Volume 7, Issue 3, July 2020 ISSN: 2348-8565 (Online)

International Journal of Modern Engineering and Research Technology

Website: http://www.ijmert.org Email: editor.ijmert@gmail.com

# Substrate Temperature Influenced Electrical, Dielectric and Optical Properties of $HfO_2$ Films Formed by Magnetron Sputtering

**S. Venkataiah**
*Research Scholar*
*Department of Physics,*
*Sri Venkateswara University,*
*Tirupati (A.P.), India*
*E-mail: svt487@gmail.com*

**Uthanna S**
Assistant *Professor*
*Department of Physics,*
*Sri Venkateswara University,*
*Tirupati (A.P.), India*
*E-mail: uthanna@rediffmail.com*

## ABSTRACT

*DC magnetron sputtering technique was employed for deposition of hafnium oxide ($HfO_2$) thin films on quartz and p-silicon substrates held at different temperatures in the range 30–450°C. The deposited films were characterized for their chemical composition, chemical binding configuration, and crystallographic structure and optical properties. The films formed at substrate temperatures less than 350°C were amorphous nature while those deposited at 350°C and above were of polycrystalline with monoclinic $HfO_2$. X-ray photoelectron spectrum showed the characteristic core level binding energies of $HfO_2$. Optical band gap of the films increased from 5.58 eV to 5.88 eV with increase of substrate tempe-rature from 30°C to 450°C Gate capacitor with configuration of Al/$HfO_2$/p- Si was fabricated and studies the electrical and dielectric properties.*

***Keywords:***— *Hafnium oxide, thin films, DC magnetron sputtering, electrical, optical properties.*

## I. INTRODUCTION

Hafnium oxide ($HfO_2$) considered being a potential high-k dielectric material among the silicon dioxide, zirconium oxide, titanium oxide, tantalum oxide, barium strontium oxide and zirconium titanium oxide. It has advantages of good electrical properties and better chemical stability and compatibility with the silicon the base for the integrated circuit technology [1]. $HfO_2$ is a wide band gap, high refractive index material useful as visible, near infrared antireflection coatings, band pass filters and heat mirrors for energy efficient windows [2, 3]. High dielectric constant made it a potential candidate as gate dielectric in field effect transistor in random access memory devices [4, 5]. Amorphous $HfO_2$ thin films formed on polymer substrates find application in flexible thin film capacitor and fibre optical wave guides. Various physical thin films deposition techniques namely vacuum evaporation [6], electron beam evaporation [4, 7], pulsed laser deposition [8], DC magnetron sputtering [9, 10] and RF magnetron sputtering [1, 11, 12] and chemical methods, atomic layer deposition [13], sol-gel process [14] and chemical vapour deposition [15] were effectively employed for deposition of $HfO_2$ thin films. Among these deposition methods, DC reactive magnetron sputtering considered to be the industrially employed technique for deposition of films in the presence of reactive gas of oxygen by sputtering metallic target to form metal oxide films on large area substrates.

In this investigation, $HfO_2$ thin films were deposited on to quartz and p-type silicon substrates by DC reactive magnetron sputtering method by sputtering of hafnium target in the presence of reactive gas of oxygen and sputter gas of argon at different substrate temperatures in the range 30°C - 450°C. The effect of substrate temperature on the structural, electrical, dielectric, and optical properties of $HfO_2$ films was systematically studied. Metal oxide semi-conductor (MOS) structure with configuration Al/$HfO_2$/p- Si was fabricated by depositing aluminium films on $HfO_2$ by vacuum evaporation and studied the electrical and dielectric properties of the MOS gate capacitor.

