Influence of Annealing Temperature on the Structural and Optical Characteristics of Spin Coated ZrO_2 Thin Films on Glass and ITO Substrates

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Abstract—**Zirconium dioxide (ZrO_2) thin film was prepared on glass and ITO substrate by spin-coating method to study the influence of annealing temperature on the structural and optical properties. The X-ray diffraction (XRD) revealed that the films are polycrystalline in nature with preferred orientation of (111) and (-111) planes. The structural analysis shows that the films are cubic and monoclinic in nature and also verified by the scanning electron microscopy (SEM) images. The crystallite size was calculated using Debye Scherrer's equation. The optical absorbance of the deposited film was recorded using UV-Vis-NIR spectrometry. The optical transmittance spectra indicate an average 80% transmittance in the visible region of spectrum. The optical band gap of deposited film was ranged from 5.35 eV to 5.68 eV. The photoluminescence properties of both ZrO_2 thin films coated on glass and ITO substrates were studied.**

Keywords- Zirconium dioxide thin films; Spin coating method; annealing temperature; X-ray diffraction; Scanning electron microscopy; Photoluminescence; optical properties

I. INTRODUCTION

Thin films materials play a vital role in the development of civilizations based on high technologies. Among different material classes of oxides have various functional electro-physical properties (electro physical, optical etc.), which allows us to use these materials as a basis for synthesis of many film materials. At the present stage of development of photonics, optoinformatics, optotechniques and laser optics, the requirement of optics properties of films extended [1,2]. Zirconium dioxide is being investigated for its future potential applications as an insulator in transistor in nanoelectronic devices [3, 4]. It is also used to replace SiO_2 as the gate dielectric material in metal-oxide-semiconductor devices because of its high dielectric constant (~ 25), good thermal stability on silicon and large band gap (5.6 eV). Zirconia-based ceramics are often used as thermal insulator because of low thermal conductivity (2.2 W/mK) over temperatures ranging from cryogenic to > 1200^{o} C., e.g., for thermal barrier coating (TBC) [5]. Zirconia based thin films have good adhesion to substrates such as glass, ceramics, silicon, sapphire etc., and also high corrosive resistance [6-8]. Zirconium dioxide is the most popular electrolyte material for solid oxide fuel cells and electrochromic devices due to its high ionic conductivity [9]. Zirconium dioxide is used as a thin film coating on the laser facets from degradation and to ensure long-term reliable operation [10]. Zirconium dioxide is non-magnetic and highly resistant against acids and alkaline. Zirconia based thin films have a high mechanical stability and it serves to improve the properties (especially the scratch resistance) of varnishes and coatings applied as top coats to automobiles.

Zirconium dioxide thin film can be prepared by a wide variety of techniques including sputtering[11], chemical vapor deposition[12], sol-gel process[13], spray deposition and e-beam evaporation[14]. Every method has its own advantages and disadvantages. Spin coating is a fast, easy and cost effective method to generate homogeneous thin films. In this study, we have investigated the influence of annealing temperature on the structural and optical characteristics of spin coated ZrO_2 thin film on glass and ITO substrates.

II. EXPERIMENTAL

ZrO_2 thin film was prepared from the film-forming solutions (FFSs). The FFSs was prepared from 99.9% ethanol (Changshu Yanguan Chemical, China) and Zirconium Oxychloride $ZrOCl_2.8H_2O$ (98.0% Loba Chemie); of solution concentration 0.1mol/L. The solution was stirred at 40^{o}C for 3 hrs using magnetic stirrer to yield clear and homogeneous solution. Then the solution was allowed for aging at room temperature for one day before used for coating process. Formation of hydroxo complexes $[Zr(OH)_8\ (C_2H_5OH)\ (H_2O)_{16-x}]Cl_8$; as a result, a stable sol is formed in the solution.

$$ZrOCl_2.\ 8H_2O + C_2H_5OH \longrightarrow [Zr\ (OH)_8\ (C_2H_5OH)\ (H_2O)_{16-x}]Cl_8$$

