Electronic structure and transport in amorphous metal oxide and amorphous metal oxy-nitride semiconductors

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Recently amorphous oxide semiconductors (AOS) have gained commercial interest due to their low temperature processability, high mobility and areal uniformity for display back planes and other large area applications. A multi-cation amorphous oxide (a-IGZO) has been researched extensively and now being used in commercial applications. It is proposed in literature that overlapping In-s orbitals form the conduction path and the carrier mobility is limited due to presence of multiple cations which disrupt electronic transport. A multi-anion approach towards amorphous semiconductors has been suggested to overcome this limitation and has been shown to achieve hall mobilities an order of magnitude higher compared to multi-cation amorphous semiconductors. In this work we compare the electronic structure and electronic transport in multi-cation amorphous semiconductor, a-IGZO and multi-anion amorphous semiconductor, a-ZnON using computational methods. We show that in a-IGZO, the carrier transport path is through overlap of s-orbitals of mixed cations and in a-ZnON, the transport path is formed by overlap of outer Zn-s orbitals. We also show that for multi-component ionic amorphous semiconductors, the electron transport can be understood in terms of orbital overlap integral which can be calculated from structural information and has a direct correlation with carrier effective mass calculated using computationally expensive first principle DFT methods.

I. INTRODUCTION

High performance thin film devices with low processing temperatures and low fabrication cost are the current world’s demand for large area applications. Hydrogenated amorphous silicon (α-Si:H) has been used widely as the active channel material because of its low fabrication cost and high areal homogeneity up until last decade1–4. Since 2010, α-Si:H based thin film devices have been actively replaced with either low temperature polysilicon (LTPS) which offers higher mobility but suffers from non-homogeneity5,6 or amorphous metal-oxide based TFTs for large area applications such as display backplanes. Over the past decade, metal oxide semiconductors have been studied intensively and used in many thin film based devices7–12. In case of polycrystalline single metal oxide semiconductors, such as ZnO, SnO2, In2O3, Ga2O3 etc., the conduction band is made of large overlapping s-orbitals of metal cations (with electronic configuration (n-1)d10ns0), which remain insensitive to any M-O-M bond angle variation. Following the hypothesis proposed by Hosono et al.13,14, amorphous structures of multi-cation metal oxides are preferred for large are uniformity. Due to non-directional nature of ionic bonding in these materials, the charge carrier mobility is preserved in amorphous structures, in comparison to conventionally used α-Si, where the directional nature of covalent bonds deteriorates the mobility in amorphous structures15. One such multi-cation amorphous oxide semiconductor is amorphous indium gallium zinc oxide (a-IGZO), which has shown mobilities as high as 15 cm2/V-sec12–19 and the fabrication of devices on large area has reached commercial domain. a-IGZO based TFTs have found application in various areas such as large area AMOLED displays20,21, high-resolution photosensors22,23, flexible TFTs24,25, interactive displays26,27, etc. However, it is claimed that due to presence of multiple cations of different ionic sizes, the electronic conduction path is hindered which limits the carrier mobility28. As an alternative to multi-cation amorphous metal oxide structures, a multi-anion approach towards amorphous structures has been proposed and is being investigated experimentally and computationally28–35. Amorphous zinc oxy-nitride (a-ZnON) is one such multi-anion amorphous semiconductor which has shown a great promise as a viable replacement of a-IGZO and the electron mobilities (Hall mobilities) exceeding 200 cm2/V.s have been experimentally reported30. Challenges related to stability of the a-ZnON compositions and the fabrication of thin film transistors utilizing a-ZnON as active layer are being addressed experimentally and continuous improvements in device structures and device characteristics are being reported32,35. To realize the full potential of single cation, multi-anion approach towards amorphous semiconductors, it is essential to understand how the electronic conduction is differentiated in multi-cation and multi-anion amorphous semiconductors theoretically using computational methods and how to approach complex multi-component amorphous structures computationally to optimize for the properties that are important to realize stable, high mobility thin film transistors. In the present work, we have studied computationally generated structures of multi-anion amorphous material, a-ZnON and compared its electronic structure with that of multi-cation a-IGZO using the calculations based on first principle density functional theory (DFT) to understand
FIG. 1. Atomic arrangement in (a) a-ZnON-21 and (b) a-ZnON-11. The polyhedra shown in unit cells represent different coordination of Zn with the anions (O/N). Colors used for atoms are as follows: Zinc- grey, Oxygen- red and Nitrogen-blue. Visualization software VESTA\textsuperscript{36} is used for the visualization of the amorphous structures and polyhedra formations.