## II. EXPERIMENTAL

DC magnetron sputtering technique was employed for deposition of $HfO_2$ thin films on to quartz and p-type silicon (100) substrates held at different temperatures. The vacuum system used for deposition of the films was the combination of diffusion pump backed by rotary pump. Pure oxygen and argon were used as reactive and sputter gases respectively. Pressure in the sputter chamber was measured with Pirani - Penning gauge combination. After achieving the ultimate pressure of $5\times10^{-6}$ Torr, the reactive gas of oxygen was admitted into the sputter chamber to achieve the partial pressure of $5\times10^{-4}$ Torr. Then the sputter gas of argon was fed into the sputter chamber to obtain the sputter pressure of $6\times10^{-3}$ Torr. Hafnium (99.95% purity) with 50 mm diameter and 3 mm thick was used as sputter target for deposition of films on the substrates held at temperatures in the range 30°C - 450°C.

Thickness of the deposited films measured with Dektak depth profilometer was in the range 65 - 80 nm. Chemical composition of the deposited $HfO_2$ films was determined with energy dispersive X-ray analyzer (Oxford Instruments Inca Penta FETX3) attached to the scanning electron microscope (Carl Zeiss model EVO MAIS). Chemical binding configuration and core level binding energies of the films were analyzed with X-ray photoelectron spectroscope (Physical Electronics Model PHI 5700) and Fourier transform infrared spectrophotometer (Thermo-Nicolet model 6700). X-ray diffractometer (X'pert Pro PAN Analytical) with Cu $K_\alpha$ radiation (wavelength of 0.15406 nm) was used to determine the crystallographic structure of the films. Optical transmittance of the films formed on quartz substrates was recorded in the wavelength range 200 - 1000 nm using JASCO (modelV570) UV–Vis-NIR double beam spectrophotometer for determination of optical band gap. Metal oxide semiconductor structure with configuration of Al/$HfO_2$/p- Si was fabricated with circular capacitors of 300 μm diameter by vacuum evaporation of aluminium on the top of $HfO_2$ films. The capacitance - voltage and current - voltage characteristics of the capacitor were measured with LCR meter (MIOKI model 3532-50) and pA meter (Hewlett Packard model hp 4140B) respectively.

## III. RESULTS AND DISCUSSION

### *Chemical composition*

Figure 1 shows a representative energy dispersive X-ray analysis spectrum of the $HfO_2$ film formed on silicon substrate at 30°. The spectrum showed the characteristic kinetic energy peaks of hafnium and oxygen along with silicon. The silicon signal arises from the silicon substrate.

Chemical composition of the films was calculated from the intensity of the peaks of hafnium and oxygen and their sensitivity factors.

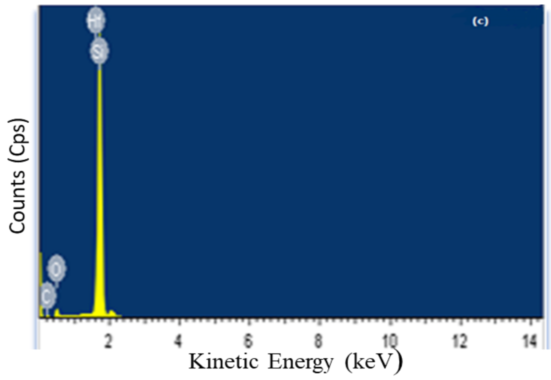


*Figure 1: EDAX spectrum of $HfO_2$ film formed at 250°C.*

The chemical composition of the films was hafnium 33.6 at. % and oxygen 66.4 at. %. It clearly indicated that the deposited films were of $HfO_2$.

**X-ray photoelectron spectroscopic studies**

Figure 2 shows the X-ray photoelectron spectrum of $HfO_2$ films formed on silicon substrate held at 250°C. The survey spectrum showed the core level binding energy peaks around 17 eV, 215 eV, 380 eV related to hafnium Hf 4f, Hf 4d and Hf 4p respectively (Figure 2a). The peak seen at about 530 eV correspond to binding energy of oxygen O 1s. The peak observed at about 284 eV related to carbon C 1s due to the contamination on the surface of the films since it exposed to the atmosphere before the XPS study. The carbon contamination was disappeared after one minute of argon ion bombardment on the films. Figure 2(b) - (d).

