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Local coordination structure and electronic structure of the large electron mobility amorphous oxide semiconductor In-Ga-Zn-O: Experiment and *ab initio* calculations

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Ionic amorphous oxide semiconductors (IAOSs) are new materials for flexible thin film transistors that exhibit field-effect mobilities of $\sim$10 cm^2 V^{-1} s^{-1} [K. Nomura *et al.*, Nature **488**, 432 (2004)]. The local coordination structure in an IAOS, In-Ga-Zn-O (*a*-IGZO), was examined using extended x-ray absorption fine structure analysis combined with *ab initio* calculations. The short-range ordering and coordination structures in *a*-IGZO are similar to those in the corresponding crystalline phase, $InGaZnO_4$, and edge-sharing structures consisting of In-O polyhedra remain in the amorphous structure. The In^{3+} 5*s* orbitals form an extended state with a band effective mass of $\sim 0.2m_e$ at the conduction band bottom.

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An ionic amorphous oxide semiconductor (IAOS) is a unique semiconductor system for low-temperature, large-area electronics because even when deposited at room temperature, the films have large electron mobilities over 10 cm^2 V^{-1} s^{-1}, which are almost comparable to those in crystalline oxide semiconductors.[1–3] Thus, IAOSs produce flexible thin film transistors (TFTs), even at room temperature, with reasonable performances such as field-effect mobilities greater than 10 cm^2 V^{-1} s^{-1},[4–7] which are better than those of *a*-Si:H and polycrystalline organics TFTs (e.g., $\sim$1 cm^2 V^{-1} s^{-1} for *a*-Si:H and $\sim$2 cm^2 V^{-1} s^{-1} for a polycrystalline pentacene TFTs).[8,9]

IAOSs have unique carrier transport properties that vastly differ from those in covalent amorphous semiconductors such as *a*-Si:H: e.g., they have (i) large Hall mobilities $\geqslant$10 cm^2 V^{-1} s^{-1}, (ii) normal definitive Hall voltages similar to a crystalline semiconductor, and (iii) high carrier doping at $>10^{20}$ cm^{-3} and degenerate conduction are possible even in amorphous phases.[10] In contrast, representative covalent amorphous semiconductors, *a*-Si:H and amorphous chalcogenides, have never archived degenerate conduction: carrier transport is controlled by nearest-neighbor hopping, or Mott's variable range hopping at low temperatures.[11] *a*-Si:H exhibits a Hall sign double anomaly, which reflects the fact that the carrier mean free path is on the order of the chemical bond length. These unfavorable features were believed to be an essential drawback of amorphous semiconductors, but the above demonstration of the high-performance IAOS TFTs has revealed that the development of a new class of amorphous semiconductors may change this perception.

To date, several *n*-type IAOSs such as In_2O_3-ZnO, CdO-PbO_2, and CdO-GeO have been discovered.[12–15] Recently, we have found that an *n*-type amorphous In-Ga-Zn-O (a-IGZO) with a molar ratio 1:1:1 is preferred for fabricating electronic devices because it has a reasonably large Hall mobilities ($>$15 cm^2 V^{-1} s^{-1}) and a good controllability of the carrier concentration over a wide range with long-time stablity.[4] *a*-IGZO is basically composed of elements that constitute a well-known *n*-type oxide semiconductors such as In_2O_3, Ga_2O_3, and ZnO. Therefore, the *ns*orbitals of these metal elements have the potential to form conduction band bottoms, which work as electron transport paths, in *a*-IGZO. To design such new amorphous semiconductors, knowledge on the local structures around the cations and the origin of the unique carrier transport properties in existing AOSs are inevitable. In this work, we examined the local coordination structures and electronic structure in *a*-IGZO films by x-ray absorption fine structure (XAFS) and *ab initio* calculations.

