Digest Journal of Nanomaterials and Biostructures Vol. 14, No. 3, July - September 2019, p. 823 - 830

FABRICATION AND CHARACTERIZATION OF MULTILAYER HfO_2/Ag/ HfO_2 FILMS

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Physical vapor deposition technique has been used to design the try-layer thin films. The commercial glass has been used as substrate for these growth. The substrate temperature of these layers has been varies from room temperature, 100 °C and 150 °. The thickness of these tri-layers has been controlled through crystal quartz monitor. The X-ray diffraction has been used to study the structural properties which shows that some amorphous to polycrystalline behavior. The surface properties of these layers have been done through Atomic Force microscopy. The transmission and reflection in UV, VIS and near IR regions had been measured using optical spectrophotometer. X-rays photospectromer (XPS) results show that binding energy decreased with increase in annealing temperature, Hafnium is changing from Ag^{+3} state to Ag^{+2}.

(Received November 22, 2018; Accepted September 19, 2019)

Keywords: HfO_2, Multilayer, AFMand XPS

1. Introduction

V. Shrotriya, discussed that how transition metal oxides used in polymer photo voltaic cells as a buffer layer. There was tri-layer in polymer based photovoltaic cell. Two layers were made up of polymer layer and indium tin oxide. [1] I.O. Usov et al. worked on tri-layer structure composed of HfO_2/MgO/ HfO_2 in thin film. 10 MeV Au ions irradiation was used in IBML at Los Alamos National laboratory. It was concluded that bulk properties like, resistance to compositional mixture, resistance to amorphization, and resistance to pronounced were in stable positioning state. In addition, first hafnium oxide layer can be transformed, cubic, or monoclinic form of HfO_2. [2] K. Marszalek et al. studied the tri layer $Al_2O_3/HfO_2/SiO_2$ and bi-layer Al_2O_3/SiO_2 anti reflective coatings and their optical properties. [3] M. Fadel et al. investigated the applications and optical properties of HfO_2 thin film. By changing the different evaporation conditions like substrate paper, evaporation rate, thickness different results were obtained. [4] By X-ray photoelectron spectroscopy (XPS) the spectral information tells that hafnium showed a strong affinity for oxygen. For the first type of sample at temperature 300 °C and second type at temperature 500 °C, the over layer was oxidized and formed HfO_2 [5].In this paper, M. Ramzan et al. analyzed the morphology of hafnium oxide (HfO_2) thin film by atomic force microscopy (AFM) . The root mean square (RMS) roughness, average roughness, surface kurtosis, surface skewness and maximum peak to valley height were studied. For all samples, RMS roughness increased with increasing grain size. But surface roughness showed opposite behavior with grain size. These thin films represented the smooth, uniform distribution of grains all around the surface. So this type of surface has very important rule as energy efficient windows in heat mirrors. [6] F L Mart´ınez, et al. studied the structural and optical properties of thin film of hafnium oxide. It was concluded that

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as compared to amorphous film, the poly crystalline films have low refractive index and high transparency. [7] A. Hakeem et al. operated the effect of vacuum annealing on optical constants and surface of hafnium oxide (HfO_2) thin film. By electron beam evaporation HfO_2 films were deposited. It was observed that by adding a metallic layer, its reflectivity can be enhanced and used as heat mirror. [8] N. V. Nguyen, et al. studied about the thickness and band gap defects of hafnium oxide. They also discussed these band gap defect states were reduced by addition of silicon. [9] L. Liu et al. worked on the synthesis of rare earth doped Hfo_2 nano tubes and their white light emission process. [10] E. S. Spiga, et al. discussed simulation and experimental study of program efficiency of HfO_2 based charge trapping memories. It was concluded that the charge distribution presented the limited trapping, near the interface with tunnel oxide. [11] It is one of the important types of physical vapor deposition. It is also known as e.beam. By applying high vapor pressure and electron bombardment, material is heated. Then on work-piece, this heated material is deposited by condensation. This process has many applications especially for coating resistor and insulating films on electric components. For scratch resistance, coating lens and filters with anti reflection, this process can also be used.