shows the narrow scan spectrum of $HfO_2$ films at the core level binding energies of Hf 4f, Hf 4d and O 1s in the binding energy ranges12-24eV, 205 - 235 eV and 526 - 536 eV. It is seen from Figure 2 (b) that the core level binding energy of 16.4 eV and 18.0 eV related to the Hf $4f_{7/2}$ and Hf $4f_{5/2}$ with spin-orbit splitting energy separation of 1.6 eV revealed the growth with tetravalent $Hf^{4+}$ state, the characteristics of $HfO_2$ [16]. In addition to this, the binding energies exhibited at 213.0 eV and 223.0 eV correspond to the Hf $4d_{5/2}$ and Hf $4d_{3/2}$ (figure 3c). From deconvolution of the peaks, the full width at half maximum of the peaks determined was 1.1 eV and 1.3 eV respectively for Hf $4f_{7/2}$ and Hf $4f_{5/2}$, which is the characteristic of $HfO_2$ films [17]. Figure 2(d) showed the oxygen O 1s core level binding energy of 529.5eV indicated the fully oxidized form of $HfO_2$.

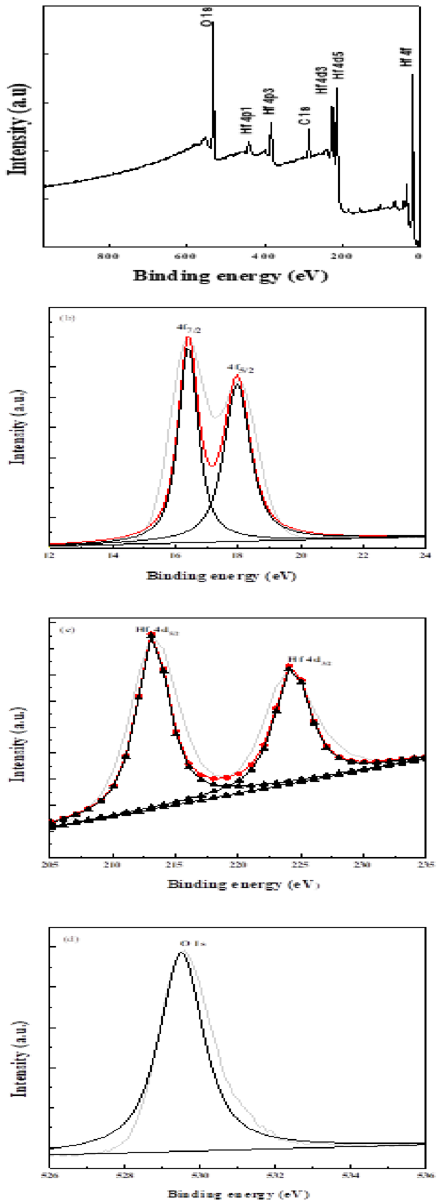


*Figure. 2 XPS spectrum of $HfO_2$ film formed at 250°C: (a) survey scan, and (b) narrow scan spectra of hafnium Hf 4f, (c) Hf 4d and (d) Oxygen O 1s*

### *Fourier transform infrared spectroscopic studies*

Chemical bonding configuration of the $HfO_2$ films deposited on silicon substrates was determined with the Fourier transform infrared spectroscopic studies. Figure 3 shows the Fourier transform infrared transmittance spectra of $HfO_2$ films deposited at different substrate temperatures. The films formed at 30°C not exhibited any absorption band because of amorphous nature. The films formed at 250° C contained a broad absorption band at 550 - 650 $cm^{-1}$ characterized the amorphous and crystalline phase of $HfO_2$ [11]. Films deposited at 350°C and 450°C contained the absorption bands at 522 $cm^{-1}$, 545 $cm^{-1}$, 604 $cm^{-1}$ and 736 $cm^{-1}$. The absorption band located at 522 $cm^{-1}$ was the vibration band of Hf - O related to monoclinic $HfO_2$ [18] and absorption bands located at 551 $cm^{-1}$ and 736 $cm^{-1}$ were the vibration mode of Hf - O in $HfO_2$ [9, 19]. From these studied it revealed that the films formed at 350°C and above were of polycrystalline with mono-clinic structured $HfO_2$.