The samples were $\sim$250 nm thick *a*-IGZO films deposited on silica glass substrates at room temperature by pulsed laser deposition (PLD) with a KrF excimer laser. Single-crystalline $InGaZnO_4$ films (*sc*-IGZO) fabricated by a reactive solid-phase epitaxy were also used for comparison (see Ref. 16 for fabrication details). High-resolution transmission electron microscopy (HR-TEM) and glazing-incidence x-ray diffraction (GIXRD) confirmed that the structure of the *a*-IGZO film was amorphous,[5] while the HR-TEM image of the *sc*-IGZO film clearly showed a layered structure, which corresponds to the crystal structure illustrated in Fig. 1.[17]

Fluorescence XAFS measurements were conducted in the BL01B1 beamline at the Japan Synchrotron Radiation Research Institute (SPring-8). The *K*-edge spectra of In, Ga, and Zn were measured at room temperature. Clear XAFS signals from all the *K*-edge spectra were observed with sharp absorption edges at 27.92 keV for In, 9.66 keV for Zn, and 10.38 keV for Ga for *a*-IGZO. The extended x-ray absorption fine structures (EXAFS) were analyzed using REX 2000 software.[18] After the $\chi(k)$ spectra were extracted by removing the background using the Cook and Sayers method, Fourier transforms were performed on the normalized $\chi(k)$ with

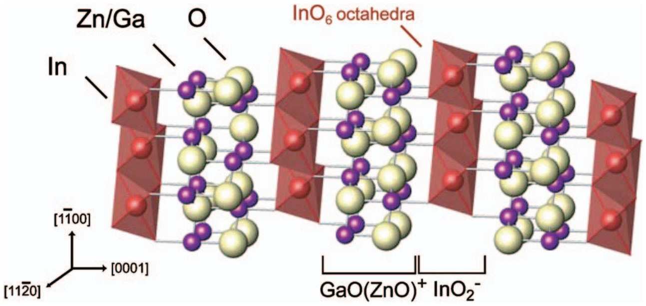

FIG. 1. (Color) Structure of $InGaZnO_4$ crystal. The red polyhedra show InO_6 octahedra, in which the coordinated oxygen ions are not shown for simplicity. The InO_2^- layer (an In^{3+} ion is located at an octahedral site coordinated by six oxygens) and the GaO^+ (ZnO) block (Ga^{3+} and Zn^{2+} ions are located at trigonal-bipiramidal sites and are each coordinated by five oxygens. The four oxygen ions are located at 0.192 nm and the other oxygen ion at 0.227 nm.) are alternately stacked along the ⟨0001⟩ direction.

k^3 weighting of a Hanning window in the k region from 30–120 nm^{-1} to obtain radial distribution functions.

Figures 2(a)–2(c) show the Fourier-transformed (FT) EXAFS spectra of the *sc*-IGZO and *a*-IGZO films. For *sc*-IGZO, the In K-edge spectrum has two peaks. As illustrated in Fig. 1, IGZO crystal is composed of alternating stacks of InO_2^- and $GaO(ZnO)^+$ layers. The In^{3+} ions in the InO_2^- layer form InO_6 octahedra, which are two-dimensionally connected in an edge-sharing network. Therefore, the nearest-neighbor In-O distance is 0.218 nm and the In-In distance is ~0.330 nm,[19] both of which show good agreement with the peak positions observed in the FT EXAFS spectra (0.217 nm and 0.328 nm). The Ga and Zn ions occupy the trigonal-bipiramidal sites in the $GaO(ZnO)^+$ layers in an IGZO crystal. In these sites, the Ga and Zn ions are coordinated by five oxygen ions where four of the oxygen ions are at a distance of 0.192 nm and the other oxygen ion

