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Electronic states of Mg, Sn-doped Ga_2O_3 thin films on ultra-smooth sapphire substrates using a NiO seed layer

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1. Summary (Note: Please include conclusions)

For analyzing band gap of Ga_2O_3 thin films with amorphous state and crystalized state, we measured their valence band using synchrotron XPS and Ga *L* edge and O *K* edge using NEXAFS. We found that from the amorphous state to the crystalize state, the main change is on the conduction bands. Both Ga *L* edge and O *K* edge shift to the higher energy value and the features of the spectra are also changed. This may be related to the short-range order in the amorphous state and the long-range order in the crystallized state. Using the same method, we studied the doped Ga_2O_3 thin films, such as Sn doped Ga_2O_3 (Sn-Ga_2O_3) and Mg doped Ga_2O_3 (Mg-Ga_2O_3). Sn-Ga_2O_3 thin film has the expanded valence band over the Fermi level and Ga *L* edge shifts to the higher energy, because the tetravalent Sn in Ga_2O_3 denotes electrons. The valence band of Mg-Ga_2O_3 shifts to the higher binding energy and the conduction has the expanded Ga *L* edge to the Fermi level, because the bivalent Mg in Ga_2O_3 denotes holes.

2. Purpose of experiment and background

In these years, the thermodynamically stable β phase of gallium oxide (Ga_2O_3) film has attracted the increasing interest as one of TCOs (transparent conducting oxide) thin films. [1] In fact, Ga_2O_3 is a transparent insulator with band gap of 4.85 eV. But with the donor doping, such as Si^{4+}, Sn^{4+}, or oxygen vacancy, it can be tuned to high electrical conductivity (38 S/cm) and colorful transparency. [2-4] These behaviors make it promising in the potential applications of solar-blind photodetectors, [5] solar cells, [6] and also field effect transistors. [7] Recently, based on the previous NiO (111) epitaxial seed layer on sapphire substrate, we obtained device-qualified crystalized Ga_2O_3 (Cry-Ga_2O_3) from amorphous Ga_2O_3 (Am-Ga_2O_3) using KrF excimer laser annealing, and also Sn doped Ga_2O_3 (Sn-Ga_2O_3) and Mg doped β-Ga_2O_3 (Mg-Ga_2O_3) epitaxial thin films. In order to examine the electronic structure and band gap of Ga_2O_3 thin films epitaxially grown on the ultra-smooth sapphire substrates, we will investigate the core level, valence band and conduction band of Am-Ga_2O_3, Cry-Ga_2O_3 (also marked as Ga_2O_3), Sn-Ga_2O_3, Mg-Ga_2O_3 thin films.

3. Experimental（Note: Description of sample，method of experiment and analysis, etc.）

The NEXAFS and XPS data of Pd@HKUST-1 and HKUST-1 were recorded at BL12, SAGA Light Source. During NEXAFS experiment, both a total electron yield and a fluorescence yield were collected. The total electron yield mode can probe the materials with the order of several nanometers beneficial for the study of nanomaterials. While the probing depth for fluorescence measurements of the order of 100 nm for the fluorescence X-rays, used for the bulk references. The overall resolution is 0.1 eV. For the valence band measurement, we used Synchrotron X-ray source. For the core level measurement, we used Al Kα source. The detector of photoelectron is 16-input muti-channel detector (MCD). The peaks were calibrated by C 1s from the absorbed air on the sample surface. The spectrum resolution is 0.1 eV

4. Results and Discussions

1) Band gap change of amorphous Ga_2O_3 (Am-Ga_2O_3) and crystallize Ga_2O_3 (Cry-Ga_2O_3) thin films

From the UV-Vis optical spectra, we have obtained the optical bandgaps of the amorphous and the epitaxial Ga_2O_3 thin films are 4.3 eV and 4.9 eV, respectively. Here we measured the XPS and NEXAFS to investigate the change of electronic states near the Fermi level. The valence bands of Am-Ga_2O_3 and Cry-Ga_2O_3 are shown in Fig. 1. The valence band maximum of these two thin films is overlapped. But the weight centers of these valence bands are a little different, 5.6 eV for Am-Ga_2O_3 and 5.7 eV for Cry-Ga_2O_3. That means the valence band of Cry-Ga_2O_3 shifts to the higher binding energy compared with that of Am-Ga_2O_3. For the conduction bands, the Ga *K* edge and O *L* edge are shown in Fig. 2 and Fig. 3, respectively. There are three main peaks in L_3 edge located at 1119.0 eV, 1122.4 eV and 1118.0 eV. In the spectrum of Cry-Ga_2O_3, the first peak at 1119.0 eV shifts to the higher photo energy and the absorption edge shifts to 1118.24 eV from 1118.05 eV. The second and the third peaks shift to the lower photon energy. And the third peak becomes much sharper. These features may be related to Ga 3*d*, 4*s*, 4*p*