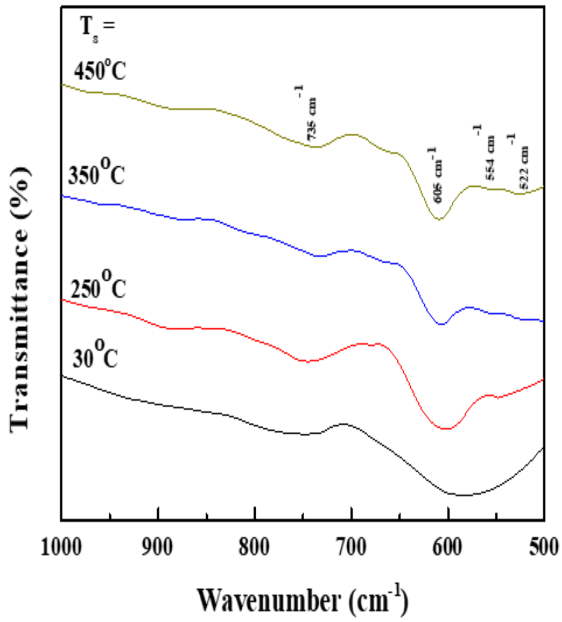


*Figure 3: FTIR transmittance spectra of $HfO_2$ films formed at different substrate temperatures.*

### *Structural studies*

X-ray diffraction profiles of the $HfO_2$ films formed at different substrate temperatures are shown in Figure 4. The films deposited at room temperature and at 250°C were of amorphous in nature. The films formed at substrate temperature of 350°C showed the diffraction peak at 2θ values at 28.33° related to the reflection ($\bar{1}11$) of monoclinic phase of $HfO_2$ [20]. The films deposited at 450°C contained the diffraction peaks at 28.19°, 35.22°, 41.31° and 50.46° correspond to ($\bar{1}11$), (200), (102) and ($\bar{1}22$) reflections of monoclinic $HfO_2$ [1] and in accordance with the JCPDS Data Card No. 06-0318.

The crystallite size (D) of the films was calculated from X-ray diffraction peak of ($\bar{1}11$) using the Debye - Scherrer's relation [21],

$$D = 0.9\lambda/\beta\cos\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where λ is the wavelength of copper X-ray radiation, β the full width at half maximum intensity of X-ray diffraction peak and θ the diffraction angle. The crystallite size calculated from the peak of ($\bar{1}11$) increased from the 16 nm to 22 nm with increase of substrate temperature from 350°C to 450°C respectively due to improvement in the crystallinity of the films.

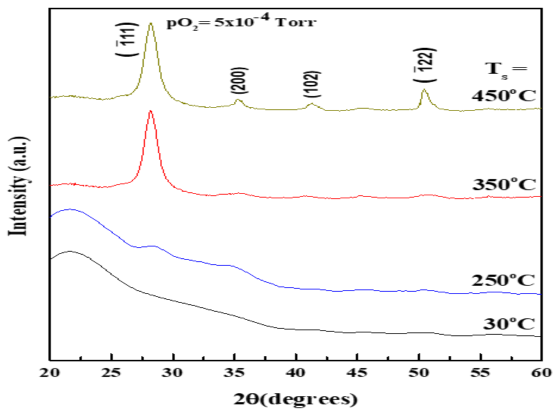


*Figure 4: X-ray diffraction profiles of $HfO_2$ films formed at different substrate temperatures.*

### *Optical properties*

The optical transmittance of the films formed on quartz substrates was recorded in order to study the optical absorption and to determine the optical band gap. Figure 5 shows the optical transmittance spectra of $HfO_2$ films formed at different substrate temperatures. The films were transparent (85 - 90%) in the visible wavelength region. The fundamental optical absorption edge of the films shifted towards lower wavelengths side with increase of substrate temperature. The optical absorption coefficient (α) was determine from the optical transmittance (T) and thickness (t) of films using relation [22],