key differences between the two and the relation between structural and electronic properties for multicomponent amorphous materials. The structure of the papers is as follows; In Sec-II, the structural details of computationally generated a-ZnON structures is discussed, which will insure the validity of the as generated amorphous structures with different compositions. Following this, in Sec-III the electronic structure of a-ZnON is examined and compared with that of already well-studied multi-cation a-IGZO to highlight the differences in electronic conduction in multi-cation and multi-anion amorphous semiconductors. Interdependence of the structural and electronic properties of multi-component amorphous materials is described in the Sec-IV, in which direct correspondence of structural details with physically measurable quantities like electron mobility and the effective mass is accentuated. Conclusions drawn based on this work are summarized in Sec-V.

II. STRUCTURE OF AMORPHOUS ZINC OXY-NITRIDE (a-ZnON)

Amorphous structures of zinc oxy-nitriles (Zn\textsubscript{x+1.59}O\textsubscript{2}N\textsubscript{2}) are generated for two stoichiometries of x:y (O:N) ratios of 2:1 (Zn\textsubscript{2}O\textsubscript{24}N\textsubscript{12}) and 1:1 (Zn\textsubscript{60}O\textsubscript{24}N\textsubscript{24}), hereafter referred to as a-ZnON-21 and a-ZnON-11 respectively. We used an evolutionary algorithm based code USPEX (Universal Structure Predictor: Evolutionary Xtallography)\textsuperscript{37–39} to generate the amorphous structures following the methodology proposed by Suhas et al.\textsuperscript{40}. The large number of structures obtained from USPEX for each composition are sorted and the structures having no undesirable bonds and density > 85% of theoretical density of corresponding crystalline structures are selected for further analysis. Details of the structure generation and sorting are provided in supplementary information (SI-I) and the representative unit cells for both the compositions of a-ZnON are shown in Fig.1.

We performed detailed structural analysis of selected structures to calculate average bond lengths (ABL) and average coordination number (ACN). The average bond lengths for Zn-O and Zn-N bonds for both compositions were found to be very close to the bond lengths in c-ZnO and c-Zn\textsubscript{3}N\textsubscript{2}. The polyhedra shown in Fig.1 suggest that most of the Zn atoms are seen to have either 3 or 4 coordination with anions (O/N). The average coordination number (ACN) for Zn with O and N was found to be ∼ 3.5 in both compositions, which is slightly less than the values in case of c-ZnO and c-Zn\textsubscript{3}N\textsubscript{2} (both having 4 coordinated Zn atoms with respective anions\textsuperscript{41–43}). We attribute this difference to the fact that the amorphous structures have density in the range of 85%-91% of theoretical density resulting in more open structure. We also calculated radial distribution function (RDF) and running coordination number (RCN) for the selected amorphous structures and found absence of any long-range order and hence these structures were confirmed to be amorphous in nature. Detailed structural analysis of a-
III. ELECTRONIC STRUCTURE OF a-ZnON AND a-IGZO

By nature amorphous structures lack long range periodicity and hence, their electronic properties are best studied computationally considering repetitive units of large unit cells under density functional theory which is applicable to periodic structures. The electronic structure calculations are performed using plane-wave code Quantum Espresso with Perdew-Burke-Ernzerhof (PBE) ultrasoft pseudo-potentials\textsuperscript{44–46} with kinetic energy cut-off of 50 Ry which is used to truncate the plane wave basis expansion for electronic bandstructure calculations, along with a denser 4x4x4 Monkhorst-Pack k-point grid for the relevant reciprocal space integration.