When the solution is applied on the substrate, chloride ions remain in the solution and are not contained in the thin FFS layer on the substrate surface. The solution is anchored to the substrate via the interaction of zirconium hydroxo complexes with the surface hydroxide group. Schematically, subsequent dehydration in a thin layer can be represented as follows [15],

$$[Zr(OH)_2\,(C_2H_5OH)_x\,(H_2O)_{4x}](OH)_2 \longrightarrow Zr(OH)_4.\,H_2O \longrightarrow$$

$$\longrightarrow ZrO_2.H_2O \xrightarrow{200^oC} ZrO_{2\,(amorphous)} \xrightarrow{400^oC} ZrO_{2\,(cubic)}$$

Glass substrate which was used for deposition were sonicated in dilute *HCl* for five minutes and then rinsed with acetone and wash with distilled water. The glass substrate was kept in hot air oven for 3 hrs at 70^{o}C to make it completely dry. The prepared solution was dropped onto glass and ITO (Sigma Aldrich) substrate which was rotated at 1000 rpm for 30 seconds, 3000 rpm for 50 seconds and 1000 rpm for 30 seconds using spin coater. After each coating (consists of three steps), the film was dried at 200^{o}C for 2 minutes to remove the organic residuals. At 200^{o}C, the film is amorphous in nature. The process was repeated for 10 times to get the desired thickness. The film was annealed in air at 300^{o}C, 400^{o}C and 500^{o}C for 1 hr.

The structure of pure ZrO_2 film was analyzed by X-ray diffractometry (SHIMADZU-XRD 6000) with Cu K_a radiation and Scanning Electron Microscopy (JEOL-JSM-5610LV). The optical absorbance of all ZrO_2 films annealed at 300^{o}C, 400^{o}C and 500^{o}C temperatures were measured at room temperature using UV-Vis-NIR spectrometer (JASCO).

III. RESULT AND DISCUSSION

A. Structural Characterization

The X-ray diffraction measurement is carried out in order to investigate the crystallization behavior of ZrO_2 thin films as the function of annealing temperature. Fig. 1(a) shows the XRD pattern of ZrO_2 thin films prepared on glass substrate and annealed at different temperature (300^{o}C, 400^{o}C and 500^{o}C). From the XRD pattern shown in Fig. 1(a), it is observed that the films are polycrystalline in nature. As the annealing temperature increases from 300^{o}C to 400^{o}C, the intensity of preferred (111) and (200) planes increases and the other peaks almost disappear; which indicate cubic structure (JCPDS 89-9069) of the film. The crystalline of the film increases as the (111) peak intensity increases with increase in annealing temperature from 300^{o}C to 400^{o}C. Again, when further increase in annealing temperature to 500^{o}C, phase transition from cubic to monoclinic structure (JCPDS 65-1022) with preferred orientation of (-111) plane of the film is observed. This is due to the increase in crystallinity of the samples which is the influence of annealing temperature on the film. Fig 1(b) shows the XRD pattern of ZrO_2 coated on ITO substrate, which revealed a monolayer cubic structure of ZrO_2 layer thin film is formed with preferred orientation of (111) plane (JCPDS 89-9069) . As the annealing temperature further increased to 400^{o}C, the intensity of (111) planes has increased as compare to the sample annealed at 300^{o}C; which shows improving crystallinity of the film. As we furthermore increase the annealing temperature to 500^{o}C, the intensity of the preferred (111) plane getting reduced and the peak at 2θ value 28.2185 of (-111) plane came to the picture. This may be the mixed phase of cubic and monoclinic structures which is the influence of annealing temperature to the samples. The grain size 'D' of the crystallites has been calculated using Debye Scherrer's formula [16],

$$D = k\lambda/\beta\cos\theta \qquad (1)$$

where $k = 0.9$ is the Scherrer constant, λ=0.15405 nm is the X-ray wavelength, β is the peak width of half maximum and θ is the Bragg's diffraction angle. The dislocation density δ which represents the amount of defects in the film was determined using the formula [17],

$$\delta = 1/D^2 \qquad (2)$$

TABLE 1**:** Grain size and dislocation density of ZrO_2 thin films coated on glass and ITO and annealed at different temperatures

Annealing Temperature (°C)	**Grain size (nm)**		**Dislocation Density (δ) × 10^{15}(lines/m^2)**	
	ZrO_2: Glass	***ZrO_2: ITO***	***ZrO_2: Glass***	***ZrO_2: ITO***
300	19.16	2.32	2.72	0.019
400	24.74	21.19	1.63	2.23
500	25.83	13.79	1.50	5.26

