The impact of orbital hybridization on the electronic structure of crystalline InGaZnO: a new perspective on the compositional dependence

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We report an investigation of the electronic structure of crystalline InGaZnO (IGZO) using X-ray absorption spectroscopy (XAS) and ab initio density functional theory calculations. The electronic properties of the conduction band vary significantly with the composition of InGaZnO$_4$, In$_2$Ga$_2$ZnO$_5$, and this is strongly correlated with the XAS spectra. Detailed analyses of the orbital character reveal crystal field splitting under characteristic local structural distortions of the ZnO$_5$ coordinate bonds, which breaks the In p/d orbital degeneracy and preferentially lowers the energies of the In p$_z$ and d$(3z^2 - r^2, x^2-y^2)$ orbitals near the Zn ions. The In s−p/d orbitals hybridize and contribute to the low-energy features of the In 5s orbitals. Therefore, the strong dependence of the electronic structure on the composition can be understood in terms of the abundance of distorted ZnO$_5$ coordination near the In$^{3+}$ ions. In the case of amorphous IGZO, however, the XAS study and the ab initio calculations consistently show that the dependence of the electronic structure on the composition is significantly weaker than it is for crystalline IGZO, which is due to the lack of distinct symmetry in the s−p/d mixed orbitals. This work demonstrates that orbital hybridization is significant in determining the detailed low-energy electronic structure of crystalline IGZO.

I. Introduction

There has been significant effort in developing alternatives to amorphous Si (a-Si) for thin-film transistors (TFTs) used in next-generation liquid-crystal displays (LCDs) and organic light-emitting diode (OLED) displays. The most promising materials are oxide semiconductors, which typically contain post-transition metal elements, such as Zn, Ga, Sn, or In. Correspondingly, the highly electronegative cations are capable of determining the electronic properties, which can lead to electrical behavior that is superior to that of a-Si. Indium gallium zinc oxide (IGZO) has attracted much research interest because of the high electron mobility (~10 cm$^2$ V$^{-1}$ s$^{-1}$) in amorphous IGZO (a-IGZO), which is one of the most significant features of merit for applications in flexible and/or large-area transparent devices.

The favorable electrical properties of a-IGZO result from the dispersive and isotropic nature of the 5s orbitals in the In$^{3+}$ ions, which are electron donors. However, a-IGZO has fundamental issues in terms of stability in response to external stress. The device performance may vary significantly following the application of a bias or illumination with ultraviolet (UV) or visible light; it is expected that the vulnerability of the soft material is responsible for this degradation. The softness of the bonds and consequent formation of deep defect levels in the amorphous material may result in undesirable effects, such as temperature bias illumination instability. Crystalline IGZO (c-IGZO) may be superior to a-IGZO in terms of stability at the expense of losing the flexibility and uniformity at the atomic scale due to the presence of grain boundaries. Indeed, Sharp recently developed an LCD panel for iPads based on (partially) crystalline IGZO rather than a-IGZO. It is therefore important to understand the electronic structure of c-IGZO to facilitate further improvement of the electrical properties of TFTs.

In spite of the growing importance of c-IGZO, most fundamental studies of IGZO have focused on the amorphous system only. This may be because a-IGZO is easier to fabricate at or near room temperature by sputtering. The electrical properties of a-IGZO vary depending on the composition of the cations, which is due to the lack of distinct symmetry in the s−p/d mixed orbitals. This work demonstrates that orbital hybridization is significant in determining the detailed low-energy electronic structure of crystalline IGZO.
and each cation appears to play a role in determining the electrical properties. For example, an abundance of Ga results in a low carrier concentration because of the high oxygen binding energy, which is essential for use as a semiconductor; however, it also results in low electron mobility. It is generally accepted that a large In content results in a high n-type carrier concentration and high electron mobility because of the large overlap of the In 5s orbitals. However, IGZO containing a very large In fraction becomes metallic. The role of Zn remains unclear, but it has been argued that it may stabilize the amorphous structure with its preference for tetrahedral coordination.

In this work, we study the electrical properties of c-IGZO, considering the influence of the crystal symmetry on the electrical properties of c-IGZO, in particular, the electronic structure of the conduction band (CB), since the majority of carriers in IGZO are electrons. We examine the electronic structure of the CB of c-IGZO composed of In : Ga : Zn = 1 : 1 : 1 (InGaZnO₄) and 2 : 2 : 1 (In₂Ga₂ZnO₇). The orbital-resolved local density of states (DOS) of the CB is obtained both theoretically using density functional theory (DFT) calculations, and experimentally using X-ray absorption spectroscopy (XAS). We investigate the significance of the orbital hybridization on the CB structure and the dependence on the composition of the material. We show that the In 5s orbital states near the CB minima are strongly hybridized with the In 5p and 5d orbitals, preferentially along the c-axis of IGZO, which depends critically on the Zn concentration near the In ions. The amorphous counterparts of a-InGaZnO₄ and a-In₂Ga₂ZnO₇ are also employed in order to highlight the influence of the structural relaxation.

