Available online at https://li02.tci-thaijo.org/index.php/ssstj

Suan Sunandha Science and Technology Journal

XANES, XPS and Raman Studies of Hafnium Oxide Thin Films fabricated by RF Magnetron Sputtering at Different Power

Ekachai Chongsereecharoen*, Yotin Kallayalert, Wichai Kongsri

Faculty of Science and Technology, Valaya Alongkorn Rajabhat University under The Royal Patronage, Pathum Thani 13180, Thailand
***Corresponding author e-mail: ekachai@vru.ac.th**

Received: *23 May 2023* / **Revised:** *15 June 2023* / **Accepted:** *20 June 2023*

Abstract

Hafnium oxide layer was deposited on unheated silicon wafer and glass substrates at different power by using RF magnetron sputtering technique. The structural property was investigated by Raman spectroscopy. Moreover, HfO_2 structure in monoclinic major phase especially at high RF power was found from the Raman spectra in vibrational modes. In addition, oxidation state of hafnium oxide thin films was gained by synchrotron-based X-ray absorption spectroscopy (XAS) using Hf L3-edge of XANES techniques and X-ray photoelectron spectroscopy (XPS) as well. The XANES and XPS results show that the oxidation state of HfO_2 films is unchanged at different powers. The thin film prepared at higher power tends to have lower oxygen vacancy.

Keywords: Hafnium oxide thin films, Raman spectroscopy, XANES, XPS

1. Introduction

Hafnium oxide (HfO_2) has been considered as an alternative metal oxide material besides SiO_2 for high κ-gate dielectric material because of its great dielectric constant, excellent chemical and thermal stabilities, and high bandgap (Park & Kang, 2006). HfO_2-based materials are also a promising candidate for high index optical coatings, resistive-switching memory and ferroelectric field effect transistors (FeFET) (Ali et al., 2020). Semiconductor company introduced hafnium-based oxides as a replacement for silicon oxide in field-effect transistors' gate insulators. There are three phases of HfO_2: cubic, tetragonal, and monoclinic. The lowest energy structure of them is monoclinic HfO_2. Nevertheless, the implementation of Hafnium Oxide encounters various obstacles, including elevated defect density, increased threshold voltage, and concerns regarding dependability. Recent research has indicated that oxygen vacancies are the most active defects. The creation of oxygen vacancies in hafnia films and bulk samples can occur as a result of growth, deposition, and doping procedures. The presence of an oxygen vacancy in defective HfO_2 results in the emergence of a defect level situated at the edge of the conduction band. The electronic transition is obviously impacted by the new defect level. The presence of principal traps in HfO_2 implies that the optimal approach for deposition and postprocessing conditions should involve the elimination or neutralization of these defects (Gangqiang, Sanqi, & Tingting, 2013; Xiong, Robertson, Gibson, & Clark, 2005). Due to their simple binary oxide with non-perovskite structure and ferroelectric properties after doping by various dopants, such as Si, Zr, Al, and La, Hafnia –based materials have attracted considerable interest in the research field of ferroelectrics (Böscke, Müller, Bräuhaus, Schröder, & Böttger, 2011). The advantage of HfO_2 for transistors is its high dielectric constant, which is greater than SiO_2 (Luo et al., 2019). In recent times, several methods exist for producing HfO_2 thin films (Kukli et al., 2002). Magnetron sputtering is one of suitable methods to fabricate HfO_2 thin films because the film properties are controllable (Aygun & Yildiz, 2009; Cantas, Aygun, & Basa, 2014). The dielectric constant and other properties of a material are dependent on its deposition method, composition, and microstructure (Biswas, Sinha, & Chakraborty, 2016; Gao et al., 2016).

To gain a better understanding of the evolution of power dependent properties of Hafnia thin films fabricated by RF sputtering, in this work, we conducted detailed structural study using Raman

Suan Sunandha Science and Technology Journal

spectroscopy and chemical composition study by X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES) analysis. The structural sensitivity of X-ray diffraction techniques diminishes when the particle size of films achieves a few nanometers or when the films exhibit amorphous characteristics with short-range order. XPS is a well-known measurement method for probing the chemical environment and the electronic structure of a wide range of samples. X-ray absorption spectroscopy (XAS) is an essential elemental characterization technique due to its exceptional sensitivity to the local electronic and atomic structure. This technique effectively addresses the challenge of characterizing the local structure and electronic properties of diminutive, poorly crystalline, or low-conductive film/powder samples.