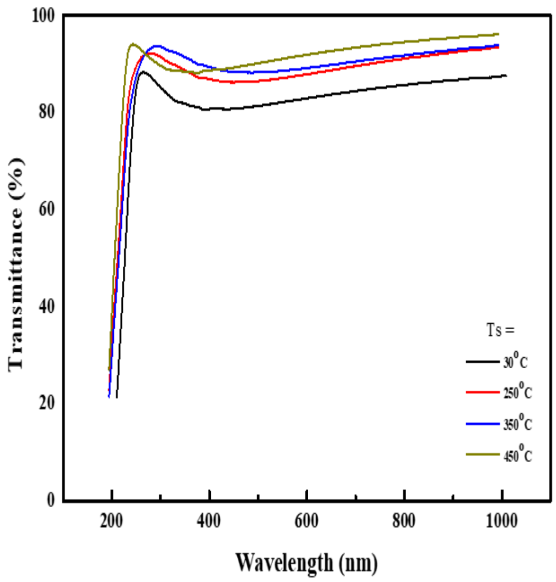


*Figure 5: Optical transmittance spectra of $HfO_2$ films formed at different substrate temperatures.*

$$\alpha = - (1/t) \ln (T) \qquad (2)$$

In order to determine the optical band gap ($E_g$). The optical absorption in the films was fitted to the Tauc's relation,

$$(\alpha h\nu) = A (h\nu - E_g)^2 \qquad ((3)$$

where A is the edge with parameter, hν the photon energy and $E_g$ the optical band gap of the films. Figure 6 shows the plots of $(\alpha h\nu)^2$

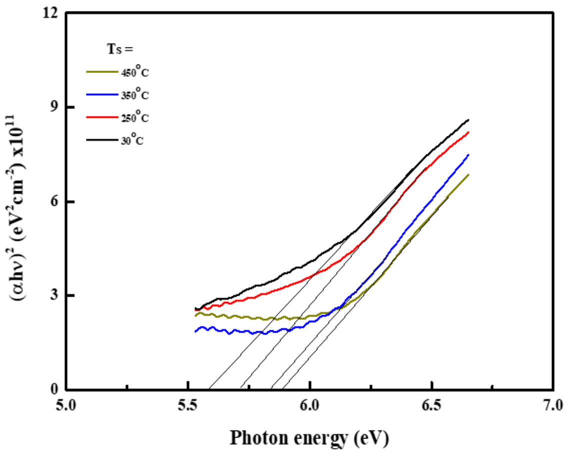


*Figure 6: Plots of $(\alpha h\nu)^2$ versus photon energy of $HfO_2$ films formed at different substrate temperature.*

band gap of the films was evaluated from the Tauc's plots increased from 5.52 eV to 5.88 eV with increase of substrate temperature from 30°C to 450°C respectively due to the transformation from amorphous to crystal-lline phase $HfO_2$. It was reported that the optical band gap of the films increased from 5.51 eV to 5.85 eV [23] and from 5.64 eV to 5.90 eV [24] due to transformation from amorphous to crystalline $HfO_2$ films.

### *Electrical and dielectric properties*

Metal-oxide-semiconductor capacitor with configuration of Al/$HfO_2$/p- Si was fabricated to study the electrical properties of the $HfO_2$ films. Figure 7 shows the capacitance - voltage characteristics of the thick $HfO_2$ films formed at different substrate temperatures (at 1 MHz) by applying bias voltage from + 3 to − 3 V. From the plots, it was observed that the accumulation capacitance increased from 38 nF to 46 nF with the increase of substrate temperature from 250°C to 450°C. This could be due to the reduction in the physical thickness of the $HfO_2$ layer with respect to substrate temperature. Besides, it is clear from the figures that with increase of substrate temperature, accumulation of capacitance improve the interface stability of $HfO_2$/Si [25]. On the other hand, there was slight shift in the flat band voltage by increasing the substrate temperature. The appropriate reason for this could be the decrease of dipole density and oxygen defect density at bottom interface of $HfO_2$/Si in MOS device [26]. In this investigation, there was small shift in the flat band potential with increase of substrate temperature which could be due to effective reduction in the oxygen vacancies in the bulk of $HfO_2$ layer, and at interface of $HfO_2$ and Si substrate. Dielectric constant was calculated from the capacitance - voltage curves using the relation,