2. Experimental details

The metal layers were required mainly for high transmittance in visible and high reflection in IR region and good electrical conductivity. Au, Ag and Al show low absorptivity in the visible region and good electrical conductivity. Among these Ag was selected as metal layer in present I/M/I structure. Marienfeld glass (sold lime glass of 3.hydrolytic) was used as substrate to deposit the I/M/I multilayer structures. Before depositing the surface of the substrates were cleaned ultrasonically by acetone and isopropyl alcohol with ratio (3:1) and dried in Ar environment. Films were deposited by using BOS Edward AUTO500 e-beam evaporation system on Marienfeld (commercial) glass by maintaining the substrate temperatures of 30 °C (B1), 100 °C (B2) and 150 °C (B3). Metal layer of ~5nm deposited from pure silver wire (99.98%) and sandwich between two dielectric layers about 10nm of Hafnium oxide (99.98%) by using graphite crucible by e-beam evaporation to form I/M/I structure under vacuum 10^{-5} mbar. Films thickness was monitored by calibrated quartz crystals monitor (Edward FTM7). The surface morphology and structural analysis of the films was measured by the Agilent 5100 atomic force microscopy in tapping mode and X-rays diffractometer (PANalytical X'pert PRO) equipped with Cu $K_\propto$ radiation in 2θ range 20-80. The optical transmittance and reflectance of thin films in the wavelength range 300-3000nm were measured using Perkine Elmer Lambda 9 type UV/Vis/NIR dual beam spectrometer.

3. Results and discussion

At different Substrate temperature i.e. RT, 100 °C and 150 °C, HfO_2 thin multilayer having thickness 20nm was grown on commercial glass substrate. X-ray diffraction (XRD) pattern of B1.com, B4-com and B7-com was shown by Fig. 4.1, 4.2, 4.3 respectively. Pattern of these multilayer's present different peaks. A broader peak exhibits low intensity and amorphous nature while narrow peak presents high intensity and mostly polycrystalline nature of I/M/I structure.

Indexing of diffraction peaks were done by using JCPDS card 06-0318 corresponding to HfO_2 monoclinic structure [space group P21/c [12], JCPDS card 04-0787 Ag and lattice parameters; a=5.12 Å, b=5.18 Å and c=5.25Å.

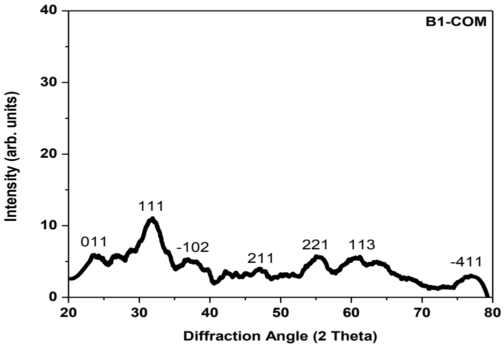

Fig. 1. XRD pattern of HfO2/Ag/HfO$_2$ multilayered films with a scan area of 5 x 5 μm^2 at RT (substrate temperature).

At substrate room temperature for B$_1$.com, peaks shows low intensity and amorphous structure but when substrate temperature increased from 0 °C to 100 °C, narrow peaks were observed which presents polycrystalline I/M/I structure. So the better crystalline behavior was noticed by increasing substrate temperature [13].

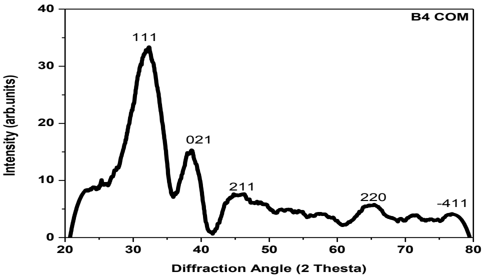

Fig. 2. XRD image of HfO2/Ag/HfO$_2$ multilayered films with a scan area of 5 x 5 μm^2 at 100^{0}C (substrate temperature).

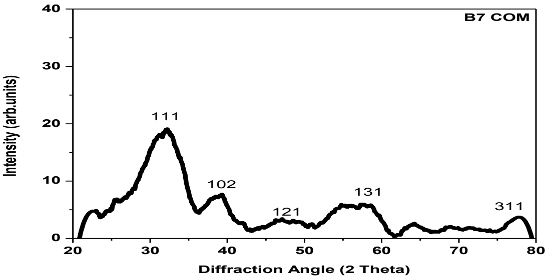

Fig. 3. XRD pattern of HfO2/Ag/HfO$_2$ multilayered films with a scan area of 5 x 5 μm^2 at 150^{0}C (substrate temperature).