II. Methods
A. Density functional theory

The DFT calculations of crystalline InGaZnO₄ and In₂Ga₂ZnO₇ were performed using the Vienna Ab initio Simulation Package (VASP) with projector-augmented wave (PAW) pseudopotential. The PBEsol functional was employed to calculate the exchange correlation energy, and the remaining computational parameters were the same as those in ref. 33. The 500 eV of cutoff energy for plane wave basis and the 7 × 7 × 1 k-point mesh grid for Brillouin zone integration were employed for both compositions. Here, the calculated cells contained 3 In, 3 Ga, 3 Zn, and 12 O atoms for InGaZnO₄ and 4 In, 4 Ga, 2 Zn, and 14 O atoms for In₂Ga₂ZnO₇. The calculated values of the lattice constants were a = 3.32 Å and c = 25.78 Å for trigonal InGaZnO₄ (R₃m), and a = 3.32 Å and c = 29.25 Å for hexagonal In₂Ga₂ZnO₇ (P6₃/mmc), which is consistent with the results of the X-ray diffraction measurements (see Section III, A). Supercell calculations were carried out to simulate amorphous InGaZnO₄ and In₂Ga₂ZnO₇. To obtain the amorphous structures, we carried out first-principles molecular dynamics (MD) simulations. In order to generate the final amorphous structure more efficiently, we first determined the cubic supercell with the gravimetric density 2–5% smaller than that of the crystalline phase, and then, randomly distributed the atoms with certain constraints on the interatomic spacing, which allows shortening of the melting time. We built two different cubic supercells containing 16 and 10 formula units of InGaZnO₄ and In₂Ga₂ZnO₇, which were then heated at 2000 K for 5 ps and cooled quickly to 300 K at a rate of ~300 K ps⁻¹. Amorphous structures were obtained by full relaxation of the cell volume and atomic positions.

B. X-ray measurements

Polycrystalline InGaZnO₄ and In₂Ga₂ZnO₇ powders (Toshiba Manufacturing Inc.) were used for the X-ray measurements. The crystallinity of the powders was examined by X-ray diffraction (XRD) using a MiniFlex II (Rigaku) diffractometer. The chemical properties of each of the ionic species in the IGZO system were investigated using X-ray photoelectron spectroscopy (XPS; see Fig. 2); it was confirmed that in both samples, the valences were
In\textsuperscript{3+}, Ga\textsuperscript{3+}, Zn\textsuperscript{2+}, and O\textsuperscript{2−}. Soft X-ray absorption spectroscopy at the O K-edge, Ga L\textsubscript{3}- and Zn L\textsubscript{3}-edges was carried out using pelletized powder samples at the 2A beamline in the Pohang Light Source in total electron yield mode. For more details of the analyses of the Ga L\textsubscript{3}- and Zn L\textsubscript{3}-edge XAS spectra, see Section III. D.

III. Analysis and discussion

A. Characterization of the IGZO powders

Crystallinity. Fig. 1 shows X-ray diffraction (XRD) patterns of polycrystalline In\textsubscript{3}Ga\textsubscript{2}Zn\textsubscript{2}O\textsubscript{9} and In\textsubscript{2}Ga\textsubscript{2}Zn\textsubscript{2}O\textsubscript{7} powders. Each diffraction pattern was assigned according to the crystal symmetries of the respective systems, i.e., R\textsubscript{3}m for In\textsubscript{3}Ga\textsubscript{2}Zn\textsubscript{2}O\textsubscript{9} and P\textsubscript{6}\textsubscript{3}/mmc for In\textsubscript{2}Ga\textsubscript{2}Zn\textsubscript{2}O\textsubscript{7}. For In\textsubscript{2}Ga\textsubscript{2}Zn\textsubscript{2}O\textsubscript{7}, most of the XRD patterns can be assigned to the P\textsubscript{6}\textsubscript{3}/mmc phase, except for a small contribution (less than 5%) from a segregated phase of In\textsubscript{2}O\textsubscript{3}, whereas in the case of In\textsubscript{3}Ga\textsubscript{2}Zn\textsubscript{2}O\textsubscript{9}, all of the patterns may be attributed (almost perfectly) to a single R\textsubscript{3}m phase. This indicates that the powder samples were pure and crystalline. The lattice constants extracted from these data are \(a = 3.30\) Å and \(c = 26.00\) Å for In\textsubscript{3}Ga\textsubscript{2}Zn\textsubscript{2}O\textsubscript{9} (R\textsubscript{3}m), and \(a = 3.31\) Å and \(c = 29.42\) Å for In\textsubscript{2}Ga\textsubscript{2}Zn\textsubscript{2}O\textsubscript{7} (P\textsubscript{6}\textsubscript{3}/mmc), which are consistent with previous reports.\textsuperscript{35}