The representative pseudo-bandstructures (a-d) and the corresponding orbital-resolved partial electronic density of states PDOS (e-h) for the two compositions of a-ZnON and two compositions of a-IGZO are shown in Fig.2. All these amorphous structures were generated in the same way as discussed earlier, except for a-IGZO-2217* (2217 represents the atomic ratios of In, Ga, Zn and O) structure, which is obtained from the previous work of Divya et al.\textsuperscript{47} a-IGZO-1114 (1114 represents the atomic ratio of In, Ga, Zn and O) structures are taken from the previous work of Suhas et al.\textsuperscript{40} and all these structures have densities in the range of 85%-91% of the theoretical densities of their crystalline counterparts. An apparent band gap at gamma point shows the semiconducting nature of these structures. An important difference to notice in the PDOS of a-ZnON and a-IGZO is that while in the later, the valence band edge is made of oxygen-2p orbitals (red), in case of the former, the valence band edge is made of nitrogen-2p orbitals (blue) which is consistent with observations reported in literature\textsuperscript{29,31,33,48–51}. The conduction band of a-ZnON is primarily made of Zn-4s orbitals, while in a-IGZO, the conduction band edge is dominated by In-5s orbitals and contribution from other metal s orbitals (Zn-4s and Ga-4s) can be seen in the inset of PDOS plots.

Most of the literature on a-IGZO reports that the conduction band minima is formed by overlapping In-5s orbitals and electron conduction path is through overlapping In-5s orbitals\textsuperscript{48–51}, while one of the earliest article on a-IGZO reported overlapping Zn-4s orbitals as conduction path\textsuperscript{52}. To further explore the roles of Zn-4s and Ga-4s orbitals, we calculated the percentage contribution of various orbitals at conduction band minima (Table.I) and plot orbital resolved conduction bands (metal-s orbitals only) in the vicinity of conduction band minima in Fig.3 for both compositions of a-IGZO and a-ZnON structures.

From Table.I, we can see that the contribution of Zn-s orbitals is about 50% at conduction band minima (CBM)
FIG. 3. (Color online) Orbital-resolved electronic band structures; (a), (b), (c) for s-orbitals of three metal cation (In, Ga and Zn respectively) in a-IGZO-1114 composition; (d), (e), (f) for a-IGZO-2217 composition and (g) & (h) for the contribution towards CBM from s-orbitals of Zn metal cation for a-ZnON-21 and a-ZnON-11 compositions respectively. Fig(i) shows the difference in curvature of the CBM for a-IGZO and a-ZnON structures (Color bar shows the color gradient for fractional contribution from different orbitals under consideration).

| Orbital         | PDOS % | Orbital         | PDOS % | Orbital         | PDOS % | Orbital         | PDOS % | Orbital         | PDOS % |
|-----------------|--------|-----------------|--------|-----------------|--------|-----------------|--------|-----------------|--------|
| Zn-s            | 55.53  | Zn-s            | 49.90  | In-s            | 29.10  | In-s            | 35.76  | In-s            | 35.76  |
| N-s             | 14.79  | N-s             | 21.09  | O-s             | 22.78  | O-s             | 22.23  | O-s             | 22.23  |
| O-s             | 13.01  | O-s             | 7.24   | Zn-s            | 20.11  | Ga-s            | 16.29  | Ga-s            | 16.29  |
| O-p             | 3.59   | N-p             | 4.62   | Ga-s            | 14.92  | Zn-s            | 11.71  | O-p             | 11.02  |
| N-p             | 2.55   | O-p             | 2.31   | O-p             | 9.50   | O-p             | 11.02  |                 |        |

TABLE I. Contributions of various orbitals towards the conduction band minimum (at the Γ-point) in two different compositions of a-ZnON and a-IGZO. These values are calculated for a representative structure from each type and composition.