2. Experimental Details

Hafnium oxide layers were deposited on cleaned glass and silicon substrates by RF magnetron sputtering at room temperature by using HfO_2 ceramic target (99.999%, 3-inch diameter). Before deposition, the background pressure in the chamber was evacuated to about 1×10^{-4} Pa. The deposition pressure was controlled at 1×10^{-4} Pa. Argon was employed as sputtering gas and fixed at 10 sccm of flow rate. The spatial separation between target and substrate was kept at 70 mm. The operating time was set for 60 min. The RF sputtering power used during the deposition process varied between 50 to 200 Watt.

The structural study of the prepared films was examined by Raman spectroscopy (SENTERRA, Bruker). Raman spectra were obtained utilizing a 532 nm laser excitation, 25 mW power, and 25 µm ×1000 µm window, with a Raman shift resolution of 0.5 cm^{-1} over a range of 50–2700 cm^{-1}. The chemical composition was analyzed by means of XPS and XANES. XPS measurements were conducted utilizing a PHI5000 Versa probe II (ULVAC-PHI, Japan) that was installed with a hemispherical electron energy analyzer at Chiang Mai university, Thailand. A monochromatic Al Kα X-ray gun operating at an energy of 1486.6 eV was employed as the excitation source. The survey scans of XPS acquired over a range of 0 to 1400 eV with pass energy of 117.40 eV and energy step of 1.0 eV. High resolutions XPS spectra were gathered with pass energy of 46.95 eV and energy step of 0.05 eV to probe the elements of interest. The calibration of the binding energy for all XPS spectra was conducted utilizing the C1s peak at 284.8 eV. The peak deconvolution process involved the application of the Sherly background subtraction method and the linear combinations of Gaussian-Lorentzian function. Moreover, the local structure was investigated by synchrotron-based XANES with electron energy of 1.2 GeV at the BL5.2: SUT-NANOTEC-SLRI XAS beamline of the Synchrotron Light Research Institute, Thailand. The XANES measurements were performed by fluorescent mode at room temperature. The spectra of Hafnium L3-edge were obtained within an energy range of 9530-96400 eV, with a 0.2 eV energy increment. The XAS data was normalized and subtracted background by the ATHENA program included in the IFEFFIT package.

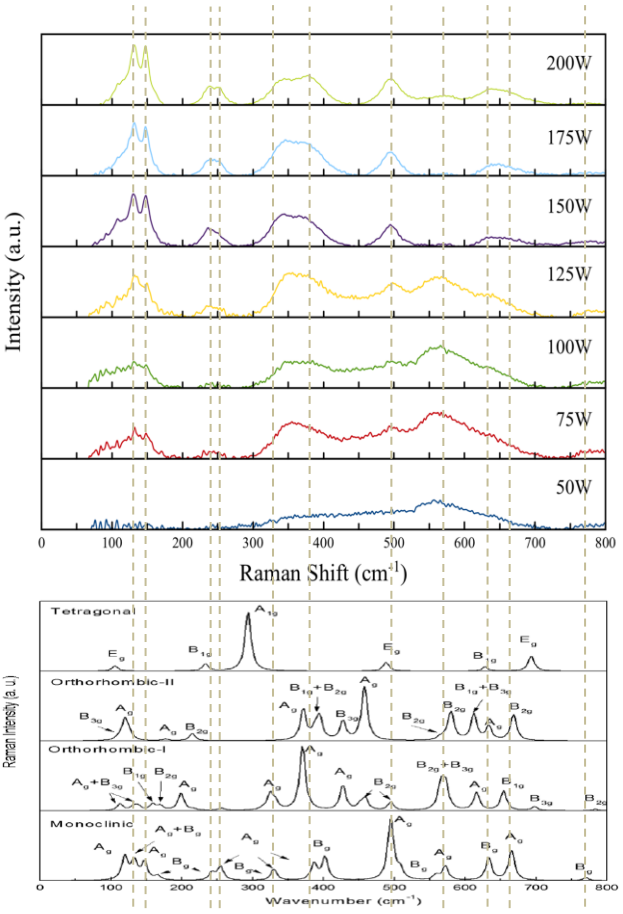

Figure 1. The RF power dependent Raman spectra of Hafnium oxide thin films compared with the calculation results from Zhou et al.'s work (Zhou, Shi, Zhang, Su, & Jiang, 2014).