Chemistry. The chemical properties of the In, Ga, Zn, and O ions were examined using the core level XPS. Samples were pelletized to minimize the contribution of surface effects. Fig. 2 shows normalized core level peaks for each of the ions. It is clear that the binding energies (BE = \(E - E_F\); \(E_F\) is the Fermi level) of the core levels were almost identical for the two compositions. (The small high-BE-shoulder in the O 1s XPS spectra may be attributed to contamination by states at the surface of the pellet.) This indicates that the chemistry of all ionic species does not vary with the composition. In particular, the fact that O 1s BEs are identical in the two samples suggests that the significant variation of the O K-edge XAS data originates from structural variations, rather than differences in the chemistry of the O ions.

B. Crystal structure

Fig. 3a shows the crystal structure of In\textsubscript{3}Ga\textsubscript{2}Zn\textsubscript{2}O\textsubscript{9} and In\textsubscript{2}Ga\textsubscript{2}Zn\textsubscript{2}O\textsubscript{7} obtained from the DFT calculations following relaxation. In In\textsubscript{3}Ga\textsubscript{2}Zn\textsubscript{2}O\textsubscript{9}, two bipyramidal MO\textsubscript{5} clusters (where M is either Ga or Zn) are entangled to form a rigid M\textsubscript{2}O\textsubscript{2.5} unit, leaving InO\textsubscript{6} to
form an InO\textsubscript{1.5} unit and the stacking sequence of the In atom along the c-axis is the same as the [111] direction of the face-centered-cubic structure (ABCABC...), which leads to the formation of a unit cell in rhombohedral symmetry (R\textsubscript{3}m). In In\textsubscript{2}Ga\textsubscript{2}ZnO\textsubscript{7}, only two out of the three MO\textsubscript{1.5} clusters are mixed, and one MO\textsubscript{3} remains as a MO\textsubscript{1.5} unit constituting a unit cell of hexagonal symmetry (P\textsubscript{6}3/mmc). These structures agree well with the present XRD experiments and previous studies on the structure of such compounds.\textsuperscript{36-38} There are several ways to arrange Ga and Zn atoms in the M\textsubscript{2}O\textsubscript{2.5} or MO\textsubscript{1.5} units. In order to find an energetically favorable arrangement among them, we analyzed some of the structural features of the c-IGZO considered in the previous theoretical and experimental studies, and compared the energies between those competing structures.

It is found that there exist two important features in the detailed structures of the IGZO system. One is the arrangement of the Ga/Zn atoms in the M\textsubscript{2}O\textsubscript{2.5} units sandwiched between the InO\textsubscript{1.5} units as shown in Fig. 3a. We modeled several equivalent structures of InGaZnO\textsubscript{4} and performed DFT calculations to examine which configuration is the most stable. Fig. 3a shows the reference structure wherein both the Ga and Zn “planes” (the atomic layers perpendicular to the c-axis) appear in the same M\textsubscript{2}O\textsubscript{2.5} unit and they alternate along the c-axis. This reference structure (GaZnO\textsubscript{2.5}) can be compared to a case where each M\textsubscript{2}O\textsubscript{2.5} unit can include either Ga or Zn atoms separately (as in an alternating array of GaO\textsubscript{2.5} + ZnO\textsubscript{2.5}). Our test calculation showed that the energy of the reference model is 100 meV per atom lower than the case of the separate occupation. It is found that in the latter case there exists an in-plane strain on both Ga and Zn layers due to the difference between the bond lengths in the Ga- and Zn-containing clusters. This results in a significant increase of energy. Therefore, it is favorable to mix Ga and Zn atoms within the same M\textsubscript{2}O\textsubscript{2.5} unit.

Meanwhile, the occupation of the Ga/Zn atoms can also alternate along the a- or b-axis. This is also modeled with a 2 × 1 × 1 supercell in which Ga and Zn atoms form stripe patterns when viewed from the c-axis. This structure was found to have almost the same but slightly lower energy (by only 10 meV per atom), suggesting no clear preference in the lateral alternations within the M\textsubscript{2}O\textsubscript{2.5} unit. This is consistent with the experimental finding of random distribution of the Ga/Zn atoms in InGaZnO\textsubscript{4}. This cation disorder was found to play a critical role in limiting the electron mobility in c-IGZO,\textsuperscript{39,40} However, it was reported that when the composition of Zn is much higher than Ga or Zn atoms separately (as in an alternating array of the M\textsubscript{2}O\textsubscript{2.5} units for the case of In\textsubscript{2}Ga\textsubscript{2}ZnO\textsubscript{7}).