for a-ZnON structures, while for a-IGZO, contribution from different metal-s orbitals is comparable or not insignificant which also follows the composition (higher Zn-s contribution for a-IGZO-1114 composition with higher Zn concentration compared to a-IGZO-2217 composition with less Zn concentration). From Fig. 3 also we can see that the contribution of different metal-s orbitals is comparable for a-IGZO compositions in the vicinity of conduction band minima and hence we argue that the electronic transport in a-IGZO should be through overlapping s-orbitals of different metal cations rather than only In-5s orbitals as cited in several papers48–51. Contribution from Zn-s orbitals towards CBM for two a-ZnON compositions and a comparison plot of conduction band
curvature for $a$-IGZO and $a$-ZnON (thus comparing the effective mass of the two qualitatively) is also shown in Fig.3. From Fig.3(i) the composite conduction band plot for $a$-IGZO and $a$-ZnON, we can estimate the effective mass of electrons in the conduction band from the curvature of the plot and we find that the effective mass for $a$-ZnON is expected to be lower (higher curvature) compared to $a$-IGZO and if we assume scattering time constants to be similar for the two amorphous materials, electron mobilities would be higher in $a$-ZnON compared to $a$-IGZO which is consistent with several recent experimental studies where hall electron mobilities as high as 100-200 cm$^2$/Vs for $a$-ZnON are reported\textsuperscript{30,35} which are much higher than reported values for $a$-IGZO ($\sim 15$ cm$^2$/V.s\textsuperscript{15–19}).

### IV. ORBITAL OVERLAP INTEGRAL AND ELECTRONIC CONDUCTION

In the previous discussion we argued that in $a$-IGZO the electronic conduction path must be through overlapping metal-s orbitals and overlapping Zn-4s orbitals in $a$-ZnON. The ease of electron transport (electron mobility) must therefore depend on the nature of overlap between these orbitals. In the following discussion, we attempt to quantify the overlap between outermost s orbitals of different metal cations in these amorphous semiconductors and relate the overlap to physically verifiable quantities such as electron mobilities. Orbital overlap integral (or overlap integral, OI) between different orbitals is a measure of overlap between single electron wavefunctions in these orbitals. Orita et al.\textsuperscript{52} argued that for electron transport in oxide semiconductors, the orbital overlap integral (OI) for metal-s orbitals should be larger than 0.4 and the fraction of metal ions forming the conduction path should be above a percolation threshold of 20%. From the second condition, it is evident that in $a$-IGZO compositions (1114 and 2217), no single metal ion can form the electron conduction path and hence in $a$-IGZO the conduction path must be through overlapping s orbitals of different metal cations, while in $a$-ZnON, the conduction path is through overlapping Zn-4s orbitals. To understand the contribution of different metal-s orbitals and their overlap, we have calculated overlap integrals between outermost s orbitals of different pairs of metal ions for both compositions of $a$-IGZO and $a$-ZnON following Mulliken's formulation for overlap integrals for Slater-type atomic orbitals (STOs)\textsuperscript{53}. The formulation used in our calculation is given in supplementary information (SI-III) and the numerical integration is carried out using MATHEMATICA\textsuperscript{54}. Different structures for the two compositions of $a$-IGZO and two compositions of $a$-ZnON were analyzed to calculate pairwise orbital overlap integrals. A cut-off distance of 4 Å was chosen to be the radius of the interaction sphere around each metal cation and all other cations in the interaction sphere are assumed to have overlapping s orbital with the metal ion in the center. Table.II shows the number of metal ion pairs, their average distances R (Å) and orbital overlap integral (OI) for outermost s orbitals calculated at average distances for the two compositions of $a$-IGZO and $a$-ZnON. In an additional column in Table.II we also show the total contribution from that particular metal ion pair per unit volume (Number of Pairs * OI / volume), which can be compared between different compositions and the sum over all pairs is considered for $a$-IGZO. We notice a marked difference in overlap integrals for same metal cations (Zn-Zn, In-In and Ga-Ga) with similar average cation-cation distance compared to the values reported by Orita et al.\textsuperscript{52}. We ascribe this difference to the slight difference in the way the orbital overlap integrals are calculated. Moreover, the constraint of overlap integral to be more than 0.4 to form a conductive path in\textsuperscript{52} by Orita et al. is an empirical one. The range of pairwise orbital overlap integrals in Table.II from 0.13 to 0.30 should all form the conducting pathways for electron transport however with varying ease of electron transport between two overlapping orbitals with higher overlap integral providing less resistance to electron transport.