While at 150 °C, peaks exhibited intermediate behavior b/w amorphous and polycrystalline nature. Some Ag peaks were also observed. Films produced at various substrate temperature shows preferred orientations along different directions for HfO$_2$. These are shown in Table 2 for B$_1$.com, B$_4$-com and B$_7$-com structure.

Table 1: X-rays diffractions preferred plane of HfO2/ Ag /HfO2 thin films at different substrates temperature

S.NO.	Sample	Substrate (glass)	Substrate Temperature (˚C)	Preferred planes
1	B1-com	Commercial	RT	(011), (111), $(4\bar{1}1)$
2	B4-com	Commercial	100	(111), (021), (211)
3	B7-com	Commercial	150	(111), (102), $(1\bar{3}1)$

By using atomic force microscopy (AFM) technique, morphology of HfO_2 thin multilayer was determined.

Fig 4.4, 4.5 and 4.6 presents two and three dimensional images of (5µm × 5µm) of HfO_2/Ag/HfO_2 thin films. These films were prepared at different substrate temperature i.e. RT, 100 °C and 150 °C respectively, and deposited at commercial glass substrate. These micrographs tell that HfO_2 films do not demonstrate continuous long trenches or splotches, which were revealing of fracture free and pinhole-free face.

For I/M/I films, a granular surface was noticed. The arbitrary distribution of grains in projection and size indicated an arbitrary nucleation method. Arbitrary orientation of grains exhibits identical grain growth [14-15]**.** As set by the polycrystalline diffraction peaks (XRD), these images describe of grains that shows columnar growth with favored preferences.

Table 2. The roughness factors for the HfO_2/ Ag /HfO_2 thin films at various substrate temperature.

Sampli.ID	Roughness average (Ra) Nm	RMS roughness (Rq)Nm	Max.roughness valley depth (R_v) Nm	Max.roughness peak height (R_p)Nm	Kurtosis (R ku) nm	Skewness (R_{sk})Nm	RMS-grain-wise(nm)	Max. height roughness (R_t)Nm
B_1-com	2.64	3.11	8.99	5.23	2.382	-0.477	4.87	14.21
B_4-com	1.51	1.85	4.13	5.10	2.557	0.264	4.61	9.23
B_7-com	3.44	4.33	9.45	12.01	3.223	0.287	5.o4	21.46

The increase in substrate temperature is very useful for changing solid from amorphous to polycrystalline phase and very helpful for optical applications especially in energy efficient windows, heat mirrors etc. The root mean square surface (RMS) tells about light scattering and quality of surface under discussion. By applying Gwyddion software, measurements of roughness of AFM data have been studied as listed in table 2. Mean height as calculated over the complete measured length/area can be calculated by average roughness (Ra) [8]. It shows 2.64nm, 1.51nm and 3.44nm (Ra) for thin films prepared at RT, 100 °C and 150 ºC respectively. The values of surface roughness for HfO_2 multilayer thin films were 3.11nm, 1.85nm and 4.33nm. Peaks dominancy on the surface has been observed by low value of skewness (R_{sk} = from -0.477 to o.264 nm) , But the kurtosis (R_{ku}) value presents that division of grains over the scanned area has comparatively few high peaks and low valleys which intend a rough surface[16]

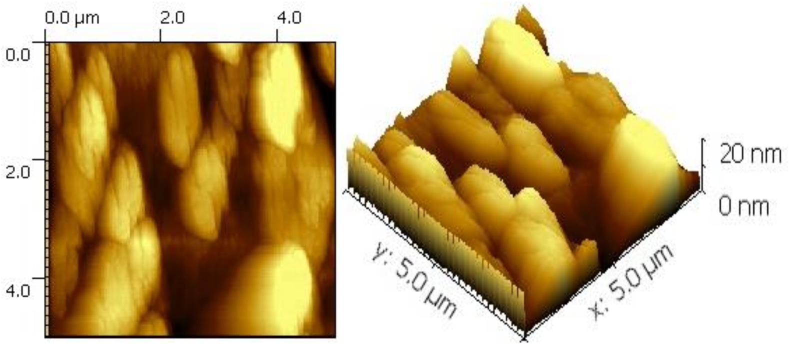

Fig. 4. Two- and three-dimensional AFM images of HfO_2/Ag/HfO_2 multilayered films with a scan area of (5μm × 5μm) at RT (substrate temperature).