In a previous study of Da Silva et al. (ref. 42), the local structures of the M\textsubscript{2}O\textsubscript{2.5} units were explained in terms of the inversion domain boundary (IDB) that connects the reversed polarity of the oxygen tetrahedra between neighboring InO layers. According to IDB theory, only Ga atoms can form IDB with the fivefold bipyramidal configuration because Ga atoms have more valence electrons than Zn atoms. A switching test, in which the Ga and Zn atoms are replaced by each other, resulted in an energy increase of ~200 meV per atom, indeed showing the stability of the ordered structure.

The second characteristic feature in the structure is that in the case of In\textsubscript{2}Ga\textsubscript{2}ZnO\textsubscript{4} with P\textsubscript{6}3/mmc symmetry, the MO\textsubscript{1.5} units should be introduced being compatible with the hexagonal symmetry (see Fig. 3a). Since a metal atom in the MO\textsubscript{1.5} unit is connected with oxygen atoms in the above and below InO\textsubscript{1.5} layers, its local structure forms the trigonal bipyramid and at the same time constitutes the IDB. This suggests that the Ga atoms should occupy primarily the MO\textsubscript{1.5} units rather than the M\textsubscript{2}O\textsubscript{2.5} units and the local structure of Ga in the MO\textsubscript{1.5} unit should appear to be the same with that in the M\textsubscript{2}O\textsubscript{2.5} unit, in both InGaZnO\textsubscript{4} and In\textsubscript{2}Ga\textsubscript{2}ZnO\textsubscript{7}. We also performed a switching test in which the Ga atoms in the MO\textsubscript{1.5} unit and the Zn atoms in the M\textsubscript{2}O\textsubscript{2.5} unit are interchanged and found that the energy increases by 230 meV per atom. This again suggests the reliability of our reference model structure.

All the results of the aforementioned tests strongly suggested that the simple reference structure shown in Fig. 3a is an appreciably stable configuration. Therefore, we utilized the reference structures to evaluate the structure effect in the IGZO system. And we examine the mixing effects of Ga/Zn sites by employing the 3 × 3 × 1 supercells of InGaZnO\textsubscript{4} and In\textsubscript{2}Ga\textsubscript{2}ZnO\textsubscript{7}, distributing the Ga and Zn atoms randomly in the M\textsubscript{2}O\textsubscript{2.5} units (while distributing the Ga atoms only in MO\textsubscript{1.5} units for the case of In\textsubscript{2}Ga\textsubscript{2}ZnO\textsubscript{7}).

We observed that the angle between the Ga–O bonds both along and perpendicular to the c-axis was almost 90°. This suggests that the GaO\textsubscript{3} clusters were not distorted in either InGaZnO\textsubscript{4} or In\textsubscript{2}Ga\textsubscript{2}ZnO\textsubscript{7}. The structural rigidity remained whether the Ga\textsuperscript{3+} ions occupied the M\textsubscript{2}O\textsubscript{2.5} or the MO\textsubscript{1.5} unit forming the IDB. The length of each bond is numerated in Fig. 3a. All the Ga–O bond lengths were close to 2 Å (1.91 Å to 1.97 Å; see Fig. 3a). However, the ZnO\textsubscript{3} clusters were significantly distorted with an O\textsubscript{A}–Zn–O\textsubscript{P} angle of 106° for both systems (where O\textsubscript{A} denotes apical and O\textsubscript{P} in-plane oxygen atoms). This instability of the bipyramidal local structure (contrary to the case of the Ga ions) may be caused by the complicated nature of the interactions of the shallow Zn 3d levels (where the binding energy is approximately ~10 eV) with the Zn 4sp CB orbitals.\textsuperscript{44} Four of the Zn–O bonds (three in-plane bonds and one apical bond) had similar or slightly larger lengths as the Ga–O bonds (Zn–O: 1.97–2.00 Å), while the remaining single Zn–O bond toward the GaO\textsubscript{3} cluster entangled within the M\textsubscript{2}O\textsubscript{2.5} unit was elongated by approximately 30% (~2.5 Å). This structural distortion has an important consequence, which will be described shortly.