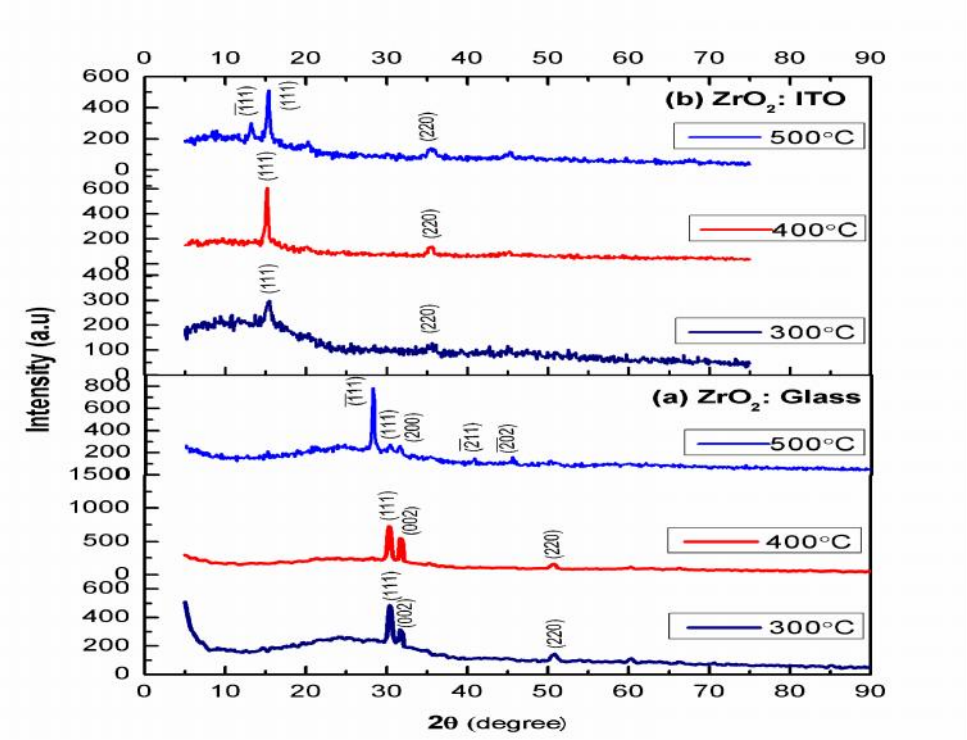

Figure 1. XRD spectra of ZrO_2 thin films coated on (a) glass, (b) ITO substrates and annealed at different temperatures

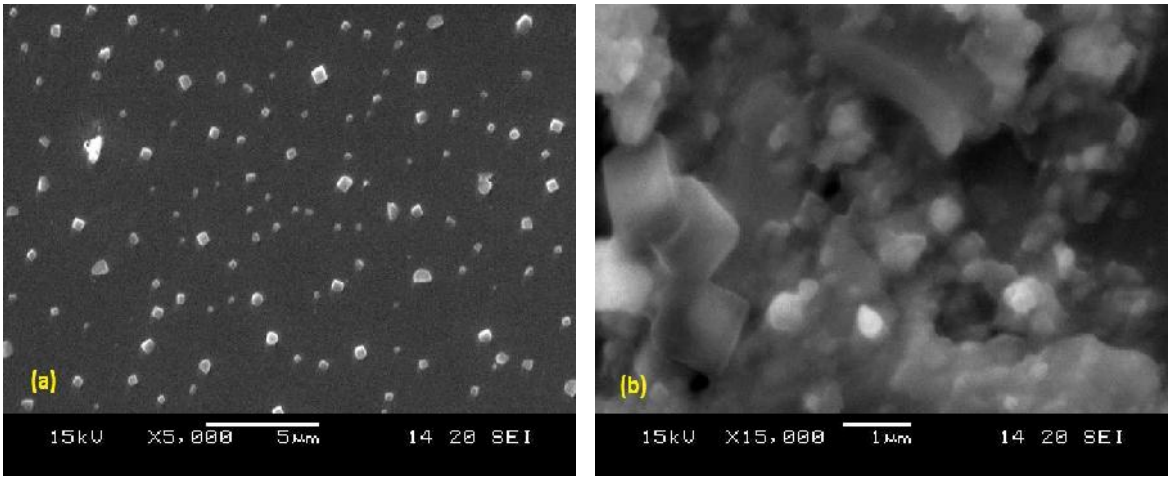

Figure 2. SEM image of ZrO_2 thin films coated on (a) glass and (b) ITO substrates

Fig. 2 shows the Scanning Electron Microscopy (SEM) of ZrO_2 thin film coated on glass and ITO, to inspect the rough morphology, particle size and distribution of particles on the surface of film. From Fig 2(a, b) it is seen that the particles are cubic in shape. Also, it is observed that the particles size increases with increase in annealing temperature which correlated with Table 1 of the XRD result.

