovalent silver. This leads to a narrower band gap for the material that contains copper rather than silver when the trivalent cation species are the same. In fact, a comparison

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**Figure 4.** Variation of optical band gap of the (1–$x$)ZnO–$x$(AgGaO$_2$)$_{1/2}$ alloys (red dots and line) as a function of the alloying level, $x$, together with that reported for the (1–$x$)–$x$CdO alloys (green dots and line) for comparison.

**Figure 5.** Schematic illustration of the chemical bond between an oxide ion and a monovalent silver or copper ion in (a) β-AgGaO$_2$ and (b) β-CuGaO$_2$. 

![Image of electronic band structures](image-url)
between the delafossite $\alpha$-AgGaO$_2$ and $\alpha$-CuGaO$_2$ semiconductors indicates that the band gap of $\alpha$-CuGaO$_2$ is smaller than that of $\alpha$-AgGaO$_2$ [48, 60, 61]. Consequently, wurtzite-derived $\beta$-CuGaO$_2$ is expected to have a band gap narrower than that of $\beta$-AgGaO$_2$ and the energy range covered by the wurtzite and its derived oxide semiconductors will expand into the near-infrared region.

The solid state reaction at high temperatures between Cu$_2$O and Ga$_2$O$_3$ results in delafossite $\alpha$-CuGaO$_2$. Wurtzite-derived $\beta$-CuGaO$_2$ (the space group Pna$_2$1) can be obtained by an ion-exchange of Na$^+$ ions in the precursor $\beta$-NaGaO$_2$ with Cu$^+$ ions in CuCl under an evacuated atmosphere to avoid the oxidation of Cu$^+$ to Cu$^{2+}$ [29, 62]. $\beta$-CuGaO$_2$ is a black material and its absorption edge appears at 1.47 eV in the near-infrared region as shown in Figure 6. Oxide semiconductors are mainly wide band gap materials, and this is an important feature for their use in oxide semiconductors. $\beta$-CuGaO$_2$ is a rare oxide semiconductor with a narrow band gap in the near-infrared region unlike the common oxide semiconductors.

Theoretical calculations of the electronic band structure, as shown in Figure 7, indicate that $\beta$-CuGaO$_2$ is a direct band gap semiconductor unlike $\beta$-AgGaO$_2$ and $\beta$-AgAlO$_2$ [29, 52]. The direct band gap and high density of states around the VBM because of the significant contribution of Cu 3d states enables the intense absorption of light. Because $\beta$-CuGaO$_2$ possesses these optical features and its band gap matches the band gap required to achieve the theoretical maximum conversion efficiency for a single-junction solar cell, as shown in the inset of Figure 6 [63], it is a promising light absorbing material in thin-film solar cells, similar to CdTe and Cu(In, Ga)Se$_2$.

The intentional doping of $\beta$-CuGaO$_2$ has not been reported and, therefore, its detailed electrical transport property is not yet understood. However, the sign of the thermoelectromotive force measured at room temperature was positive. This indicates that the material is a $p$-type semiconductor without intentional doping. This is similar to copper-containing delafossite oxides [64–67]. The $p$-type electrical conduction and the small lattice mismatch of $\beta$-CuGaO$_2$ with ZnO, i.e., 0.6% in the $ab$-plane and 1.4% along the $c$-axis are promising for the fabrication of a $p$-$n$ heterojunction between $p$-type $\beta$-CuGaO$_2$ and $n$-type ZnO. We are now investigating methods to control its electrical properties and to fabricate thin films of $\beta$-CuGaO$_2$ for the development of optoelectronic devices that work in the near-infrared region.

5. Summary and outlook

Wurtzite-derived ternary I–III–O$_2$ semiconductors have expanded the energy range that oxide semiconductors cover as shown in Figure 8. The included range is not only the UV region but also the visible and near-infrared regions. This is similar to II–VI chalcogenides and III–V pnictide semiconductors. The electronic transport properties of oxides are limited compared with chalcogenides and pnictides because of their ionic nature. However, oxides have some advantages...
over chalcogenides and pnictides, such as their abundance and the non-toxicity of oxygen. Additionally, oxides maintain excellent stability in air and water under ambient conditions. Consequently, oxide semiconductors are very attractive materials for optoelectronic applications that work in the visible to near-infrared region in addition to the visible to UV region.

The $\beta$-NaFeO$_2$ structure has lower crystal symmetry than the chalcopyrite structure. The structural deviation from the ideal wurtzite structure, i.e., the distortion of cation and oxygen tetrahedra from an ideal tetrahedron increases with an increase in the size difference between the monovalent and trivalent cations. The structural distortion was studied and is discussed in terms of crystal structural chemistry [68]. A few reports exist about the relationship between structural distortion and physical properties [62, 69]. Because the structural distortion inevitably influences the nature of the chemical bonds and eventually their physical properties, a determination of the relationship between structural features and physical properties is a valuable and important challenge.

In this paper, we focused on the band gap engineering of oxide semiconductors with wurtzite and derived structures. We thus describe oxides that contain cations of main group elements with $ns^0$ and/or $n\,(n+1)d^{10}ns^0$ electronic configurations. In addition to these oxides, ternary oxides may contain trivalent transition metallic ions. The multiferroic ferromagnetic and ferroelectric property has been reported for $\beta$-NaFeO$_2$ [70]. This area also needs to be developed further for wurtzite-derived I–III–O$_2$ oxides.

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