Suan Sunandha Science and Technology Journal

3. Results and Discussion

Raman spectra of the HfO_2 thin films with different sputtering power are investigated as shown in Figure 1. The Raman experimental result was compared with the calculation results from Zhou et al.'s work (Zhou et al., 2014). The results revealed that all films are in a monoclinic/ orthorhombic-I phase mixture. In the preparation with the sputtering power more than 100W, HfO_2 film structure is obviously the majority in Monoclinic phase (Wu et al., 2012). As the sputtering power increased, the amount of activated Ar+ ions per unit time raised. As a result, more target atoms with higher average kinetic energies were sputtered per unit of time. As a result, the deposition rate rises linearly with sputtering power. The extra energy will be transmitted to the substrate and released as heat since the density of the film cannot be indefinitely increased. When temperature during deposition in the chamber is higher, a partial transformation into the monoclinic phase occurs (Pathak et al., 2020).

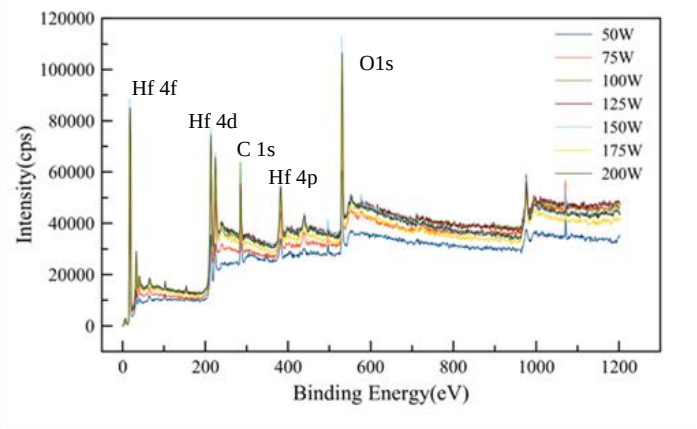

Figure 2. Survey XPS spectra of Hafnium oxide thin films prepared at different RF power.

XPS was utilized to examine the surface compositions of Hafnium oxide film samples. In Figure 2, the XPS survey spectra shows that Hf (4f, 4d, 4p), O and C are present on all films' surfaces. XPS typically has an analysis depth of less than 5 nanometers. There is no surface contamination observed in all samples within sensitivity of the instrument. The adsorption of atmospheric carbon on the surface is expected to be responsible for the presence of carbon. The high-resolution XPS spectra at Hf4f and O1s binding energy regions are shown in figures 3 and 4, respectively. The Hf 4f 7/2 and Hf 4f 5/2 peaks of all films were observed at binding energies of about 16.6 and 18.4 eV, respectively, confirming the formation of HfO_2 on the surfaces (Lin & Liao, 2013; Luo et al., 2018). The O1 s peaks of all films were deconvoluted into two peaks at the binding energies of 530.3 and 532.0 eV which are associated with the Hf–O bond of O–Hf–O and the O–O bond of non-lattice oxygen, which was made possible by the suboxides with Hf, respectively. The large proportion of the non-lattice oxygen peak in the O 1s spectra indicates that the HfO_2 film layer surface contained more defects (Biswas et al., 2016; Luo et al., 2018; Perevalov, Aliev, Gritsenko, Saraev, & Kaichev, 2013). The XPS result in figure 4 shows that the intensity of non-lattice oxygen peak decreased with increasing sputtering power. Therefore, it is noted that the HfO_2 films with low RF power have more defects.

