Electronic structure of interstitial hydrogen in wide gap semiconductor IGZO and ZnO

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In-Ga-Zn-O (IGZO) and ZnO are wide gapped oxide semiconductors. The former works as transparent semiconductor in amorphous form and commercially used in display devices. In such applications, the switching properties of the thin film transisters (TFT) formed and the stability under light illumination are important. It has been identified that hydrogen plays an important role in those features. Recent research with infrared transmission spectroscopy and *ab initio* calculations combined suggests that two hydride ions (H^-) goes into the oxygen vacancy and creates the deep levels in the energy scheme of IGZO [1]. Independently, hydrogen treatment of IGZO gains n-type doping and is used in forming electronic contacts in the applications.

We employ positive muons (μ^+) from accelerator facilities and investigate the position and the electronic state of hydrogen in IGZO and ZnO using the muon spin relaxation (μSR) method. We use J-PARC MLF for investigation of IGZO bulk polycrystalline and ZnO single crystalline specimens, and PSI-LEM (Low Energy Muon) facility for IGZO amorphous films. We found that muon takes the diamagnetic states (electron closed shell, such as H^+ or H^- state). The former H^+ state is most likely taking the O-H bonding state because of the large electron affinity of the oxide ion. The latter H^- is in a inert state without bonding to other ions. The diamagnetic feature of the muon (=implanted hydrogen) does not depend on whether the specimen is polycrystalline of amorphous film as long as it is in the insulating composition. The position of H^+ or H^- state are further confirmed with the observed nuclear dipolar field and its calculation: in IGZO, the species with a nuclear magnetic moment is In and Ga, and the dipolar fields are consistent between the experimental observation and the calculated one for stable hydrogen position as *ab initio* calculation suggests. The position is at the bond center of the Zn-O. This indicates muon resides in the ZnO block of the IGZO crystal structure.

In single crystalline ZnO, it has become possible at J-PARC MLF to measure the local symmetry of the hyperfine parameter of muon from the crystal axis dependence of the applied magnetic field. The local symmetry of the shallow hydrogen state of muon in ZnO has been identified. It coincides with the symmetry of the Zn-O bond center and O-H anti-bonding site and most likely consistent with the hydrogen site of IGZO with the same local ZnO structure.

The observation of muons taking the diamagnetic state in IGZO is the direct evidence for the interstitial hydrogen serving as an electron doner [2]. Within the framework of Element Strategy, we have been measuring μSR of functional oxide materials, such as C12A7 electride [2]; this could lead to general understanding of the role of hydrogen in these oxides.

Reference

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