$$C = k\varepsilon_o A/t \text{ ........................ } (4)$$

where C is the capacitance, $k$ the dielectric constant of the material, $\varepsilon_o$ the permittivity of free space and A the area of the capacitor. The dielectric constant increased from 22 to 25 with increase of substrate temperature from 250°C to 450°C. The improvement in the crystallinity of the $HfO_2$ films that is the reduction in full width at half maximum is the evidence for the improvement of the dielectric constant.

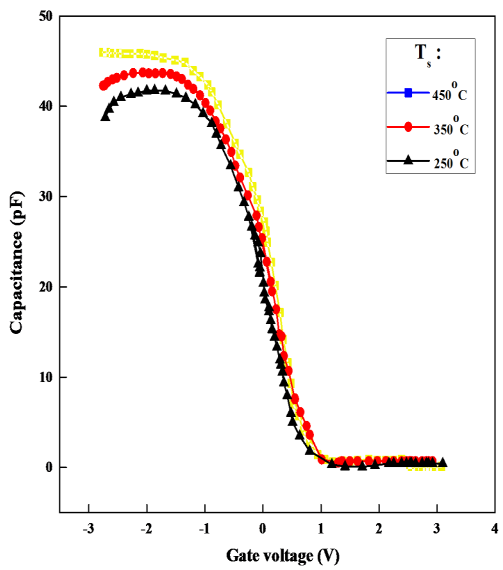


*Figure 7: Capacitance - voltage characteristic of Al/ $HfO_2$/Si capacitors formed at different substrate temperature.*

Figure 8 shows the leakage current versus applied voltages on the top electrode in analogy with the current - voltage curves of diodes to the MOS capacitor. From the figure, it is observed that leakage current density (at 1 V) decreased from $5.1\times10^{-4}$ A/cm$^2$ to $4.8\times10^{-5}$ A/cm$^2$ with increase of substrate temperature from 250°C to 450°C respectively. It implies that the deposition of $HfO_2$ films on Si substrate at high substrate temperatures showed a significant impact on suppressing the defects in gate insulator resulted in the improvement of interface quality between the gate insulator $HfO_2$ and substrate.

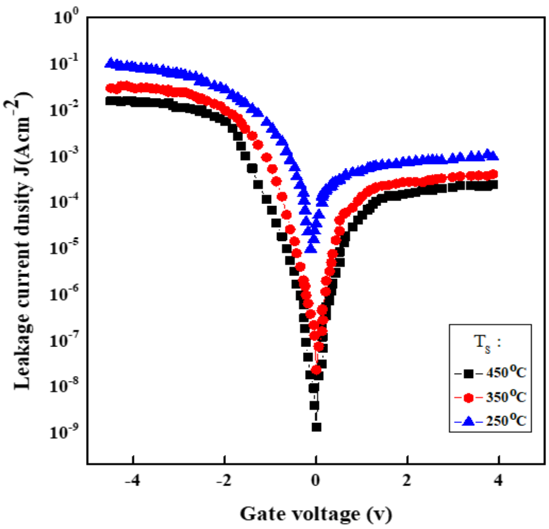


*Figure 8: Current - voltage characteristic of Al/$HfO_2$/Si capacitors formed at different substrate temperatures.*

## IV. CONCLUSIONS

Thin films of $HfO_2$ were deposited on to quartz and p- silicon substrates held at different temperatures in the range 30°C-450°C by sputtering of hafnium target in an oxygen partial pressure of $5\times10^{-4}$ Torr using DC magnetron sputtering technique. EDAX analysis of the films confirmed the growth of $HfO_2$. X-ray photoelectron spectrum showed the characteristic core level binding energies of $HfO_2$. The films deposited at substrate temperatures up to 250°C were amorphous in nature. Films formed at

