Microscopic Mechanism of the Negative Bias and Illumination Stress Instability of Amorphous Oxide TFTs

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Abstract

The microscopic origin of the negative bias and illumination stress (NBIS) instability of amorphous oxide semiconductors is revealed by first-principles calculations. We find that the excited holes during the stresses generate O_2 peroxide defects in the oxide channel with increasing the Fermi level. The peroxide defects exhibit meta-stability.

Author Keywords

oxides; instability; first-principles calculations

1. Introduction

Amorphous oxide semiconductors (AOS) have outstanding properties of high electron mobility, visible light transparency, flexibility, and suitability for low temperature processing [1]. In flat-panel displays, to overcome the mobility limit of amorphous Si, the substitution of the thin-film transistor (TFT) channel materials to AOS has been pursued intensively. At the same time, the transparent flexible TFTs realized by the AOS have attracted great attention for emerging new electronic devices and displays. The facing bottleneck of the AOS TFT applications is the AOS instabilities under negative bias and illumination stress (NBIS) [2-9]. By NBIS or only by illumination stress (IS), the threshold voltage (V_{th}) of the AOS TFT is largely negative-shifted. The NBIS is important because it is applied steadily to the AOS TFTs under normal off-state stand-by condition in active matrix liquid crystal displays.

In order to understand the microscopic origin of the NBIS instability, extensive experimental and theoretical studies have been performed, and a few plausible models have been suggested. (i) Holes are generated by light illumination and trapped at the interface between the AOS channel and the gate insulator and injected into the gate insulator [2,3]. (ii) NBIS desorbs surface O atoms (reduction) and accordingly dopes electrons [4]. (iii) Photo-ionized O-vacancies (V_O) persist with slow electron recombination [5-11]. Since the interface (or gate insulator) hole trap model (i) cannot explain the IS instability, which has been observed not only in AOS TFTs but also in AOS thin films without a gate insulator through persistent photo-conductivity (PPC), there has been considered to be a mechanism intrinsic in AOS materials [3,12]. According to the surface O reduction model (ii), an overlying passivation layer on AOS TFT has been adopted. Although somewhat improved, the NBIS or IS instability is still serious even with avoiding the surface effect. The V_O (iii) can give photo-carriers and be a hole-trap, but the meta-stability of the ionized V_O remains unclear. In order to explain the long recovery time of V_{th} in AOS TFT and long PPC of AOS (an order of day at room temperature), the energy barrier from the meta-stable state to the stable state should be very high. Experimentally reported activation energy is in the range of 0.9~1.0 eV [12].

Here, we propose a new microscopic mechanism of the NBIS instability of AOS TFTs based on first-principles calculations, which explains the Vth shift and slow recovery. We find that the O-O bonding peroxide defects are formed by excited holes. The chemical nature is in detail described. The peroxide defects generate electron carriers with increasing the Fermi level. The activation energy for the structural recovery from the peroxide to normal amorphous structure is calculated to be 0.97 eV, which is in a good agreement with the experimental values.

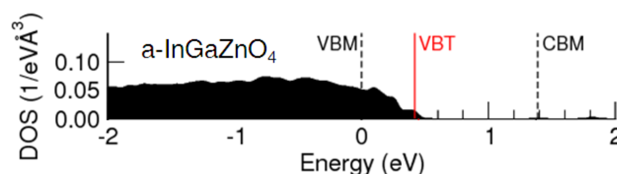

Figure 1. Calculated electronic density of states of amorphous $InGaZnO_4$

2. Methods

First-principles calculations are performed as implemented in the Vienna ab initio simulation package (VASP) code [13]. The projector-augmented wave (PAW) pseudopotentials [14] and the plane-wave basis set with a kinetic energy cutoff of 400 eV are used. The local-density approximation (LDA) [15] with the on-site Coulomb energy (U) [16] of 6 eV for metal d states is mainly used for the exchange correlation energy. The Heyd-Scuseria-Ernzerhof (HSE) hybrid functional is also used with the standard mixing parameter of 0.25 (25% from Hartree-Fock) and the screening parameter fixed to 0.2 $Å^{-1}$ [17]. The amorphous $InGaZnO_4$ as a representative AOS are mainly investigated with the 168-atomic cubic supercell. The LDA band gap of the amorphous $InGaZnO_4$ is 0.97 eV, and the HSE band gap is 2.55 eV. The HSE value is more close to the experimental (optical) band gap of 3.17 eV [18].