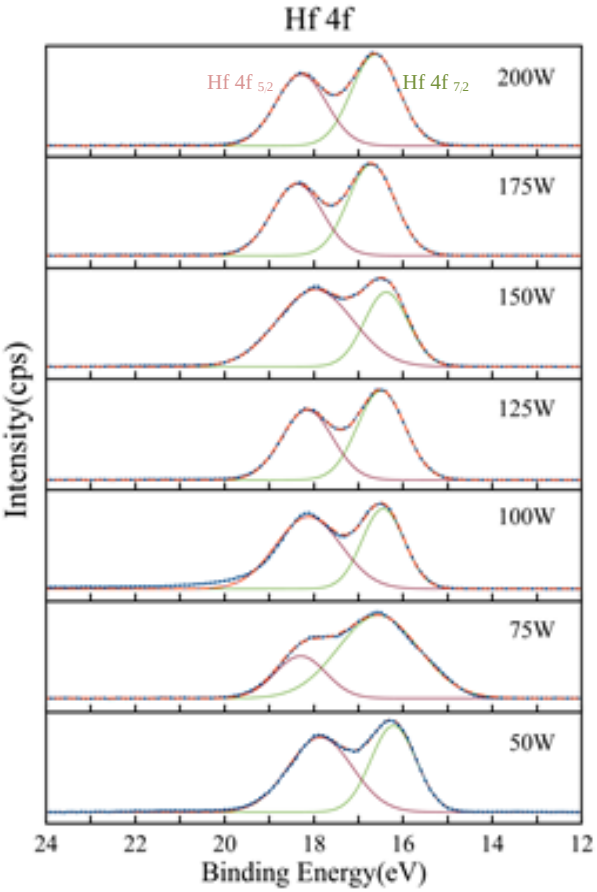

Figure 3. Hf 4f XPS spectra of the Hafnium oxide films prepared at various power.

The normalized Hf L3-edge XANES spectra of the Hafnium oxide films prepared at different power are shown in Figure 5. The benefit of XANES is that it is sensitive to the local environment surrounding the probing atoms and can therefore be used to determine the chemical composition and oxidation states of the probing atoms. It is evident from Figure 5, XANES spectra of all samples reveal similar features and identical energy position of Hf L3-edge.

Suan Sunandha Science and Technology Journal

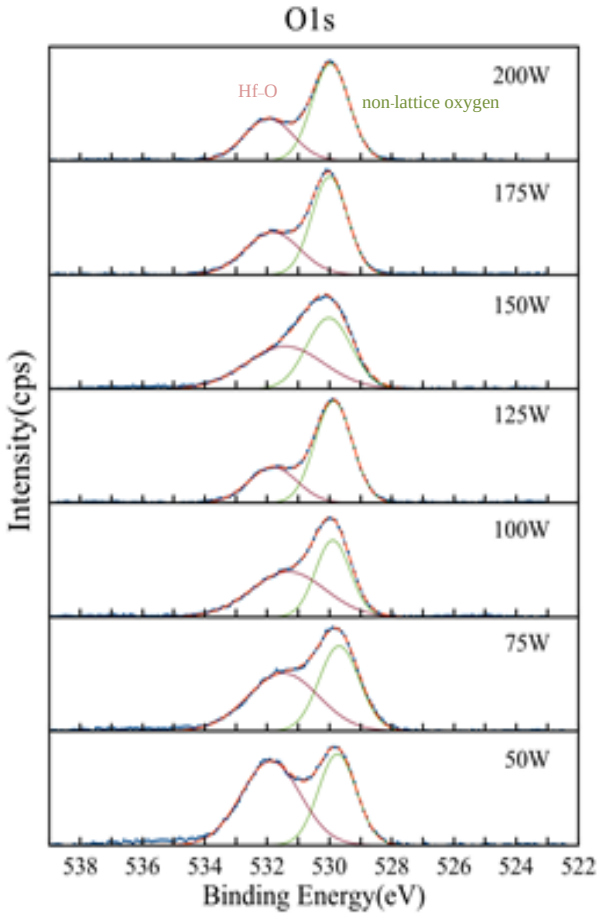

Figure 4. O1s XPS spectra of the Hafnium oxide films prepared at various powers.

