X-ray Absorption Spectroscopy and Its Simulation for Some Disordered Oxide Systems

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Abstract. The local structural properties of representative amorphous oxides, ZnO, HfO$_2$, ZrO$_2$, and In$_2$Ga$_2$ZnO$_7$ were investigated by using X-ray absorption spectroscopy and an ab-initio theoretical calculation (FEFF). The X-ray absorption near-edge structures of the amorphous systems were compared with those of their crystalline counterparts, and were interpreted in terms of weakened structural orders (in the case of ZnO, HfO$_2$, and In$_2$Ga$_2$ZnO$_7$) or fundamentally different local structures (ZrO$_2$; monoclinic-like local structure favoured in amorphous phase in contrast to the tetragonal structure in crystalline film).

1. Introduction

X-ray absorption spectroscopy (XAS) is a nondestructive way to probe the chemistry and structural properties of materials of interest by shining x-rays with various photon energies near the absorption edge energies and measuring the absorption coefficients [1]. Since the core level photoionization process itself involves the creation of localized holes on the inner orbitals very near to the nucleus, the XAS spectrum essentially reflects the short-range local structures near the photon-absorbing atom.

Amorphous materials have no long-range orders so that structural characterization using diffraction techniques is not feasible. However, the structural orders can survive in a short range no matter how significant the randomness in the atomic positions is. Thence XAS has a strong advantage in providing structural information in a highly disordered system. In particular, the X-ray absorption near-edge structures (XANES) reflect the geometry of the local coordination. Therefore, one can find clues on the local structural evolution in amorphous phases in comparison to the crystalline phases. This study demonstrates the methodology of structure identifications in amorphous oxide systems with examples of four kinds of oxide systems, that are close to the industrial application; HfO$_2$, ZrO$_2$, ZnO, and In$_2$Ga$_2$ZnO$_7$. HfO$_2$ and ZrO$_2$ are the representative high dielectric constant materials which can be used as the gate oxides in metal-oxide-semiconductor field-effect transistors. Besides, they also show ferroelectric behaviors. On the other hand, ZnO and InGaZnO are transparent semiconductors, which can be used as the electrodes or semiconducting channels in optoelectronic devices. All these oxides are now fabricated in industry level, and controlling the structural orders or defects is now very important. The XANES of amorphous systems are compared with those of the crystalline counterparts, and the features are interpreted being aided by an ab-initio theoretical simulation, FEFF. Although not as much accurate as density functional theory-based calculations (like DV-Xα), FEFF can provide fair insights on how the local structure can influence the electronic structure and the orbital configuration.
2. Methods

2.1. X-ray Absorption Spectroscopy
All the XAS measurements were performed at hard X-ray beamlines in Pohang Light Source in Korea. The samples were prepared by thin-film techniques of either rf sputtering (ZnO and In$_2$Ga$_2$ZnO$_7$) or atomic layer deposition (HfO$_2$ and ZrO$_2$), except for commercial polycrystalline In$_2$Ga$_2$ZnO$_7$ powder (Toshima Manufacturing Inc.). For thin film samples (ZnO, HfO$_2$, ZrO$_2$, and In$_2$Ga$_2$ZnO$_7$ film), fluorescence yield mode was used, while for powder sample (In$_2$Ga$_2$ZnO$_7$), transmission yield mode was used. The photon energies were calibrated before recording the experimental spectra.

2.2. XANES Simulation
The XANES simulation was performed by using an ab-initio real-space multiple scattering code, FEFF [2,3]. For the spectra of ZnO, ZrO$_2$, and In$_2$Ga$_2$ZnO$_7$, FEFF8 was employed, while for the spectra of HfO$_2$, an older version, FEFF6 was used. The contribution of each of the virtual electron scatterings in the X-ray absorption process can be included or excluded in the simulated spectrum. One convenient way is to consider all the multiple scattering paths up to the infinite number of “legs” in the scattering paths (for instance, 2 for Zn→O→Zn and 3 for Zn→O→O’→Zn) within a given radius of scattering range with respect to the photon-absorbing atom. This is often called full multiple scattering (FMS) mode. Generally, the FMS radius ($R_{FMS}$) represents the degree of structural order so that a higher (lower) value of $R_{FMS}$ is for the more ordered (disordered) system. Alternatively, the number of legs can be restricted to a fixed number. For example, the signals from the single backscatterings only can be collected by confining the number of legs to be 2. In this work, the amorphousness was mimicked overall either by reducing the $R_{FMS}$ value or confining the number of legs to be 2.