350°C and above were of polycrystalline with monoclinic structured of $HfO_2$. The crystallite size of the films increased from 16 nm to 22 nm with increase of substrate temperature form 350°C to 450°C. Optical band gap of the films increased from 5.58 eV to 5.88 eV with increase of substrate temperature from 30°C to 450°C. Gate capacitor with configuration of Al/$HfO_2$/p-Si was fabricated and studies the electrical and dielectric properties. The dielectric constant of the capacitor increased from 22 to 25 with increase of substrate temperature. The leakage current decreased from $5.1\times10^{-4}$ A/cm$^2$ to $4.8\times10^{-5}$ A/cm$^2$ with increase of substrate temperature from 250°C to 450°C.

## ACKNOWLEDGMENT

One of the authors, S. Venkataiah is thankful to the University Grants Commission, New Delhi for the award of UGC-BSR-RFSMS Research Fellowship. Dr. S. Uthanna is thankful to University Grants Commission for award of UGC-BSR Faculty Fellowship.

## REFERENCES:

[1] M. Vargas, N.R. Murphy and C.V. Ramana, Tailoring the index of refract-tion of nanocrystalline hafnium oxide thin films Appl. Phys. Lett., 104 (2014) 10197.

[2] J. Buckley, B.D. Salvo, G. Ghibaudo, M. Gely, J.F. Damlencourt, F. Martin, G. Nicotra and S. Deleonibus, Investigation of $SiO_2$/$HfO_2$ gate stacks for application to non-volatile memory devices, Solid State Electron., 49 (2005) 1833.

[3] T.J. Bright, J.I. Watjen, Z.M. Zhang, C. Muratore and A.A. Voevodin, Optical properties of $HfO_2$ thin films deposited by magnetron sputtering: From the visible to the far-infrared, Thin Solid Film, 520 (2012) 6763.

[4] M. Ranzan, A.M. Rana, E. Ahmed, M.F. Wasiq, A.S. Bhatti, M. Hafeez, A. Ali and M.Y. Nadeem, Optical characterization of hafnium oxide thin films for heat mirrors, Mater. Sci. Semicond. Process., 32 (2015) 22.

[5] M. Nath and A. Roy, Interface and electrical properties of ultra-thin $HfO_2$ film grown by RF sputtering, Physica B 482 (2016) 43.

[6] D. Franta, I. Ohlidal, D. Necas, F. Vizda, O. Caha, M. Hason and P. Pokorny, Optical characterization of $HfO_2$ thin films, Thin Solid Films, 519 (2011) 6085.

[7] S. Jeena, R.B. Tokes, S. Tripathi, K.D. Rao, D.V. Udupa, S. Thakur and Sahoo, Influence of oxygen partial pressure on microstructure, optical properties, resi-dual stress and laser induced damage threshold of amorphous $HfO_2$ thin films, J. Alloy. Compd., 771 (2019)373.

[8] H. Liu, G. Wang, Z. Zhang, K. Pan and X. Zhang, Synthesis of negative thermal expansion $HfW_2O_8$ thin film using pulsed laser deposition, Ceram. Intl., 40 (2014) 13855.

[9] G. Aygun, A. Cantas, Y. Simsek and R. Turan, Effect of physical growth conditions on the structural and optical properties of sputtered grown thin $HfO_2$ films, Thin Solid Films, 519 (2011) 5820.

[10] V. Dave, P.K. Mishra and R. Chandu, Nanostructured hafnium oxide thin films for sensing carbon monoxide: An Experimental

Investigation, Mater Today: Proc., 5 (2018) 23286.

[11] K.C. Das, S.P. Ghosh, N. Tripathy, D.H. Kim, T.J. Lee, M. Myoung and P. Kar, Evolution of microstructural and electrical properties of sputtered $HfO_2$ ceramic thin films with RF power and substrate temperature, Ceram. Intl., 42 (2016) 138.