The InO\textsubscript{6} octahedral cluster (InO\textsubscript{1.5} unit) was trigonally distorted with almost the same In–O bond length of ~2.2 Å. Besides the six In–O bonds, there were two additional long In–O bonds along the c-axis (shown by the thick dashed lines in Fig. 3a). Although the two bonds were significantly longer than the six short In–O bonds, they may still contribute to the crystal fields on the In\textsuperscript{3+} ions. Hence, oxygen coordination of the In\textsuperscript{3+} ions should be regarded as effectively 6 + 2. As shown in Fig. 3a, the distortion of the ZnO\textsubscript{3} cluster results in an elongation of the long In–O bond (to 3.60 Å) pointing towards the Zn atom. The increase in the In–O bond length due to the ZnO\textsubscript{3} distortion was almost the same as the increase in the Zn–O bond length,
reflecting the dominant role of the ZnO$_5$ distortion in the change in the [InO$_5$]O$_2$ coordination. This elongation lowered the Coulomb interaction between the electrons at the O and In ions. Therefore, the energies of the In orbital states that participated in the long bonds were preferentially lowered.

Fig. 3b shows the [InO$_5$]O$_2$ coordination in the presence of the Ga$^{3+}$ and/or Zn$^{2+}$ ions nearby. By distorting the ZnO$_5$ cluster, the Zn$^{2+}$ ions can attract the oxygen atom, which results in a longer In–O bond, so as to bring the oxygen ion away from the InO$_5$ cluster. Meanwhile, the Ga$^{3+}$ ions do not induce such an elongation of the In–O bond. Thus, the average distance between the InO$_5$ cluster and the O$^{2–}$ ion shared by the ZnO$_5$ should increase with increasing Zn population near the InO$_5$ cluster. The Zn population near the InO$_5$ cluster generally increased as a function of the Zn concentration. For instance, with a low Zn concentration, the nearest cations to the InO$_6$ cluster were mostly Ga$^{3+}$, so the average InO$_6$–O bond length along the c-axis was shorter. Conversely, with a high Zn concentration, the nearest cations were mostly Zn$^{2+}$, so that the average InO$_6$–O length along the c-axis was longer. In addition, the Ga-rich phase has more MO$_{1.5}$ units (M is mostly Ga), which might hinder such distortion of the InO$_6$ clusters. Therefore, a high Zn concentration will result in a lower average InO$_6$–O bond length.

It is found that in the random-mixed configuration, the bond angles of O–Ga(Zn)–O and the bond length are not uniquely defined as in the ordered structures. However, the elongation of the average InO$_6$–O bond length under Zn-rich conditions (in this case, InGaZnO$_4$) is clearly observed (not shown). This suggests that random mixing does not devaluate the effects of the local structural distortions.

The influence of the local structure on the electronic structure is shown schematically in Fig. 3c. Here, only s–p hybridization is shown for clarity, although s–d hybridization is also significant. If it were not for the additional two long In–O bonds, the InO$_5$ coordination would possess $D_{4h}$ point group symmetry under trigonal crystal fields. A trigonal crystal field splits the triply degenerate p levels into p$_x$, p$_y$, and p$_z$ orbitals. The d orbital states are split into three states of an $A_g$ singlet (3z$^2$ – r$^2$), an e$^2$$_g$ doublet, and an e$^2$$_u$ doublet with increasing energy (not shown in the figure). When the lengths of the additional two In–O bonds increased, the Coulomb potential decreased at the In$^{3+}$ site along the c-axis so that the p orbitals aligned along the c-axis (i.e., p$_z$, 3z$^2$ – r$^2$, and zxy/yz levels, where the z direction is parallel to the c-axis) and were slightly reduced in energy (see the center part of Fig. 3c). In other words, the symmetry of the orbital configuration was lost when the In–O bond increased in length due to a high Zn concentration near the In$^{3+}$ ions.

It appears that the arrangement of the orbitals in energy was not particularly important to the actual electrical properties, since thermal carrier generation occurred mostly at the low-lying In 5s orbital states. However, the In 5s orbital had a complex electronic structure, which was mixed with the p/d orbitals. From molecular orbital theory, we may expect a strong mixing effect among the s and p/d orbitals in the O coordinated cluster. For example, the In$^{3+}$ ions can have sp$^3$d$^2$ hybridized orbital states under the crystal field of an octahedral O coordination. Since the hybridized states possess a relatively localized and directional p/d character, they should be sensitive to the details of the local coordination.

In particular, the low-energy part of the In 5s structure is dominated by strongly hybridized s–p/d orbitals. The right-hand side of Fig. 3c shows the energy order of the hybridized s–p orbital states and the evolution thereof in response to changes in the atomic composition. Here, only the in-phase s–p hybridized states (|s| + |p|), which have mainly the s orbital character, are shown for clarity. The levels of the out-of-phase hybridized states (|s| – |p|) should exist at higher energies, and the s–d mixing effect is expected to be similar. The diagram clearly shows that the energy of the CB minimum (In 5s) can be lowered by increasing the Zn concentration. This tendency was observed in both the experimental and theoretical data.