3. Results and discussion

3.1. ZnO

Figure 1 shows the Zn K-edge XANES of (a) amorphous ZnO and (b) crystalline (wurtzite) ZnO, and their FEFF simulations [4].

Figure 1. Zn K-edge XANES of (a) amorphous ZnO and (b) crystalline (wurtzite) ZnO, and their FEFF simulations [4].

The ZnO films were prepared by sputtering on Si wafer [4]; the as-grown film with 2 nm thickness was amorphous (a-ZnO), while the film with 50 nm thickness after annealing was crystalline having wurtzite structure (w-ZnO; P6$_3$/mc). FEFF simulation was done assuming the wurtzite structure and the results were attached in the respective figures [4]. For w-ZnO, full multiple scattering up to $R_{FMS} = 5.0$ Å was considered, while for a-ZnO, single scatterings within half path length of 4.0 Å (i.e. Zn→O→Zn and Zn→Zn’→Zn only) were considered. The simulation well reproduced the major features (highlighted by arrows) in the experimental data. This suggests the preferential loss of multiple scattering events due to structural disorders in amorphous ZnO. Thus, it can be told that the amorphousness would suppress the virtual electron hopping and degrade the electrical property of ZnO for use as a transparent semiconductor [4].
3.2. HfO$_2$

![Figure 2](image)

**Figure 2.** Hf L$_3$-edge XANES of (a) amorphous HfO$_2$ and (b) crystalline (monoclinic) HfO$_2$, and their FEFF simulations [5].

Figure 2 shows the Hf L$_3$-edge XANES of (a) amorphous and (b) crystalline HfO$_2$ films and their simulated spectra, taken from Ref. [5]. The HfO$_2$ films were prepared by atomic layer deposition on Si wafer [5]; the as-grown film with 10 nm thickness was amorphous (a-HfO$_2$), while the film after annealing was crystalline having a monoclinic crystal structure (m-HfO$_2$; P2$_1$/c). FEFF simulation was done assuming the monoclinic structure. For m-HfO$_2$, multiple scatterings with the number of legs less than 8 in a radius of 5.0 Å were considered, while for a-HfO$_2$, only the single scatterings such as Hf→O→Hf and Hf→Hf'→Hf (the number of legs is 2) are considered within the same range. The simulation well reproduced the major features (highlighted by the arrow) in the experimental data in Fig. 2. This suggests the preferential loss of multiple scattering events in amorphous HfO$_2$, similar to the case of ZnO in Fig. 1.

3.3. ZrO$_2$

![Figure 3](image)

**Figure 3.** Zr K-edge XANES of (a) amorphous ZrO$_2$ and (b) crystalline (tetragonal) ZrO$_2$, and their FEFF simulations [6].

Figure 3 shows the Zr K-edge XANES of (a) amorphous and (b) crystalline ZrO$_2$ films with their simulated spectra taken from Ref. [6]. The ZrO$_2$ films with 8 nm thickness were prepared by atomic layer deposition on Si wafer [6]. The as-grown film was amorphous (a-ZrO$_2$), while the annealed film became crystalline having a tetragonal crystal structure (t-ZrO$_2$; P4$_2$/nmc). FEFF simulation was done with R$_{FMS} = 6.0$ Å for both a-ZrO$_2$ and t-ZrO$_2$. The experimental spectrum of t-ZrO$_2$ was reproduced very well by the theoretical spectra based on the tetragonal local structure (see the arrows in the figure), whereas that of a-ZrO$_2$ was not. Meanwhile, the spectrum of a-ZrO$_2$ was very similar to that of ZrO$_2$ powder having a monoclinic structure and was well reproduced by the simulation based on the
monoclinic-like local structure model as shown in Fig. 3(a). This suggests the amorphousness in ZrO$_2$ hinders the metastability of the tetragonal structure in ZrO$_2$ so that a monoclinic-like local structure is favoured. Thus, the benefit of the high dielectric constant in tetragonal ZrO$_2$ can be suppressed in amorphous ZrO$_2$.