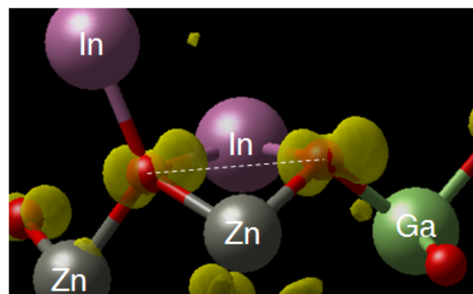

Figure 2. Charge density of the VBT state of amorphous InGaZnO4

3. Results

The valence band tail (VBT) states of AOS are investigated. The calculated density of state of amorphous $InGaZnO_4$ is shown in

Figure 1. We find the valence band tail extends over about 0.5 eV above the VBM of crystalline $InGaZnO_4$. The calculated charge density of the top-most VBT state is shown in Figure 2. It can be seen that the VBT state is characterized by the localized O-O ppσ* anti-bonding state. The reason why the VBT states have the ppσ* character is obvious. In AOS, the upper valence bands are characterized by the O-2p anti-bonding states. In inter-site p-p coupling, the σ-σ* level splitting is much larger than the π-π* splitting, and the ppσ* forms the highest energy level (see Figure 3). Since the VBT states are the highest among the anti-bonding states, they become to have at least partly the O-O ppσ* anti-bonding character.

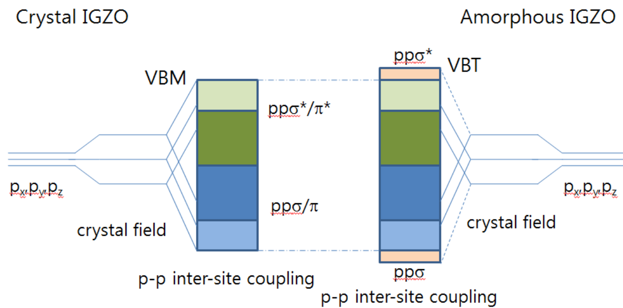

Figure 3. Schematic diagram of oxygen p bands of crystal and amorphous In-Ga-Zn-O

When the anti-bonding state is empty by excited holes, the two oxygen atoms prefer to be bonded. We calculate the total energies in presence of two holes in the supercell as a function of the O-O distance, as shown in Figure 4. When the O-O separated configuration changes to O_2 bonded peroxide configuration, the total energy is found to be lower by about 1.0 eV. That is, in presence of holes, the peroxide defect formation is preferred. The atomic structures of the normal amorphous structure and the peroxide structure are shown in Figures 5(a) and (b), respectively. In the peroxide configuration, we put two electrons into the supercell. In this neutral charge state, the total energies as a function of the O-O distance are shown in Figure 4. As expected, the O-O separated normal amorphous structure is found to be more stable than the peroxide state. In normal amorphous structure, we could not find any O-O bond configuration. Only with the holes, the peroxide structure is found to be formed as shown in Figure 5(b). In the recovery process from the O_2 peroxide to O-O separated normal amorphous structure, the energy barrier is found to be significant. It is 0.69 eV in LDA+U calculations and 0.97 eV in HSE calculations. Experimentally, the recovery of the AOS TFTs after NBIS is known to be very slow, and it takes a few days at room temperature. Experimentally measured activation energy is in the range of 0.9~1.0 eV [12]. Our calculated 0.97 eV in HSE is in a very good agreement with the experimental range. Therefore, the peroxide model for the instability problem explains quantitatively, and is supported by, the experimental aspects.

In terminology of defects in crystalline semiconductors, the peroxide formation can be considered as a formation of a V_O and O-interstitial (O_i) pair (O Frenkel-pair). The O_i is in a split-interstitial form with bonding to a host O atom (O-O_i), and charge neutral. The V_O is a (2+) donor, and thus the two electrons can be considered to be doped by the created V_O. Lee and co-workers [12] measured reversible and very slow photocurrent decays in amorphous In-Ga-Zn-O. They obtained the activation energy of 0.9~1 eV for the photocurrent decays, and proposed a (photo-reduced) meta-stable donor model. As a possible atomic configuration, a weak O atom in amorphous In-Ga-Zn-O is suggested, which can be easily photo-reduced. According to our peroxide model, the weak O atoms can be those with making the ppσ*-like VBT states, which can be easily dimerized by the excited VBT holes. Takechi and co-workers [19] performed UV photo-field effect experiments on amorphous In-Ga-Zn-O, and also pointed out a reversible structural change that requires some relaxation time. They conjectured the generation of V_O and O interstitial [19], which is an O Frenkel-pair.