B. Optical Properties

The variance of absorbance (A) as a function of wavelength (ranged 200-900 nm) of ZrO_2 thin films on glass and ITO substrates was recorded using UV-Vis-NIR spectrometer and is shown in Fig. 3. From Fig. 3(a), the absorption edge of ZrO_2 thin film on glass substrate is shifted towards the lower region of the visible light when annealing temperature increases from 300°C to 500°C. Similarly in Fig. 3(b), the absorption edge of ZrO_2 thin film on ITO substrate is also shifted towards the lower region of the visible light when annealing temperature is increases from 300°C to 500°C. But, absorption edge shift is found to be very less as compare to the shift made in ZrO_2 thin film on glass substrate which may be the effect of ITO substrate.

From the theory of optical absorption, the absorption coefficient of the films is calculated using the expression [19],

$$\alpha = 2.303A/t \qquad (3)$$

where, A is the absorbance and t is the thickness of film.

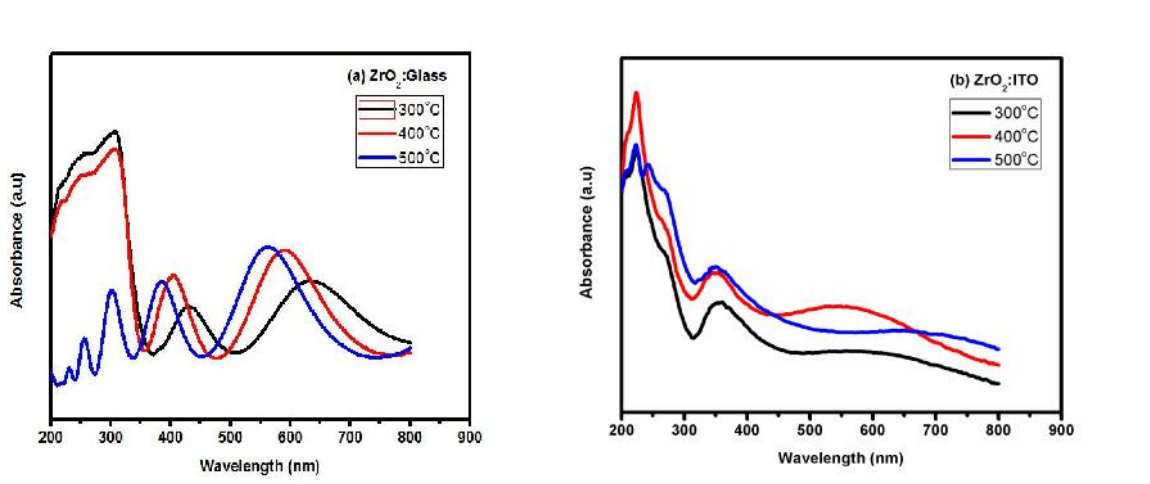

Figure 3. UV-Vis Absorption spectra of (a) ZrO_2: Glass and (b) ZrO_2: ITO thin film annealed at different temperatures

The absorption coefficient α and the extinction coefficient *k* are related by the formula,

$$k = \alpha\lambda/4\pi \qquad (4)$$

The Optical energy gap E_g and absorption coefficient α are related by the equation

$$(\alpha h\nu)^n = k(h\nu - E_g) \qquad (5)$$

where, *k* is a constant, *h* is Planck's constant, *hν* is the incident photon energy and n is a number which characterizes the nature of electronic transition between valence band and conduction band. For direct allowed transition, n=2 and n=1/2 for indirect transition.

A plot of $(\alpha h\nu)^n$ versus *hν*, then extrapolated the straight line portion of $(\alpha h\nu)^2$ to the *x*-axis at α=0. The intercepts on the x-axis will give the energy band gap (E_g) which is shown in Fig. 3.