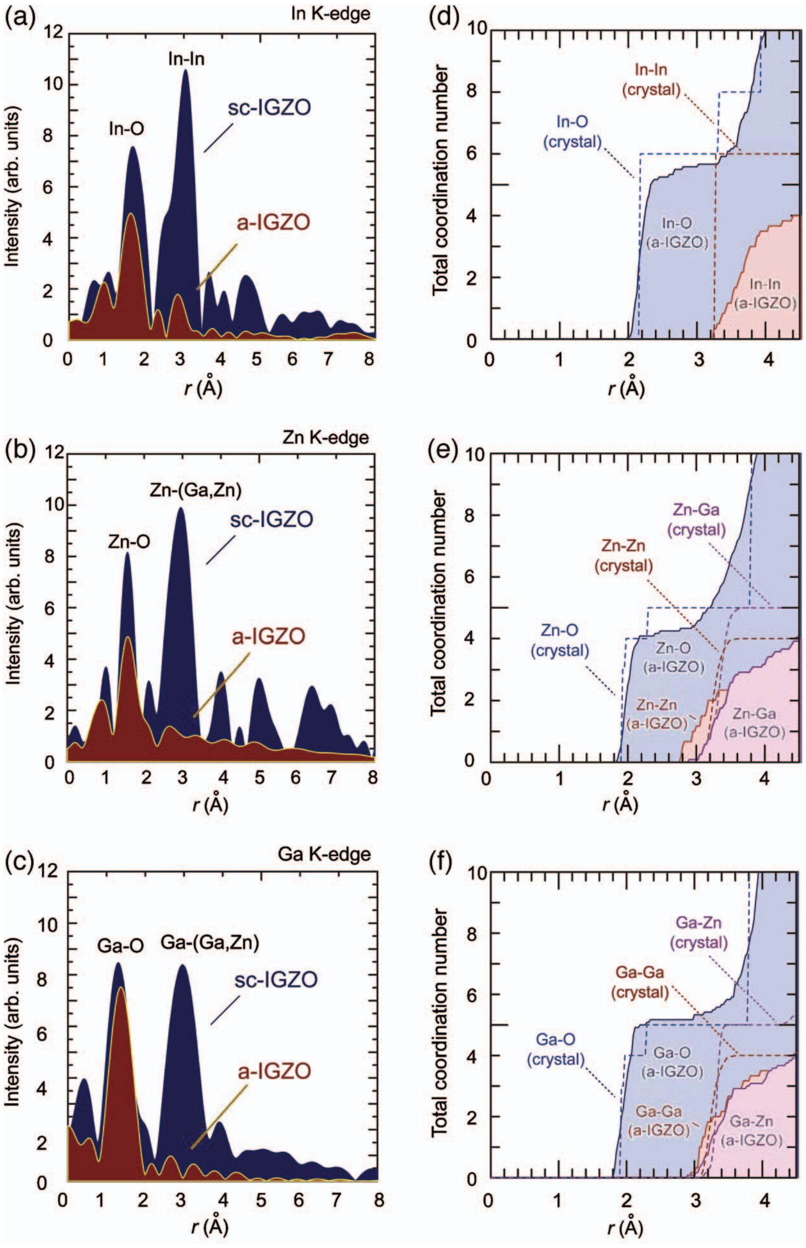

FIG. 2. (Color) Coordination structures in a-IGZO. Those in IGZO crystal are shown for comparison. (a)–(c) Measured FT EXAFS spectra. (a) In K edge, (b) Zn K edge, and (c) Ga K edge. (d)–(f) Running coordination number (RCNs) for the center ions of (d) In, (e) Zn, and (f) Ga evaluated from the LDA-relaxed a-IGZO structure.

TABLE I. Local structural parameters for a-IGZO films evaluated by EXAFS measurements. Crystallographic data for $InGaZnO_4$ crystal is shown for comparison.

	a-IGZO			IGZO crystal (PDF#38-1104)	
Coord. Sphere	r (nm)	σ (Å^2)	N	r (nm)	N
In-O	0.211	0.0077	4.5	0.218	6
Zn-O	0.195	0.0081	4.6	0.193	5
Ga-O	0.200	0.0067	4.3	0.193	5

is at a longer distance of 0.227 nm. The Zn or Ga *K*-edge spectrum also has two peaks, each of which corresponds to the first nearest oxygen and the second nearest Zn or Ga cations. The observed distances also agree well with those in the reported crystal structure.