C. Conduction band structure

Fig. 4a shows the O K-edge XAS spectra of the polycrystalline InGaZnO$_4$ and In$_2$Ga$_2$ZnO$_7$ powders. The features of the O K-edge (hv ~530 eV) are primarily attributed to empty O 2p states. Therefore, as shown in Fig. 4b, the spectra can fit the theoretical O 2p DOS if the effect of core-hole creation is neglected. Since the O 2p states can be empty only through orbital hybridization with the cations, the orbital states of these cations should be also taken into account in order to understand the features. Our XPS data (Fig. 2) showed no difference in the chemistry of each ion between the two powders. Thus, we may also exclude the possibility of a chemical shift in the XAS. Furthermore, it is well known that in the case of O K-edge XAS, the core-hole effect is minimal because the core-hole is created in the O 1s state rather than the cation core orbitals, so the effect on the final state electron configuration of the cations is negligible. Thus, we can determine the O K-edge XAS as an experimental probe for the local DOS (LDOS) of the cations.

The most important finding from the data shown Fig. 4a is that compared with InGaZnO$_4$, a noticeable enhancement of the peak labeled B and a suppression of the peak labeled A was observed in the In$_2$Ga$_2$ZnO$_7$ spectrum. It follows that there were more empty states in the low-energy region of InGaZnO$_4$. The O 2p DOSs for InGaZnO$_4$ and In$_2$Ga$_2$ZnO$_7$ are shown in Fig. 4b; the dependence of these peaks on the composition was quite consistent with those in the experimental spectra. In particular, compared with the In$_2$Ga$_2$ZnO$_7$ LDOS, feature A in the InGaZnO$_4$ LDOS was shifted to a lower energy by approximately 0.5 eV, and the intensity of feature B was reduced. This may explain the drastic spectral evolution in features A and B observed in Fig. 4a.

To assign the features of the O 2p DOS, the In 5s, 5p, and 5d DOSs and the Ga/Zn 4s DOSs are displayed in Fig. 4c and d, respectively. The In 5s DOS had a narrow bandwidth, which predominantly contributed to the low-energy (<5 eV) features. The low-energy features (A and B) shown in Fig. 4b are very similar to those in the In 5s DOS, which suggests that the CB features resulted primarily from the In 5s orbitals. Feature C was dominated by Ga/Zn 4s DOS, and features D and E
originated from the In/Ga/Zn p orbital states. Note that a small amount of In p and In d DOSs was observed in the In 5s energy range, as shown by the asterisk in Fig. 4c. This reflects the s–p/d orbital mixing effect in the In ions. As will be shown in the following section, this orbital hybridization significantly alters the low-energy features of the CB, despite the weakness of the contributions to the 5s DOS.

D. Orbital hybridization

Here, we focus on understanding the microscopic origin of the compositional dependence, particularly near the CB minimum. It is well known that in both InGaZnO$_4$ and In$_2$Ga$_2$ZnO$_7$, the atomic arrangement can be decomposed into successive connections of the metallic ions mediated by oxygen ions, as shown in Fig. 3a. The oxygen coordination of [InO$_6$]O$_2$ has a $D_3d$ trigonal distortion, and the MO$_5$ bipyramids ($D_3$) can have an M site that is shared by the Ga$^{3+}$ and Zn$^{2+}$ ions. Ga$^{3+}$ and Zn$^{2+}$ ions have the same number of electrons and similar ionic radii, so they can occupy the same crystallographic site. Hence, it is often presumed that the two ions are randomly distributed over the M sites.$^{1,36}$

However, even though the two ionic species can mix, it is not clear whether the local structures of GaO$_5$ and ZnO$_5$ clusters are identical. The local symmetry of an oxygen-coordinated metal ion cluster is determined by the coordination number itself. This is a consequence of the repulsive coulombic interactions between negative charges on the oxygen ions. Therefore, both GaO$_5$ and ZnO$_5$ clusters in InGaZnO$_4$ and In$_2$Ga$_2$ZnO$_7$ have trigonal bipyramidal coordination, whereas InO$_6$ has octahedral coordination (with a $D_{3d}$ trigonal distortion). However, the details of the local structure, such as the angle between the M–O bonds and the subtle elongation or contraction, are determined by the electronic configuration as well as by the chemical environment surrounding the clusters.