The sum of all pairwise orbital overlap integral normalized to volume (total normalized orbital overlap integral) gives us a parameter to compare different structures and compositions for their electron transport. It should be noted that the orbital overlap integral would strongly depend on the density of the amorphous structure as with increasing density the average distances between metal ion pairs would be smaller. For two different compositions of $a$-IGZO, the total normalized orbital overlap integral are very similar with slightly higher value for $a$-IGZO-1114 composition compared to $a$-IGZO-2217. From Table.II(a), it can be seen that the number of pairs for mix cations is much higher in comparison to pairs of similar cations for $a$-IGZO. The value of overlap integral is found to be the highest for Zn-Zn pair, but since the number of pairs are limited, this overlap cannot be solely responsible for the electronic conduction in the material. From the table, it is evident that, for $a$-IGZO-1114 composition the main contribution to overall electron transport comes from electron transport between In-Zn, Zn-Ga and In-Ga ion pairs, and for $a$-IGZO-2217 composition, the main contribution is from electron transport between In-Ga and In-Zn metal ions pairs. These results are also consistent with our observation of contribution of different metal s orbitals in conduction band of $a$-IGZO (Fig.2 and Table.I). For single cation amorphous structures such as $a$-ZnON, electron transport path is always through overlapping s orbitals of Zn-Zn metal ions since there is only one type of cation in this system and the average distance between Zn-Zn ions is smaller than any two pairs in $a$-IGZO which results in higher orbital overlap. Also, owing to large number of such pairs with large orbital overlap, the total normalized orbital overlap integral for $a$-ZnON is much larger (more than factor of 2) compared to $a$-IGZO and hence we may expect the electron transport to be much easier in $a$-ZnON. From
TABLE II. Pair-wise orbital overlap integral for metal cation pairs in case of (a) a-IGZO, two compositions and, (b) a-ZnON, two compositions, at their average distances within a cut off radius of 4 Å selected to be the radius of the interaction sphere.

| Pair   | No. of Pairs | R (Å) | Overlap Integral | OI*Pairs/Volume | No. of Pairs | R (Å) | Overlap Integral | OI*Pairs/Volume |
|--------|--------------|-------|-----------------|----------------|--------------|-------|-----------------|----------------|
| Zn-Zn  | 16           | 3.44  | 0.256           | 0.00357        | 3            | 3.48  | 0.248           | 0.00064        |
| In-In   | 15           | 3.60  | 0.186           | 0.00243        | 25           | 3.52  | 0.200           | 0.00434        |
| Ga-Ga  | 14           | 3.43  | 0.134           | 0.00163        | 22           | 3.31  | 0.154           | 0.00294        |
| In-Zn  | 39           | 3.48  | 0.226           | 0.00768        | 32           | 3.51  | 0.222           | 0.00615        |
| In-Ga  | 45           | 3.43  | 0.174           | 0.00681        | 56           | 3.53  | 0.157           | 0.00761        |
| Zn-Ga  | 39           | 3.28  | 0.222           | 0.00756        | 28           | 3.36  | 0.206           | 0.00500        |
| Sum    |              |       |                 | 0.02966        |              |       |                 | 0.02669        |

| Pair   | No. of Pairs | R (Å) | Overlap Integral | Pairs*OI/Volume | No. of Pairs | R (Å) | Overlap Integral | Pairs*OI/Volume |
|--------|--------------|-------|-----------------|----------------|--------------|-------|-----------------|----------------|
| Zn-Zn  | 232          | 3.27  | 0.291           | 0.06231        | 337          | 3.23  | 0.299           | 0.06693        |