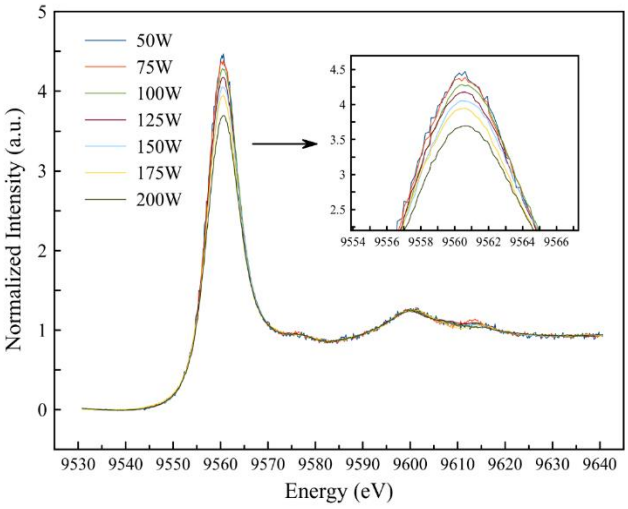

Figure 5. The normalized Hf L3-edge XANES spectra of the Hafnium oxide films are prepared at various powers.

The edge energy of Hf L3-edge was found at 6559.05eV. Additionally, the position of the absorption edge in all samples is similar to that of the HfO_2 standard, indicating that the valence state of Hf in Hf -O clusters is +4. The highest peaks at 9560 eV relate to the Hf 2p3/2 →5d transition and features above 9570 eV are due to the transition to the 6sd continuum (Botti et al., 2020; Cho, Jung, & Hwang, 2010). A significant decrease in intensity of the white line feature reflects the decrease of oxygen vacancy contents. Additionally, this XANES result is in good agreement with the previous XPS results.

4. Conclusion

Hafnium oxide thin films synthesized at different RF power by RF magnetron sputtering are in a monoclinic/ orthorhombic-I phase mixture. The majority Monoclinic structure was obtained in all samples which were confirmed by Raman and XANES results. XPS and Hf L3-edge XANES techniques were investigated, and they show well agreement with the same oxidation state of HfO_2. The samples prepared at greater power tend to have lower oxygen vacancy.

Acknowledgement

The authors would like to thank the Synchrotron Light Research Institute (Public Organization) (BL5.2), Thailand for their provision of the XAS measurement and laboratory facilities**.**

References

Ali, F., Zhou, D., Ali, M., Ali, H. W., Daaim, M., Khan, S., … Sun, N. (2020). Recent progress on energy-related applications of HfO_2-based ferroelectric and antiferroelectric materials. *ACS Applied Electronic Materials*, *2*(8), 2301-2317. doi:10.1021/acsaelm.0c00304

Aygun, G., & Yildiz, I. (2009). Interfacial and structural properties of sputtered HfO_2 layers. *Journal of Applied Physics*, *106*(1), 014312. doi:10.1063/1.3153953

Biswas, D., Sinha, A. K., & Chakraborty, S. (2016). Effects of oxygen partial pressure and annealing temperature on the residual stress of hafnium oxide thin-films on silicon using synchrotron-based grazing incidence X-ray diffraction. *Applied Surface Science*, *384*, 376-379. doi:10.1016/j.apsusc.2016.05.015

Suan Sunandha Science and Technology Journal

Böscke, T. S., Müller, J., Bräuhaus, D., Schröder, U., & Böttger, U. (2011). Ferroelectricity in hafnium oxide thin films. *Applied Physics Letters*, *99*(10), 102903. doi:10.1063/1.3634052

Botti, L., Kondrat, S. A., Navar, R., Padovan, D., Martinez-Espin, J. S., Meier, S., & Hammond, C. (2020). Solvent-activated hafnium-containing zeolites enable selective and continuous glucose–fructose isomerisation. *Angewandte Chemie*, *132*(45), 20192-20198. doi:10.1002/ange.202006718

Cantas, A., Aygun, G., & Basa, D. K. (2014). *In-situ* spectroscopic ellipsometry and structural study of HfO_2 thin films deposited by radio frequency magnetron sputtering. *Journal of Applied Physics*, *116*(8), 083517. doi:10.1063/1.4893708