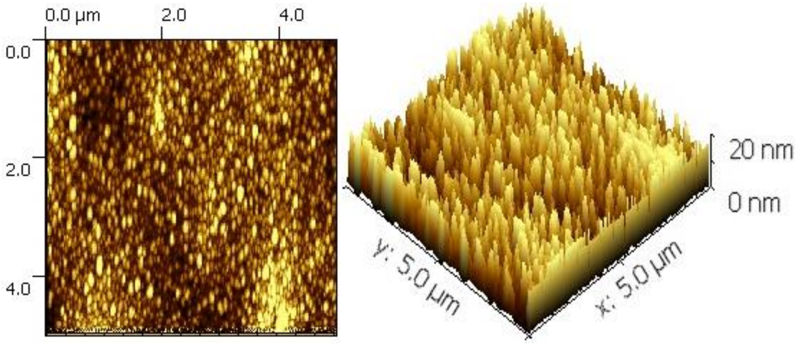

Fig. 5. Two- and three-dimensional AFM images of HfO_2/Ag/HfO_2 multilayered films with a scan area of 5μm × 5μm at 100 °C substrate temperature

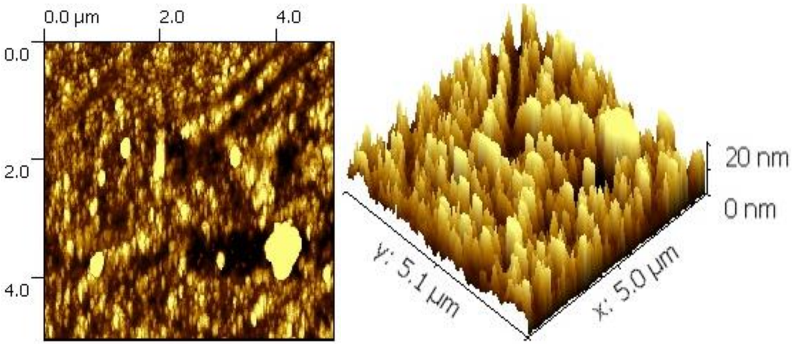

Fig. 6. Two- and three-dimensional AFM images of HfO_2/Ag/HfO_2 multilayered films at 150 °C substrate temperature.

For energy efficient applications and opto-electronics, Study of optical properties such as transmission, reflection is very important. To examine the optical properties of HfO_2 /Ag /HfO_2 multilayer thin films, UV-VIS-NIR spectrophotometer (Perkin Elmer Lambda 9) with UV-Win Lab software was used.

We plot a graph between %transmittance and wavelength for HfO_2 thin multilayer prepared at different substrate temperature i.e. RT, 100 °C and 150 °C respectively. Visible region is weakly transmitted for all three devices. But when wavelength increases from 500nm to 1000nm, transmittance shows variation up to 5%. In Near infrared region, transmittance has been improving up to 20%. But it becomes gradually decreasing after 2500 nm. By transmittance spectra, it has been observed that there is no any inter band electronic transition from valance to conduction bonds of film due to high level of transmittance in visible and IR region.[8] from graph it is clear that, by increasing substrate temperature, % transmittance has been enhanced. So substrate temperature and transmittance exhibit direct relation with each other.

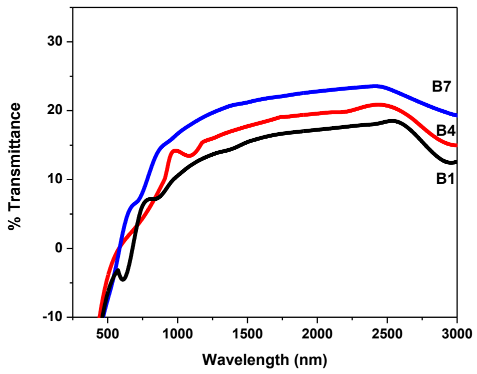

Fig. 7. Spectral transmittance of HfO_2/Ag /HfO_2multilayer thin films deposited at different temperature (substrate temperatures).