From Fig. 4 (a-c), the direct energy band gap of the ZrO_2 film coated on glass substrate annealed at different temperature was found to be 5.35 eV at 300°C, 5.41 eV at 400°C and 5.68 eV at 500°C. Similarly, in Fig. 4(d-f), the direct energy band gap of the ZrO_2 film coated on ITO substrate annealed at different temperature was found to be 5.43 eV at 300°C, 5.48 eV at 400°C and 5.44 eV at 500°C.

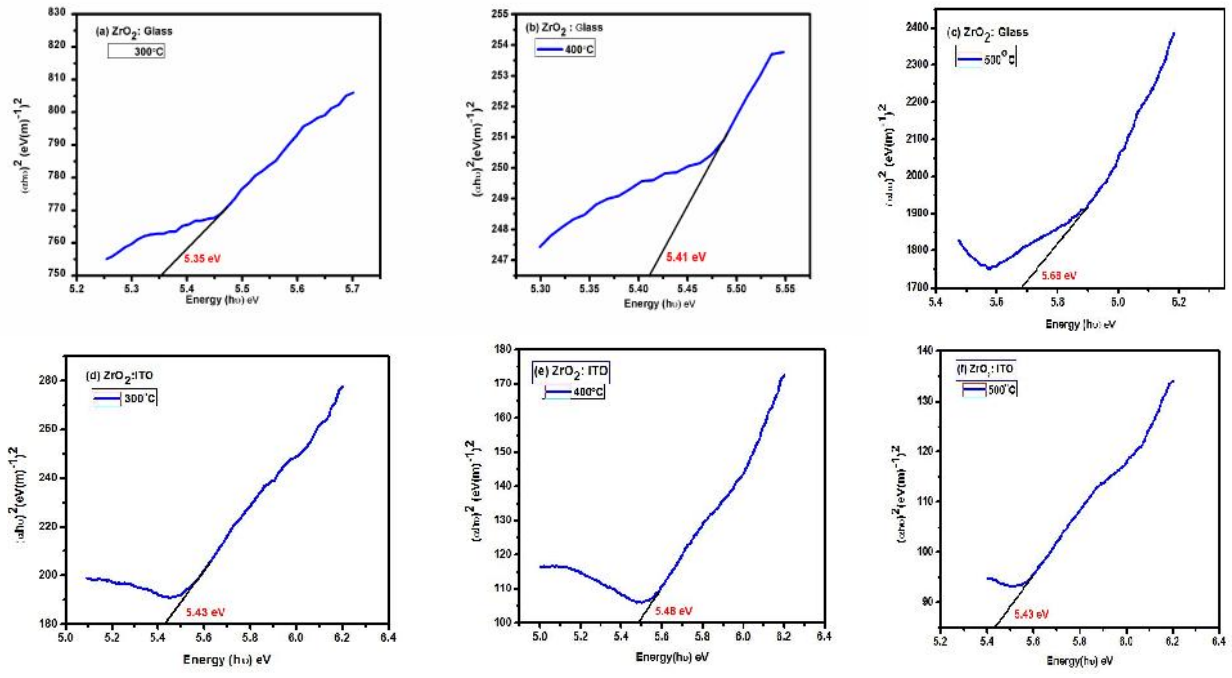

Figure 4. Tauc plot of ZrO_2 thin film on glass and ITO substrate annealed at different temperatures

Photoluminescence (PL) spectra of ZrO_2 thin films on glass and ITO substrates were measured at room temperature. The spectrum of pure ZrO_2 on glass substrate exhibits three emission peaks as shown in the Fig 4(a). The spectrum exhibits near band edge emission peaks at 237.93 nm, 239.89 nm, and 240.15 nm, for the samples annealed at 300°C, 400°C and 500°C respectively. The highly intense zirconium peaks at 445.405 nm, 444.34 nm and 445.402 nm in the ZrO_2 thin film annealed at 300°C, 400°C and 500°C respectively, and can be due to the ionized oxygen vacancies (F-centre) from the conduction band. It was also observed that the intensity of the PL bands gradually increases with the increase in annealing temperature from 300°C to 500°C. Pure ZrO_2 shows relatively high blue emission at 445.405 nm (2.78 eV), 444.34nm (2.79 eV), 445.402 nm (2.806 eV) for different samples annealed at 300°C, 400°C and 500°C respectively.

