

Comparison on the atomic and electronic structures of crystalline and amorphous Zn_2SnO_4 using density functional theory

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Zinc Tin oxide (ZTO) is one of the promising n-type oxide semiconductors which is used as the channel layers for various electronic devices. [1] It is usually used as amorphous film due to uniform deposition without grain boundary. In addition, the ternary oxide system has higher crystallization temperature of 600 °C, so the temperature window for using stable amorphous film is wider than binary oxides which have lower crystallization temperature. The mobility of amorphous film is reported as ~ 10 times higher than that of amorphous Si. [2] However, compared to polycrystalline phase, the mobility of amorphous state is lower. In this study, we investigated the differences among crystalline and amorphous zinc tin oxide in the atomic and electronic structure.

Calculations based on the density functional theory were performed using VASP code. Crystalline phase of Zn_2SnO_4 (c- Zn_2SnO_4) in the inverse spinel structure was used. Amorphous Zn_2SnO_4 (a- Zn_2SnO_4) structure was obtained by melt-quenching method based on the first principles molecular dynamics. For atomic structure analysis, radial distribution function (RDF) was used for bond lengths and coordination numbers (CNs). The RDF was obtained by averaged atomic positions which were obtained during annealing at 300 K for 1 ps. For electronic structure analysis, projected density-of-states (PDOS) and inverse participation ratio (IPR) were used.

Fig. 1(a) shows the RDF of O-Zn for c- Zn_2SnO_4 and a- Zn_2SnO_4 . The RDF was used in order to count the average bond lengths and CNs of cations. The average bond length of O-Zn obtained by RDF of c- Zn_2SnO_4 is longer than that of a- Zn_2SnO_4 . The CN of c- Zn_2SnO_4 was 5, which resulted from the half of tetrahedra (4) and the other half of octahedra (6) bonds with oxygens. However, the CN of a- Zn_2SnO_4 is 4.43 which decreased from that of c- Zn_2SnO_4 . Zn atoms in a- Zn_2SnO_4 form tetrahedra or bi-pyramid bonds with oxygens. Fig. 1(b) shows the RDF of O-Sn for c- Zn_2SnO_4 and a- Zn_2SnO_4 . The average bond length of O-Sn of c- Zn_2SnO_4 is almost similar as that of a- Zn_2SnO_4 . The CNs of c- Zn_2SnO_4 and a- Zn_2SnO_4 were almost the same as 6, and 5.89, respectively. It means the high crystallization temperature is resulted from the lowered CN and shortened bond length of Zn-O.

Fig. 2(a) and 2(b) show the IPR and PDOS for c- Zn_2SnO_4 and a- Zn_2SnO_4 . Zn 3d-O 2p hybridized orbital mainly forms the valence band maximum and Sn 5s forms the conduction band minimum. Despite of different local structure, the PDOS between tetrahedral and octahedral Zn were not different each other in c- Zn_2SnO_4 . Lower IPR value as $1/N$ means fully delocalized states to N atoms, on the other hand, higher IPR value means localized states. The IPR value at the valence band maximum in a- Zn_2SnO_4 is much higher than that in c- Zn_2SnO_4 . Especially, the interactions between O-2p in the

valence band maximum in a-Zn₂SnO₄ were dominant and they form the long valence band tail which exists as localized at the ~ 1 eV region. In addition, the conduction band minimum also showed localized states in a-Zn₂SnO₄. The calculation results correspond to the experimental reports related to the wide valence band tail and lower electronic mobility in amorphous structure. [3,4]

References

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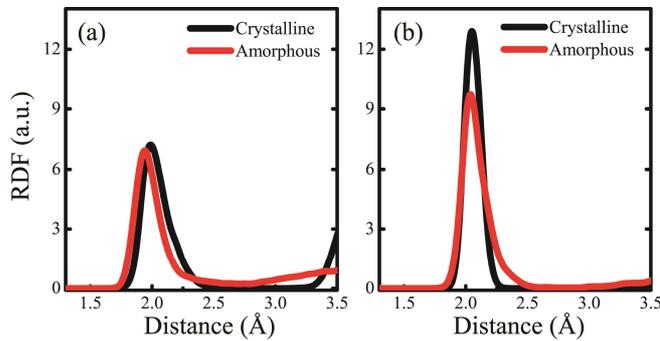


FIG. 1. The radial distribution functions of (a) O-Zn and (b) O-Sn of c-Zn₂SnO₄ and a-Zn₂SnO₄ obtained during the first principles molecular dynamics at 300 K.

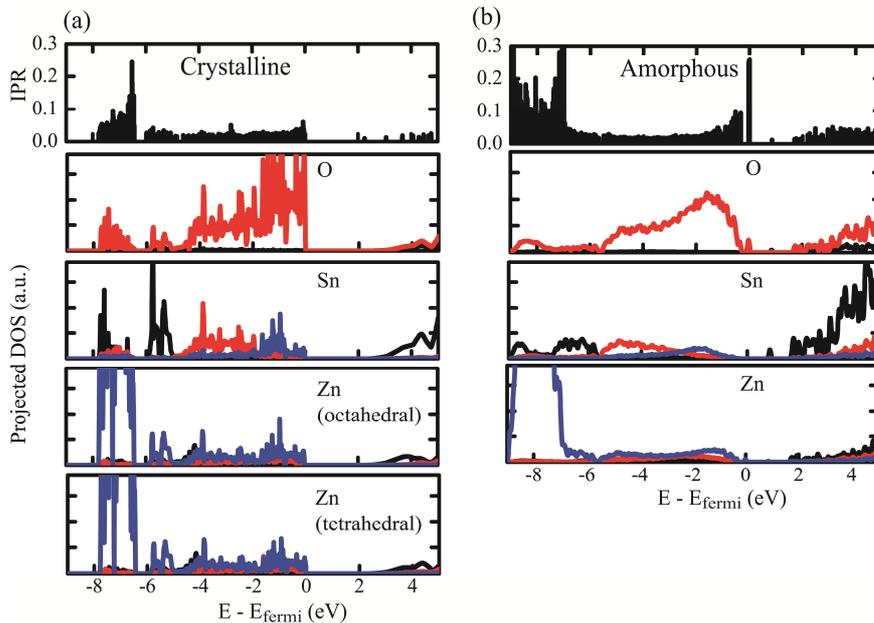


FIG. 2. The IPRs and PDOSs for (a) c-Zn₂SnO₄ and (b) a-Zn₂SnO₄. The conduction band for the PDOS was five times multiplied for better viewing. Black, Red, Blue lines indicate the s, p, and d-orbitals for the PDOS.