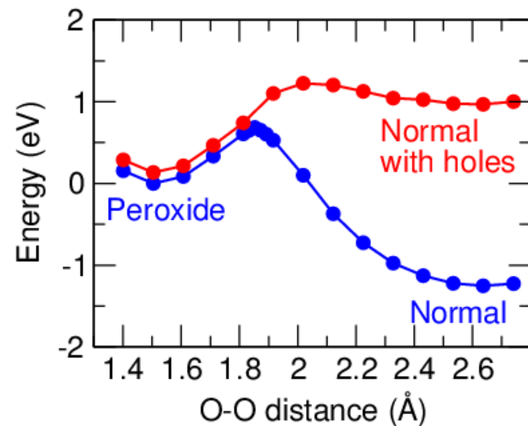

Figure 4. Total energies with respect to O-O distance (red) in presence of holes and (blue) in neutral state.

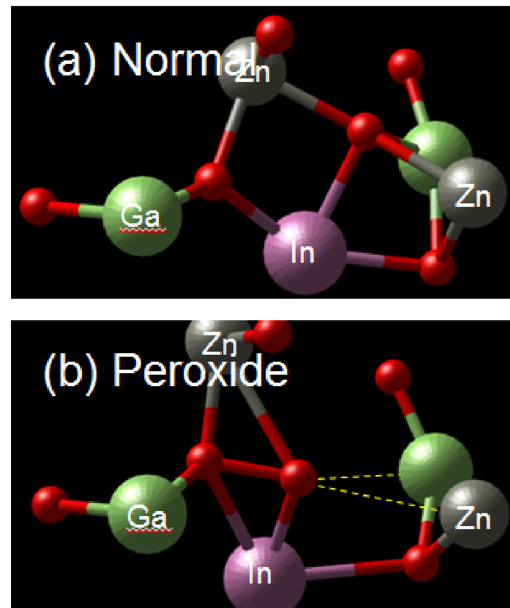

Figure 5. Atomic structures of (a) normal amorphous and (b) peroxide configurations calculated in amorphous $InGaZnO_4$

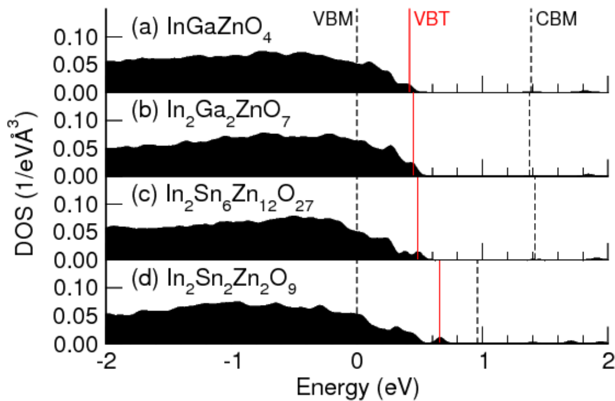

Figure 6. Calculated electronic densities of states of the as-generated amorphous a) $InGaZnO_4$, b) $In_2Ga_2ZnO_7$, c) $In_2Sn_6Zn_{12}O_{27}$, and d) $In_2Sn_2Zn_2O_9$ (LDA+U). The VBM is the valence band maximum of the crystalline $InGaZnO_4$. The VBT is the top-most valence band tail state. The CBM is the conduction band minimum of the amorphous $InGaZnO_4$.

4. Impacts

This work presents a new view point to understanding the instability problem of AOS. The given microscopic picture includes (i) the exited VBT holes, (ii) the peroxide defects, and (iii) the meta-stability. This understanding will open a new technological way to improve the stability of amorphous oxide semiconductors. From the point of view of material engineering, it is important to reduce the density of VBT states in AOS to improve the stability, since the formation of the meta-stable peroxide defects is mediated by the VBT holes. Then, what affects the VBT states in AOS? Post-annealing process has been known to reduce the density of VBT states [19]. It is because of reducing the high energy local amorphous configurations. Interestingly, we find that the densities of VBT states increase as the In and Sn ratio increases (Figure 6). It seems to be because the O atoms are weakly bound near the In and Sn, by which they are easily disordered with forming the inter-site ppσ* localization. Thus, the increase of In and Sn ratio in AOS can worsen the instability of AOS. The minimization of the localized VBT states is fundamentally important to relieve the instability problem and should be a direction in process and material design to obtain reliable AOS.

Acknowledgements

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