hybridized with oxygen bands, not the only the Ga 3*d* hybridization with O 2*s* as explained by the reference. [8] O *K* edge changes much clearer, especially the absorption edge. There is a small peak at 532.0 eV in the pre-edge region, which make the edge shift by 2.05 eV to the higher photo energy. The double peaks at 535.5 eV and 539.7 eV become much clearer and the tail at 560 eV becomes much shaper after the crystallization. In summary, the valence band, Ga *L* edge, and O *K* edge expand the valence band by 0.1 eV, 0.2 eV and 2.05 eV, respectively. Actually, the optical spectra show the crystallization expand the valence band by 0.6 eV. That hints the Ga or O is not the isolate factor to influence the band gap. There might be interaction between Ga bands and O bands.

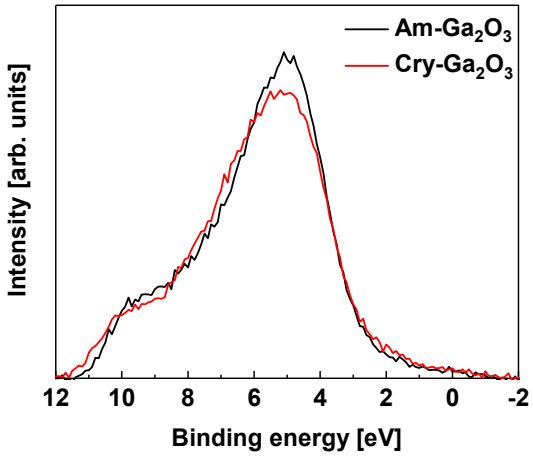

Fig. 1 XPS valence band of amorphous (Am-Ga_2O_3) and crystallized Ga_2O_3 (Cry-Ga_2O_3) thin films.

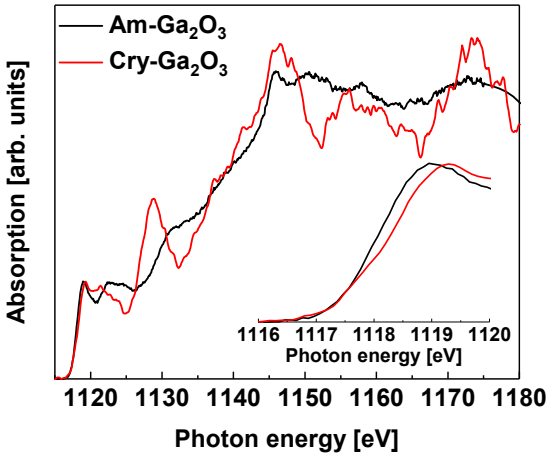

Fig. 2 NEXAFS Cu *L* edge of amorphous and crystallized Ga_2O_3 thin films. Inset shows the magnification of absorption edges.

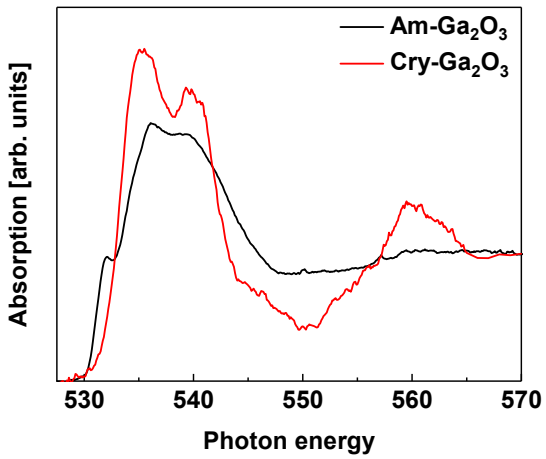

Fig. 3 NEXAFS O *K* edge of amorphous and crystallized Ga_2O_3 thin films.