[12] A. Vinod, M.S. Rathore and N. Srinivasa Rao, Effects of annealing on quality and stoichiometry of $HfO_2$ thin films grown by RF magnetron sputtering, Vacuum, 155 (2018) 339.

[13] J. Lockinger, S. Nishiwaki, B. Bissig, G. Degutis, Y.E. Romanyut, S. Buechelar and A.N Tiwari, The use of $HfO_2$ in a point contact concept for front interface passivation of Cu (In,Ga)$Se_2$ solar cells, Solar Energy Mater. Solar Cells, 195 (2019) 213.

[14] P. Jin, G. He, D. Xiao, J. Gao, M. Lin, J. Lu, Y.Liu, M. Zhang, P. Wans and Z. Sun, Microstructure, optical, electrical properties, and leakage current transport mechanism of sol-gel processed high-*k* $HfO_2$ gate dielectrics, Ceram. Intl., 42 (2016) 6761.

[15] A. Devi, S. Cwik, K. Xu, A.P. Milanov, H. Noei, Y. Wang, D. Barreca, J. Meijer, D. Rogalla, D. Khani, R. Cross, H. Parale and S. Paul, Rare-earth substituted $HfO_2$ thin films grown by metalorganic chemical vapour deposi-tion, Thin Solid Films, 520 (2016) 4512.

[16] X. Luo, Y. Li, H. Yang, Y. Liang, K. He, W. Sun, H.H. Lin, S. Yao, X. Lu, L. Wan and Z. Feng, Investigation of $HfO_2$ Thin Films on Si by X-ray photo-electron spectroscopy, Rutherford backscattering, grazing incidence X-ray diffraction and variable angle spectro-scopic ellipsometry, Crystals, 8 (2018) 248.

[17] M. Engelhard, J. Herman, R. Wallace and D. Baer, As-received, ozone cleaned and $Ar^+$ sputtered surfaces of hafnium oxide grown by atomic layer deposition and studied by XPS, Surf. Sci. Spectra., 18 (2011) 46.

[18] J.C. Hackley and T. Gougousi, Properties of atomic layer deposited $HfO_2$ thin films Thin Solid Films, 517 (2009) 6576.

[19] D.A. Neumayer and E. Catir, Materials characterization of $ZrO_2$-$SiO_2$ and $HfO_2$-$SiO_2$ binary oxides deposited by chemical solution deposition, J. Appl. Phys., 90 (2001) 1801.

[20] P. Kondaiah, S. Habibuddin and G. Mohan Rao, Studies on RF magnetron sputtered $HfO_2$ thin films for micro-electronic applications, Electron. Mater. Lett., 11 (2015) 592.

[21] B.D. Cullity, Elements of X-ray Diffraction, Addition-Wesley, Reading, MA (1978).

[22] J. Tauc, Amorphous and Liquid Semiconductor, Plenum Press, NY (1974).

[23] M. Modreanu, J.S. Parramon, O. Durang, B. Bridou, M. Stchakovsky, C. Eypert, C. Naudin, A. Knowles, F. Bridou and M.F. Ravet, Investigation of thermal annealing effects on micro -structural and optical properties of $HfO_2$ thin films, Appl. Surf. Sci., 253 (2006) 328.

[24] J.M. Khoshman, A. Khan and M.E.

Kordesch, Amorphous hafnium oxide thin films for antireflection optical coatings, Surface. Coat. Technol., 202 (2008) 2500.

[25] T. Yu C.G. Jin, Y.J. Dong, D. Cao, L.J. Zhuge, X.M. Wua, Temperature depen-dence of electrical properties for MOS capacitor with $HfO_2/SiO_2$ gate dielectric stack, Mater. Sci. Semicond. Process, 16 (2013) 1321.

[26] R. Garg, N. A. Chowdhury, M. Bhaskaran, P. K. Swamy, and D. Misraa, Electrical characteristics of thermally evaporated $HfO_2$, J. Electro -chem. Soc., 151 (2004) 1.

* * * * *