For *a*-IGZO, the In *K*-edge spectrum in (a) shows a distinct peak at 0.211 nm, which corresponds to the In-O distances in IGZO crystal. It should be noted that the peak intensity of the first peak decreases by ~40% from that of *sc*-IGZO and the second peak intensity becomes drastically weaker. The coordination numbers *N* for *a*-IGZO were calibrated using the XAFS data and the crystal structure[19] of $InGaZnO_4$, which are listed in Table I. The nearest neighbor In-O coordination number is ~4.5, which is smaller than that in the IGZO crystal ($N=6$). For the Zn and Ga *K*-edge spectrum of *a*-IGZO [Figs. 2(b) and 2(c)], only one peak is observed in each spectrum and is assigned to the nearest Zn-O and Ga-O distance, respectively. This result indicates that the medium range ordering at distances equal to or longer than the second neighbor distance is nearly lost around the Zn and Ga ions in *a*-IGZO. Similar to the In case, the nearest neighbor Zn-O and Ga-O distances are close to those in *sc*-IGZO, but the coordination numbers are somewhat smaller than those in *sc*-IGZO ($N_{\text{Zn-O}}\sim 4.6$ and $N_{\text{Ga-O}}\sim 4.3$ for *a*-IGZO, while $N_{\text{Zn-O}}=N_{\text{Ga-O}}=5$ for IGZO crystal).

In general, it is known that EXAFS has a good resolution and reliability for determining short-range structures. However, EXAFS has ambiguity and is less reliable for determining medium-range structures, especially for an amorphous system and a multicomponent system such as *a*-IGZO. Therefore, we also performed *ab initio* calculations to provide a more reliable structure model by combining the calculations and EXAFS results for *a*-IGZO. First, classical molecular dynamics (MD) simulations were performed to obtain initial trial structures for following *ab initio* structure relaxation. We employed a crystalline MD cell containing 1890 atoms and performed constant temperature, constant pressure MD simulations with 2 fs time steps using the code MXDTricl.[20] Empirical interionic potentials of the Born-Mayer type with dispersion interactions were employed. The empirical parameters were adjusted to reproduce the crystal structure of $InGaZnO_4$ and the density of the *a*-IGZO film estimated by x-ray reflectivity measurements (~ 5.9 g cm^{-3}).[21] The 1890 atoms MD cell was then melted at 5500 K and then cooled to 1 K at a rate of 12.5 K ps^{-1} to obtain an amorphous structure. Next the cell size was reduced to 84 atoms to fit the model size to our computational capacity for *ab initio* calculations. The 84 atoms MD cell was again melted and cooled to obtain a MD-relaxed amorphous structure. We confirmed that the density (5.79 g cm^{-3}) and local coordination structure of this model were essentially the same as that obtained on the amorphous structure of the 1890 atoms MD cell, guaranteeing that the reduction of the MD cell size did not affect the relaxed amorphous structure.

Then we performed *ab initio* variable-cell relaxation on the relaxed amorphous structure of the 84 atoms MD cell to obtain a quantum-mechanically stable structure. The relaxation calculations were performed by the pseudopotential and plane wave method at the local-density approximation (LDA) level using the code VASP[22] ("LDA-relaxed structure"). The relaxed structure, which is shown in Fig. 3(a), provides a similar density (5.71 g cm^{-3}) to those obtained by the MD simulations (5.79 g cm^{-3}) and the observed value (~5.9 g cm^{-3}).

Figure 2 also shows the running coordination numbers (RCNs, ionic coordination numbers integrated with respect to the ionic distance *R*)[2(d)–2(f) calculated from the LDA-relaxed structure and the structure of the IGZO crystal. It is found that the ionic distances calculated by the LDA (~0.21–0.23 nm for In-O, 0.19–0.21 nm for Zn-O, 0.19–0.21 nm for Ga-O) agree well with those obtained by EXAFS (see Table I). The RCN function shows that the coordination numbers in the LDA-relaxed *a*-IGZO structure are ~5 for In-O ($N_{\text{EXAFS}}\sim 4.5$), ~4 for Zn-O ($N_{\text{EXAFS}}\sim 4.6$), and ~5 for Ga-O ($N_{\text{EXAFS}}\sim 4.3$). These coordination numbers are consistent with the EXAFS results.