Cho, D. Y., Jung, H. S., & Hwang, C. S. (2010). Structural properties and electronic structure of HfO_2-ZrO_2 composite films. *Physical Review B*, *82*(9). doi:10.1103/physrevb.82.094104

Gangqiang, Z., Sanqi, T., & Tingting, T. (2013). Electronic structure and optical properties of monoclinic HfO_2 with oxygen vacancy. *Rare Metal Materials and Engineering*, *42*(8), 1576-1580. doi:10.1016/s1875-5372(13)60093-4

Gao, J., He, G., Deng, B., Xiao, D. Q., Liu, M., Jin, P., … Sun, Z. Q. (2016). Microstructure, wettability, optical and electrical properties of HfO_2 thin films: Effect of oxygen partial pressure. *Journal of Alloys and Compounds*, *662*, 339-347. doi:10.1016/j.jallcom.2015.12.080

Kukli, K., Ritala, M., Sundqvist, J., Aarik, J., Lu, J., Sajavaara, T., … Hårsta, A. (2002). Properties of hafnium oxide films grown by atomic layer deposition from hafnium tetraiodide and oxygen. *Journal of Applied Physics*, *92*(10), 5698-5703. doi:10.1063/1.1515107

Lin, S. S., & Liao, C. S. (2013). The hydrophobicity and optical properties of the HfO_2-deposited glass. *Ceramics International*, *39*(1), 353-358. doi:10.1016/j.ceramint.2012.06.033

Luo, J. D., Zhang, H. X., Wang, Z. Y., Gu, S. S., Yeh, Y. T., Chung, H. T, … Cheng, H. C. (2019). Improvement of ferroelectric properties in undoped hafnium oxide thin films using thermal atomic layer deposition. *Japanese Journal of Applied Physics*, *58*. doi:10.7567/1347-4065/ab0ded

Luo, X., Li, Y., Yang, H., Liang, Y., He, K., Sun, W., … Feng, Z. (2018). Investigation of HfO_2 thin films on Si by X-ray photoelectron spectroscopy, Rutherford backscattering, grazing incidence X-ray diffraction and variable angle spectroscopic ellipsometry. *Crystals*, *8*(6), 248. doi:10.3390/cryst8060248

Park, P. K., & Kang, S. W. (2006). Enhancement of dielectric constant in HfO_2 thin films by the addition of Al_2O_3. *Applied Physics Letters*, *89*(19), 192905. doi:10.1063/1.2387126

Pathak, S., Das, P., Das, T., Mandal, G., Joseph, B., Sahu, M., … Siruguri, V. (2020). Crystal structure of monoclinic hafnia (HfO_2) revisited with synchrotron X-ray, neutron diffraction and first-principles calculations. *Acta Crystallographica Section C: Structural Chemistry*, *76*(11), 1034-1042. doi:10.1107/s2053229620013960

Perevalov, T. V., Aliev, V. Sh., Gritsenko, V. A., Saraev, A. A., & Kaichev, V. V. (2013). Electronic structure of oxygen vacancies in hafnium oxide. *Microelectronic Engineering*, *109*, 21-23. doi:10.1016/j.mee.2013.03.005

Wu, R., Zhou, B., Li, Q., Jiang, Z., Wang, W., Ma, W., & Zhang, X. (2012). Elastic and vibrational properties of monoclinic HfO_2 from first-principles study. *Journal of Physics D: Applied Physics*, *45*(12), 125304. doi:10.1088/0022-3727/45/12/125304

Xiong, K., Robertson, J., Gibson, M. C., & Clark, S. J. (2005). Defect energy levels in HfO_2 high-dielectric-constant gate oxide. *Applied Physics Letters*, *87*(18), 183505. doi:10.1063/1.2119425

Zhou, B., Shi, H., Zhang, X. D., Su, Q., & Jiang, Z. Y. (2014). The simulated vibrational spectra of HfO_2 polymorphs. *Journal of Physics D: Applied Physics*, *47*(11), 115502. doi:10.1088/0022-3727/47/11/115502