3.4. In$_2$Ga$_2$ZnO$_7$

Figure 4. (a) In K-edge, (b) Ga K-edge, and (c) Zn K-edge XANES of amorphous In$_2$Ga$_2$ZnO$_7$ [7] and polycrystalline (hexagonal) In$_2$Ga$_2$ZnO$_7$ with their FEFF simulations [8].

Figure 4 shows the XANES of a transparent semiconductor, In$_2$Ga$_2$ZnO$_7$ at (a) In K-edge, (b) Ga K-edge, and (c) Zn K-edge, and their simulated spectra, taken from Refs. [7,8]. The polycrystalline In$_2$Ga$_2$ZnO$_7$ powder had a hexagonal crystal structure (h-In$_2$Ga$_2$ZnO$_7$: P6$_3$/mmc), while the sputtered In$_2$Ga$_2$ZnO$_7$ film on glass (150 nm-thick) was amorphous (a-In$_2$Ga$_2$ZnO$_7$). The spectra of the polycrystalline sample were well reproduced by the full multiple scattering simulations with $R_{FMS} = 6.0$ Å, while those of a-In$_2$Ga$_2$ZnO$_7$ could be done with much-reduced values of $R_{FMS}$, e.g. less than 4.0 Å as shown in the figure. This indicates that the structural disorders in the film were significant in spite of the relatively high thickness (150 nm). Maintaining the amorphous state even at high thickness is a useful property for flexible devices.

4. Conclusion

The X-ray absorption near-edge structure analyses aided by theoretical simulations are powerful in studying the local structural properties of highly disordered materials. Not only the evolution in the degree of structural disorders (amorphous ZnO, HfO$_2$, or In$_2$Ga$_2$ZnO$_7$) but also the local structural evolution (amorphous ZrO$_2$) can be scrutinized in comparison with their crystalline counterparts.

Acknowledgement

This work was supported by grants from the National Research Foundation of Korea (NRF-2018R1D1A1B07043427).

References

[1] “X-Ray Absorption”, edited by D. C. Koningsberger and R. Prins (Wiley, New York, 1988).
[2] J. J. Rehr, "Recent Developments in Multiple-Scattering Calculations of XAFS and XANES," Jpn. J. Appl. Phys., Suppl. vol. 32-2, pp. 8-12, 1993.
[3] A. L. Ankudinov, B. Ravel, J. J. Rehr, and S. D. Conradson, "Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure," Phys. Rev. B, vol. 58, no. 12, pp. 7565-7576, 1998.
[4] D.-Y. Cho, J. H. Kim, and C. S. Hwang, “Electron hopping interactions in amorphous ZnO films probed by x-ray absorption near edge structure analysis,” Appl. Phys. Lett., vol 98, no. 22, pp. 222108, 2011.
[5] D.-Y. Cho, T. J. Park, K. D. Na, J. H. Kim, and C. S. Hwang, “Structural disorders in an amorphous HfO$_2$ film probed by x-ray absorption fine structure analysis,” Phys. Rev. B, vol 78,
no. 13, pp. 132102, 2008.

[6] D.-Y. Cho, H.-S. Jung, J. H. Kim, C. S. Hwang, “Monocliniclike local atomic structure in amorphous ZrO₂ thin film,” Appl. Phys. Lett., vol. 97, no. 14, pp. 141905, 2010.

[7] D.-Y. Cho, J. Song, K. D. Na, C. S. Hwang, J. H. Jeong, J. K. Jeong, and Y.-G. Mo, "Local structure and conduction mechanism in amorphous In–Ga–Zn–O films," Appl. Phys. Lett. vol. 94, no. 11, pp. 112112, 2009.

[8] D.-Y. Cho, J. Song, Y. C. Shin, C. S. Hwang, W. S. Choi, and J. K. Jeong, "Influence of High Temperature Postdeposition Annealing on the Atomic Configuration in Amorphous In–Ga–Zn–O Films," Electrochem. Solid-State Lett., vol. 12, no. 6, H208-H210, 2009.