Although, we cannot directly relate the total overlap integral with measured values of hall mobilities, there is an apparent correlation between the two. Carrier mobilities in any material depend on the effective mass and the scattering time constants. The scattering mechanisms in amorphous semiconductors are not clearly understood and often difficult to measure. The carrier effective mass on the other hand can be estimated from the electronic structure of the material and can give us valuable insight regarding carrier transport in the material. From the pseudo band structures for a-IGZO and a-ZnON in Fig.2, the bottom of conduction band appears to be symmetric around Γ point and effective mass is calculated by fitting a parabola in small k-range of ± 0.1 Å⁻¹ in Γ-X direction at the minima and taking the inverse of the curvature ($\frac{1}{m^*} = \frac{1}{\hbar^2} \left( \frac{\partial^2 E}{\partial k^2} \right)$). Since, the structures are amorphous, the effective mass in three different directions might be slightly different owing to different arrangements of ions in the three directions in real space, we took the average by calculating the effective mass in all three Γ-X directions. As shown in Table.II, for the a-IGZO-1114 and a-IGZO-2217 structures, the electron effective mass was estimated to be 0.21 mₑ and 0.22 mₑ respectively. While, these two values are nearly same, they are small compared to the measured values for electron effective mass in a-IGZO of 0.34 mₑ but are in agreement with calculated values reported in\textsuperscript{17}. For a-ZnON-11 and a-ZnON-21 structures, as shown in Table.II, the estimated electron effective masses are 0.17 mₑ and 0.16 mₑ respectively which also match closely with previously reported theoretical value of 0.19 mₑ for electron effective mass in a-ZnON\textsuperscript{31}. The smaller electron effective mass observed in a-ZnON compared to a-IGZO, suggest faster electron transport in a-ZnON. Our earlier discussion on total normalized orbital overlap integral also had a similar observation and hence we expect to see some correlation between two calculated values; the effective mass and the total normalized orbital overlap integral. To explore this correlation, we plot in Fig.4, the effective mass and the total normalized orbital overlap integral for different structures of a-IGZO-1114, a-IGZO-2217, a-ZnON-21 and a-ZnON-11 compositions. Same is also shown for c-ZnO and c-Zn₃N₂.

FIG. 4. (Color online) Correlation between the effective mass and the total normalized orbital overlap integral (OI * Number of Pairs/volume) for different structures of a-IGZO-1114, a-IGZO-2217*, a-ZnON-21 and a-ZnON-11 compositions. Same is also shown for c-ZnO and c-Zn₃N₂.
estimated effective mass and calculated orbital overlap integrals for c-ZnO and c-Zn₃N₂ for comparison. From the plot, we can see a strong correlation between effective mass calculated using \textit{ab initio} method and the total normalized orbital overlap integral which is calculated from the structural information and hence, we can use the normalized orbital overlap integral as an estimate for the carrier effective mass and the carrier mobility for comparison between amorphous structures.

V. CONCLUSIONS

A multi-anion approach towards amorphous semiconductors has distinct advantages over multi-cation based amorphous oxide semiconductors. Our electronic structure comparison of the two materials systems (a-ZnON and a-IGZO) highlights the role of cations and anions in the electronic structure. We have also established that while the electronic conduction in a-IGZO is through outer s-orbitals of mixed cations and depends on composition (ratio of cations), in a-ZnON the electronic conduction path is through overlapping Zn-s orbitals and is independent of composition (ratio of anions). The ease of conduction in these amorphous structure can be estimated in terms of extent of overlap between empty s orbitals of metal cations and we have shown that orbital overlap integral has a strong correlation with the calculated carrier effective mass. Effective mass calculations based on \textit{ab initio} DFT calculation of electronic structure are computationally very expensive and can be done on one structure at a time. On the other hand, the calculation of the total normalized orbital overlap integral as an estimate for carrier effective mass can be done on for many different amorphous structures or structural averages from many amorphous structures with very small computational expense. While single structure based DFT calculation are limited in their scope, calculations based on many structures or averages of many structures, such as generated by evolutionary algorithm based codes should give us better insight into the average properties of these materials and can be used effectively while predicting properties of new compositions.

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