Fig. 5a shows the Ga L$_3$-edge XAS spectra and Fig. 5b shows the Zn L$_3$-edge XAS spectra. These reflect the Ga/Zn 4s and 4d states modified by core-hole effects. To examine the electronic structure with the core-hole effect, XAS data were simulated using an $ab$ initio real-space multiple scattering approach (i.e., FEFF8), which is based on the model structure of InGaZnO$_4$. The simulated spectra reproduce the experimental spectra for both InGaZnO$_4$ and In$_2$Ga$_2$ZnO$_7$ accurately, suggesting the validity of the assignments of the features B–E in the O K-edge XAS spectra (Fig. 4a). Feature B may be attributed to the Ga/Zn 4s orbital states, whereas features C–E may be attributed to the Ga/Zn 4d orbital states. These d state features also appear in the O K-edge XAS spectra, since the d orbital states are also hybridized with O 2p states. Note that the intensity of the Ga 4s or Zn 4s states does not vary significantly with the composition in the experimental spectra. This indicates that the considerable differences in feature A in Fig. 4a cannot be explained by changes in the Ga or Zn LDOSs. Therefore, the suppression of
feature A in In$_2$Ga$_2$ZnO$_7$ compared with InGaZnO$_4$ suggests a strong sensitivity of the In 5s band structures to the local environment, which can be explained by a strong orbital mixing effect in the In ions.

As shown in Fig. 3, the calculated data show that a substantial distortion occurred in ZnO$_2$ but not in GaO$_2$, which could lower the energy of the s–p/d mixed orbitals in the nearby In$^{3+}$ ions. The low-energy region of the LDOS revealed the effects of such local structural distortions. Fig. 6a–c (d–f) show the In, Ga, and Zn LDOSs of InGaZnO$_4$ (In$_2$Ga$_2$ZnO$_7$), respectively. All the energies were referenced to the values of the calculated electrostatic potentials. The LDOSs were normalized to the numbers of each cation to reflect the DOS per atom. Overall, the LDOSs of the InGaZnO$_4$ appeared to be similar to those of the In$_2$Ga$_2$ZnO$_7$ for each of the cations. We used the same nomenclature for features A to C as in Fig. 4. For both IGZO systems, the In 5s features were the most significant for the low-energy region, so they were primarily responsible for the electrical conduction through the empty states.\(^{45}\) The Ga 4s features were dispersed over a wide energy range, whereas the Zn 4s features were more concentrated on feature B (at approximately +5 eV), consistent with the experimental findings in Fig. 5.

Note that there are several signatures of the CB tail states in In and Ga LDOS. It is known that these long tails are characteristics of the IGZO system, and strongly affect the electrical properties.\(^{31}\) The energies of these tail states are approximately 1 eV lower in InGaZnO$_4$ than in In$_2$Ga$_2$ZnO$_7$. Because these tail states are part of the hybridized orbital states, they are related to the energy lowering in the high Zn concentration system (InGaZnO$_4$), as shown in Fig. 3c.

The DOSs of the p and d orbitals shown in Fig. 6 are magnified to highlight the contribution to the CB tails. It is clear that the p and d orbital states also exist near the minimum of the CB (at approximately +4 eV), although the DOSs were much smaller than those of the s orbitals. This reflects the orbital mixing through the sp$^3$d$^2$ hybridization in InO$_6$ and through the sp$^3$d hybridization in GaO$_2$ or ZnO$_2$ because otherwise, the p and d states would have significantly higher energies than the s states, as shown in Fig. 3c. Interestingly, the LDOSs of the five sub-shell states were very different from each other. As shown in Fig. 6a and d, only the d(3z$^2$ – r$^2$) (a$_{1g}$ symmetry) and p$_z$ states were widely spread in energy, which contributes to the tail-like In 5s states, whereas the main In 5s features consisted mainly of other p and d orbitals. The dominance of the d(3z$^2$ – r$^2$) or p$_z$ in the tail-like states among the d or p orbitals suggests a low energy of the hybridized s–d(3z$^2$ – r$^2$)/p$_z$ states compared with other s–d/p subshell hybridized states.

In the Ga LDOS shown in Fig. 6b and e, the contribution of the d(x$^2$ – y$^2$)/d(xy) and p$_x$/p$_y$ became particularly strong in the features labeled A and B. This was because of the strong s–d/p orbital mixing in the plane of the oxygen triangle in the GaO$_5$ cluster, shown in the inset of Fig. 6b. As shown in the Zn LDOS in Fig. 6c and f, the contributions of d(x$^2$ – y$^2$)/d(xy) and p(x)/p(y) remained dominant; however, they were much weaker compared with those in the Ga LDOS. This could be attributed to the weaker s–d(3z$^2$ – r$^2$)/d(xy) or s–p$_z$/p$_y$ mixing, due to the fact that the in-plane triangle in the ZnO$_2$ cluster was not in a centrosymmetric position (see the inset of Fig. 6c). Moreover, the features of the s–d(3z$^2$ – r$^2$) hybridized states in the Zn LDOS

![Fig. 6](image_url) LDOSs of the CB for (a–c) InGaZnO$_4$ and (d–f) In$_2$Ga$_2$ZnO$_7$. In 5s dominates the CB structure. A strong hybridization effect of the In s–p$_z$–d(3z$^2$ – r$^2$) orbitals can be observed. The inset shows the undistorted (distorted) GaO$_2$ (ZnO$_2$) clusters. The signatures of the CB tail states in In and Ga LDOSs are indicated by ▼ symbols in (a), (b), (d), and (e).