2) Band gap change of doped Ga_2O_3 (Ga_2O_3, Sn-Ga_2O_3, Mg-Ga_2O_3) thin films

Here we chose three samples, pure Ga_2O_3, Sn doped Ga_2O_3 (Sn-Ga_2O_3) and Mg doped Ga_2O_3 (Mg-Ga_2O_3). As shown in Fig. 4, the valence band centers are calculated as 5.6 eV, 5.9 eV and 6.2 eV. It is notable that there is also a tail over the Fermi level in the Sn-Ga_2O_3 valence band. The conduction band information shows in NEXAFS Ga *L* edge of Fig. 5 and O *K* edge of Fig. 6. The absorption Ga L_3 edges are located at 1118.24eV for Ga_2O_3, 1118.21 for Sn-Ga_2O_3, 1117.98 for Mg-Ga_2O_3. The absorption edge of Sn-Ga_2O_3 thin film is overlapped with Ga_2O_3. The absorption edge of Mg-Ga_2O_3 thin film shifts by 0.26 eV comparing with Ga_2O_3. The absorption edge of Mg-Ga_2O_3 thin film keeps as the same as that of Ga_2O_3 thin film. The absorption edges in O *K*-edge spectra are 533.16, 533.26, 533.34 for Ga_2O_3, Sn-Ga_2O_3, Mg-Ga_2O_3, respectively. Comparing with Ga_2O_3 thin film, the absorption edge of Sn-Ga_2O_3 and Mg-Ga_2O_3 thin film shifts by 0.10 eV and 0.18 eV, respectively, to the higher photon energy. In the semiconductor theory, tetravalent Sn denotes electrons and divalent Mg denotes holes. Then the absorption spectra of Mg-Ga_2O_3 thin film should have a shift to the lower photon energy. The observed O *K* edge shifts to the opposite direction. The O *K*-edge spectrum of Sn-Ga_2O_3 thin film shifts much less than Ga *K*-edge spectrum. All these results hint that the dopants influence Ga sites more than O sites. Maybe because the dopants mainly occupy the Ga sites.

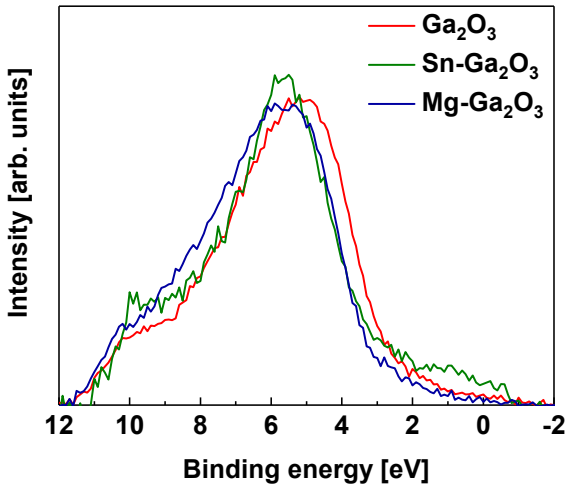

Fig. 4 XPS valence band of pure Ga_2O_3 (Ga_2O_3), Sn doped Ga_2O_3 (Sn-Ga_2O_3), and Mg doped Ga_2O_3 (Mg- Ga_2O_3) thin films.

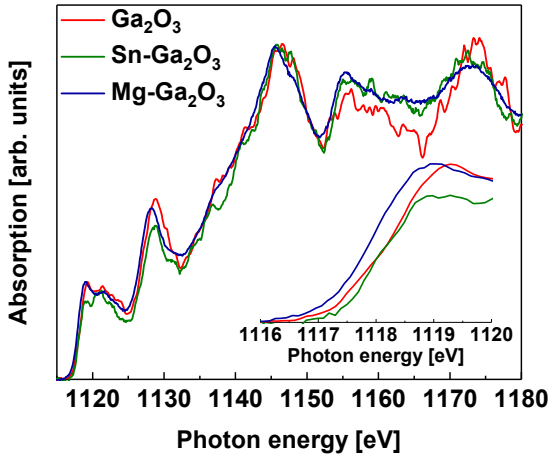

Fig. 5 NEXAFS Cu *L* edge of Ga_2O_3, Sn-Ga_2O_3, and Mg- Ga_2O_3 thin films. Inset shows the magnification of absorption edges.

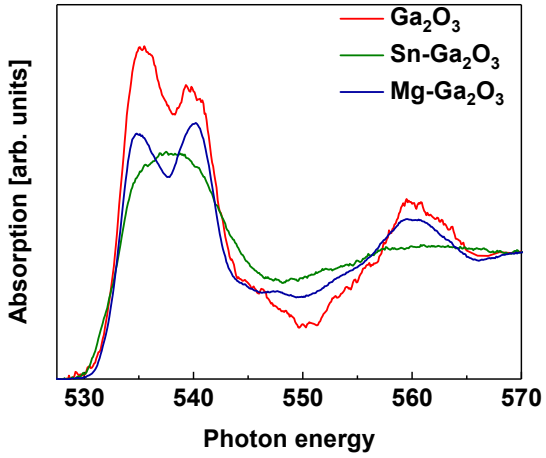

Fig. 6 NEXAFS O *K* edge NEXAFS of Ga_2O_3, Sn-Ga_2O_3, and Mg-Ga_2O_3 thin films.

5. Future issues

Using X-ray diffraction and extended X-ray absorption fine structure, we will analyze the lattice parameters of Ga_2O_3 thin films, and furthermore the atomic order and occupancy. After setting up the real lattice structure, we can calculate the density of states of these materials and comparing the experimental results with the calculated results for the further understanding.

6. References

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7. Publications, patents（Note: Typical deliverables related to this proposal.）

Not yet.

8. Keywords（Note: 2-3 words about samples and experimental methods.）

Gallium oxide, Thin film, Electronic structure

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