Here we summarize the local structure of *a*-IGZO. The nearest neighbor distances are similar to those in the IGZO crystal. The coordination numbers of In-O, Zn-O, and Ga-O are all around 4–5. This result appears reasonable for In-O and Ga-O because these cations usually occupy sixfold coordination octahedral sites in crystals. However, that of Zn-O seems slightly overestimated because Zn ions usually occupy tetrahedral sites in crystals such as wurtzite ZnO. In contrast, the LDA-relaxed structure provides a more reasonable structure: i.e., most Zn ions are coordinated by four oxygen ions while Ga ions are coordinated by ~5 oxygen ions. This difference in the coordination numbers for Zn and Ga would not be large enough to be distinguished in the present EXAFS measurements. Therefore, we conclude that the Zn ions preferentially occupy fourfold coordination tetrahedral coordination sites, while Ga and In occupy fivefold to sixfold coordination sites.

On the other hand, the distances for the second nearest neighbor coordination in the LDA-relaxed structure have a somewhat larger distribution. For the In-In coordination, the RCN changes from ~1 to ~4 as the distance increases from 0.32 to ~0.4 nm. It should be noted that the coordination number in *a*-IGZO is much smaller than that in crystalline IGZO ($N_{\text{In-In}}=6$) because the IGZO crystal has InO_2 layers composed of edge-sharing network of InO_6 octahedra. Therefore, an In ion is selectively coordinated by six InO_6 octahedra in the two-dimensional InO_2 layer. However, this