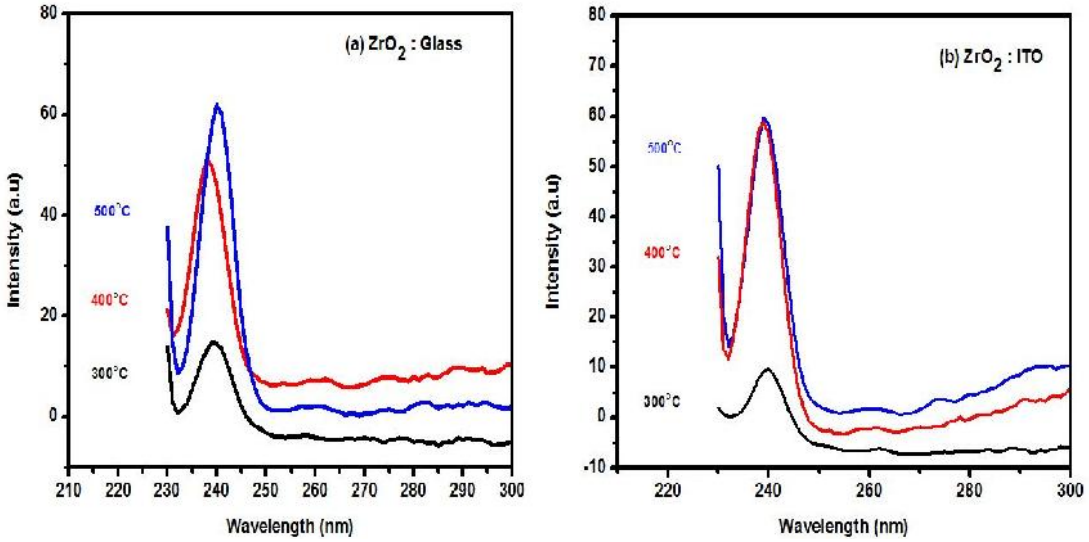

Figure 4. Photoluminescence spectra of (a) ZrO_2: Glass and (b) ZrO_2: ITO, thin films annealed at different temperatures for 1 hour

From Fig. 4(b), the PL spectra of ZrO_2 thin film coated on ITO substrate are almost similar as that of ZrO_2 thin film on glass substrate. The spectrum of pure ZrO_2 exhibits band edge emission peaks at 239.09 nm, 238.92 nm, 239.63 nm, for the samples annealed 300°C, 400°C and 500°C respectively. The highly intense zirconium peaks are observed at 443.98 nm, 444.29 nm and 443.80 nm in the ZrO_2 thin film annealed at different temperature and can be due to the ionized oxygen vacancies (F-centre) from the conduction band. It was found that there is less influence of the presence of Indium or Tin on ZrO_2/ITO thin film.

IV. CONCLUSION

Zirconium dioxide (ZrO_2) thin films having grain size of nanoscale were successfully deposited on glass and ITO substrates by spin coating technique and annealed at different temperatures ranged from 300°C to 500°C. The structural and optical properties of ZrO_2 coated on glass and ITO substrates were investigated successfully. The XRD measurement shows that the crystallization improves with increase in annealing temperature for the film coated on glass and ITO substrates. ZrO_2/glass thin film annealed at 300°C and 400°C shows cubic structure but as the annealing temperature ~ 500°C, shows phase change to monoclinic structure which was revealed by the SEM images. The XRD measurement of ZrO_2 coated on ITO substrate revealed that the formation of a monolayer of ZrO_2 thin film with preferred (111) plane on ITO substrate. The intensity of (111) plane increased with increase in annealing temperature. But some peaks are visible if the annealing temperature is further increase to 500°C. This may be the change in the phase from cubic to monoclinic structure as it happened in ZrO_2 coated on glass substrate. All the samples show good absorption in visible region at some particular wavelength with also good amount of transmittance were also observed on increasing annealing temperature. The PL properties of both ZrO_2 thin films on glass and ITO substrates were studied and found that emission peak increases with the increased in annealing temperature. The band gap was calculated and found at the range from 5.35 eV to 5.68 eV, which could be used as insulating layers in electronic applications.

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