![Fig. 7](image_url) O K-edge XAS data for amorphous InGaZnO$_4$ and In$_2$Ga$_2$ZnO$_7$ thin films (taken from ref. 36) as well as those for c-IGZO’s, and the results of the calculations, showing the contrast between amorphous and crystalline IGZO. Compared with c-IGZO, the CB minimum of a-IGZO is lowered by approximately 0.5 eV, which is primarily due to a reduction of the energies of the main In 5s features, and this contributes to a reduction in the differences between the two compositions.
were weak compared with those of the Ga LDOS, suggesting the significance of the ZnO5 distortion, and consequently resulting in a bond length change in the [InO₃]O₂ cluster.

E. Amorphous versus crystalline IGZO

Here, we compare the LDOS of c-IGZO with that of a-IGZO. Fig. 7 shows the O K-edge XAS data of amorphous InGaZnO₄ and In₂Ga₂ZnO₇ thin films (data taken from ref. 36) as well as the spectra of c-IGZOs. Overall, the changes in the spectra in response to variations in the composition (i.e., InGaZnO₄ versus In₂Ga₂ZnO₇) were similar to those of the crystalline system (shown by the dashed lines in Fig. 7). However, the spectral changes were smaller than in the crystalline systems. Furthermore, the energies of the CB minimum were approximately 0.5 eV lower than those of the crystalline counterparts. The results of calculations using large cells to mimic the amorphous state of the model systems are appended to the same figure for comparison. The lowest energy features were dominated by the In 5s states. This was similar to c-IGZO; however, the contribution of the Ga 4s states, as well as of the Zn 4s states at the low-energy region (approximately +4 eV), was less significant than with crystalline IGZO.

Careful comparison of the LDOSs of c-IGZO (Fig. 6) and a-IGZO (Fig. 7) suggests that the main peaks of the In 5s (Ga/Zn 4s) orbitals indeed shifted to lower (higher) energies for both a-InGaZnO₄ and a-InₙGa₃ZnO₇. The In 5s DOS separated out from the Ga/Zn 4s DOS suggests that the In 5s orbital can contribute to electrical conduction exclusively. It was also observed that the lower energy shift of the In 5s main peaks appeared to mitigate the contributions of the hybridized s–p/d states at energies around +4 eV. Therefore, the overall lower-energy shift of the In 5s main features made the electronic structures of the two amorphous systems much more similar to each other compared to those of the crystalline systems.

This insensitivity of the amorphous system to the composition is one of the advantages of a-IGZO for mass production, because it can lead to a weaker dependence on the deposition conditions. It has been demonstrated that the sensitivity of the electronic structure to the composition originates from s–p/d orbital hybridization in the In ions. If it were not for the orbital hybridization effect, the energies of In 5s orbitals would not be particularly sensitive to structural distortions because the s orbital itself is isotropic. The insensitivity has been regarded as one of the most important characteristics of transparent amorphous oxide semiconductors, which is in stark contrast to the covalent nature of Si. In contrast, the orbital mixing effect becomes significant in c-IGZO due to the approximately 0.5 eV increase in energy of the main In 5s features. Therefore, orbital mixing should be taken into account when describing the electronic structure of crystalline or amorphous IGZO systems.

IV. Conclusion

We have theoretically and experimentally studied the electronic structure of crystalline and amorphous IGZO using DFT and X-ray spectroscopy methods. We found a sharp contrast in the electronic structure near the CB minima, depending on the composition of the amorphous and crystalline materials. In c-IGZO, the In 5s orbitals, which constitute the CB, were strongly hybridized with In p₂ and d( 3z² − r²) orbitals, so that the low-energy CB features were sensitive to local structural variations. Non-centrosymmetric distortion of the ZnO₅ coordination resulted in an elongation of the InO₅–O bonds along the c-axis, and consequently lowered the energy of the s–p/d( 3z² − r²) mixed states. Therefore, the variation of the electronic structure in response to compositional changes could be explained by considering the distorted ZnO₅ near the In³⁺ ions. In a-IGZO, however, the main In 5s features occurred at energies that were lower by approximately 0.5 eV for both IGZO systems, which reduced the significance of orbital hybridization effects. It follows that orbital mixing should be considered for understanding the details of the low-energy electronic structure in c-IGZO systems.

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