I/M/I structures B1, B4, B7 presents negligible reflectance in UV region. It is found to be high in visible region up to 50% at 100^0C temperature. But for HfO_2 multilayer deposited at RT and 150 °C substrate temperature, visible region shows low reflectance up to 20% as compared to 100 °C substrate temperature. May be B4 exhibited this different behavior due to better deposition conditions. Reflectance presents same results as XRD. Where HfO_2 thin multilayer was show maximum intensity at 100 °C substrate temperature.

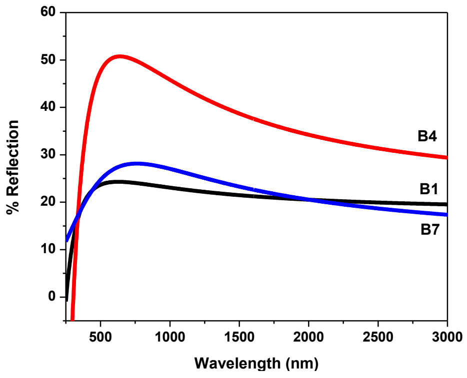

Fig. 8. Spectral reflectance of HfO_2/Ag /$HfO_{2multilayer}$thin films deposited at different temperature (substrate temperatures).

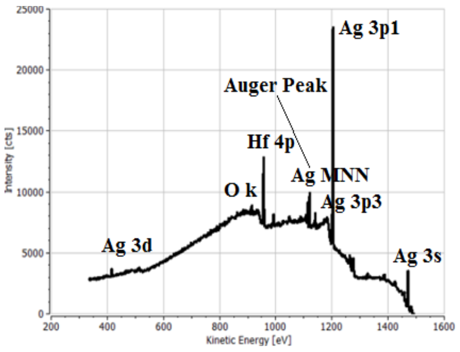

Fig. 9. XPS spectrum of HfO_2–Ag –HfO_2 multi layer films prepared at substrate temperature 100°C.

Silver's malleability and ductility, physical appearance, and value make it a common material in coinage of all metals, silver has the highest electrical and thermal conductivity, but because of silver's high cost, copper is commonly used in electrical application.[9]

Core binding energies are controlled by electrostatic connection amongst it and the core, and diminished by the electrostatic protecting of the atomic charge from every single other electron in the particle (counting valence electrons) expulsion or expansion of electronic charge subsequently of changes in holding will modify the protecting. As binding energy is decreasing with increase in annealing temperature, Hafnium is changing from Ag^{+3} state to Ag^{+2}.

More often than not, the coupling energies of the oxide and the metallic species are isolated by a couple of electron volts. Thus, when the oxide is thin (< 9 nm), it is conceivable to recognize the commitment from both oxide and metal photoelectrons. For silver, oxide thickness (d) is given as: d (nm) = 2.8 ln $((1.4(I_o/I_m))+1)$, where Io and Im are the forces (crest regions) of the oxide and metal photoelectron tops individually. Hence the oxide thickness given by above relation is 2.11 nm [17]. In figure the Ag^{3d} region has well separated spin-orbit components. Peaks have asymmetric peak shape for metal. Loss features are observed to higher binding energy side of each spin-orbit component for Ag metal.

4. Conclusions

Tri-layer $HfO_2/Ag/HfO_2$ multilayer films were fabricated at different substrate temperatures ranging from room temperature 30 °C to 150 °C by e-beam evaporation system. X-rays diffraction analysis showed that by varying the substrate temperature thin films show that some amorphous to poly crystalline behavior. XPS analysis reveals that as binding energy is decreasing with increase in annealing temperature, Hafnium is changing from Ag^{+3} state to Ag^{+2}.

AFM micrographs show the smooth and crack free surface at 100 °C. Optical parameters e.g. band gap energy, refractive index, extinction coefficient etc. of these hafnia nanofilms exhibit oscillatory trends with rising substrate temperature and thermal annealing. It was also observed that there was improvement in reflectance in visible region and transmittance in infrared region. Results correspond with the heat mirror, solar panels and transparent conducting oxide applications.

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