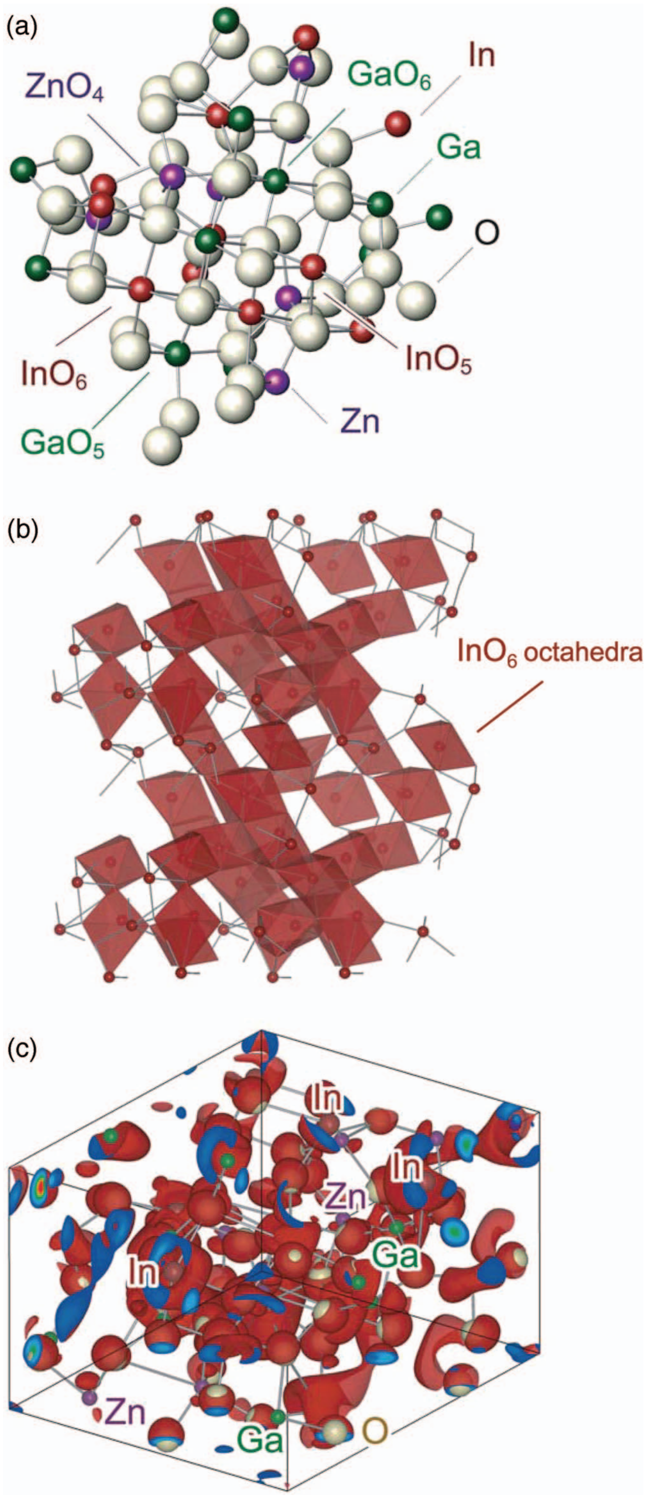

FIG. 3. (Color) (a) LDA-relaxed a-IGZO structure containing $(\mathrm{InGaZnO_4})_{12}$ atoms. MO_n (M=metal cation, n=integer) indicates a specific coordination structure with MO_n polyhedra. (b) Polyhedral view of (a). In ions are shown by the red spheres and InO_n polyhedra by the red polyhedra. (b) was drawn with the VENUS system developed by Dilanian and Izumi. (c) Red surfaces show isosurfaces of the norm of the conduction band bottom wave function $|\psi|^2$. The blue-to-red planes show cross sections of the $|\psi|^2$ on the edge planes of the cell.

selective coordination structure is destroyed in the amorphous structure, and consequently the In-In coordination number becomes close to that expected from a random cation distribution (~3.9 at R=0.4 nm).

These results explain why the measured density of *a*-IGZO is approximately 5% lower than that of the crystalline phase. The coordination numbers of the O ions around In, Zn, and Ga in a-IGZO are reduced from those in the crystalline phase, which consequently reduces the cation coordination numbers around an O ion to maintain charge neutrality. These results are visually seen in the LDA-relaxed structure shown in Fig. 3(a): i.e., InO$_6$ and GaO$_6$ octahedra coexist with less numbers of InO$_5$ and GaO$_5$ pentahedra. The low coordination number structures such as InO$_5$ and GaO$_5$ do not have oxygen vacancy sites, but have additional oxygen ions coordinated at longer distances, which causes the reduced average coordination number and the lower density in *a*-IGZO. As for the network structure of In-O polyhedra, it is worth noting that the edge-sharing network structures remain even in *a*-IGZO as illustrated by a polyhedral view in Fig. 3(b).

We also performed a supercell pseudoband calculation using the LDA-relaxed *a*-IGZO cell. The most important results are that (1) the conduction band bottom is composed of In 5*s* orbitals hybridized with O 2*p* [see the $|\psi|^2$ map at the conduction band bottom in Fig. 3(c). The extended $|\psi|^2$ densities are on the In ions.] (2) the periodic lattice of the LDA-relaxed amorphous cell has an isotropic effective masses $m^* = \sim 0.2 m_e$.[23] The results indicate that the *a*-IGZO model has no localized state in the vicinity of the conduction band bottom and the overlap between neighboring In 5*s* orbitals is rather large. The obtained effective mass is smaller than that estimated from the experimental optical data ($\sim 0.34 m_e$ was obtained from free carrier absorption in degenerated *a*-IGZO films with carrier densities $\sim 10^{20}\ \mathrm{cm}^{-3}$).[24] This discrepancy would be reasonable because the carrier electron mass typically becomes larger than the band effective mass due to the formation of polaron in a polar material.

In summary, the local coordination structures in an ionic amorphous oxide semiconductor *a*-IGZO were examined by the XAFS measurements and a structure model was constructed with the assistance of *ab initio* calculations. We found that the short-range structures, i.e., the nearest-neighbor distances, in the amorphous phase are similar to those in the crystalline phase. Coordination structures of the ions are basically similar to those in the crystalline phase, but the average coordination numbers in *a*-IGZO are reduced from those in the IGZO crystal, which yields a smaller density ($\sim 5.9\ \mathrm{g\,cm}^{-3}$). Some of In-O polyhedra maintain the edge-sharing network structures such as in the IGZO crystal, but the other In-O polyhedra are connected by corner sharing. Thus, the In ions primarily form an extended conduction band bottom and the small effective mass of $\sim 0.2 m_e$ is formed by the 5*s* orbitals of the In ions separated by 0.32–0.40 nm in the *a*-IGZO structure. This separation is somewhat large, but is similar to that in the In$_2$O$_3$ crystal, which is a well-known *n*-type semiconductor with an effective mass of $\sim 0.3 m_e$.[25]

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