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Synthesis and characterization of Nanocrystalline HfO_2

Taur SM

Department of Physics, Bharatiya Jain Sanghatana's Arts, Science and Commerce Collage, Wagholi.
Tal- Haveli, Dist- Pune, Maharashtra, India
E mail: shaileshtaur@gmail.com

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ABSTRACT

Nanostructured materials are materials consisting of nanoparticles building blocks on the scale of nanometers (i.e. 10^{-9} m). Composition, crystallinity and morphology can enhance or even induce new properties of the materials, which are desirable for todays and future technological applications. In this work, we have shown new strategies to synthesis metal oxide and metal nitride nanomaterials. The first part of the work deals with the study of synthesis of metal oxide nanoparticles. The optical properties of nanocrystalline HfO2 synthesized using a Sol-gel method. Nanocrystalline hafnium oxide having particle size of the order 10–15 nm were obtained in the present method. The nanopowder was characterized using UV-Spectroscopy X-ray diffraction studies. All these studies confirm that the phase formation is complete in the combustion synthesis and monoclinic phase [P21/a(14)] of HfO2 is obtained without the presence of any impurities or additional phases. The optical constants such as refractive index ,extinction coefficient, optical conductivity and the band gap were estimated from UV–vis spectroscopic techniques. The band gap of nanocrystalline $HfO_2$was found to be 5.1 eV.

Keywords: Band Gap, Nanocrystalline HfO_2, UV–vis, etc.

INTRODUCTION

Hafnium oxide (HfO_2) is an important ceramic material due to It's high dielectric constant (εr~ 30), high melting point (2758^{O}C) and greater chemical stability [1]. HfO_2 and its solid solutions with SiO_2 are promising replacements for SiO_2 for their potential applications as gate dielectrics [2]. Recently the optical applications of HfO_2 are gaining wide spread interest. Due to its transparency over a wide range from ultraviolet to mid-infrared, it is used as materials for heat resistant, reflective and protective optical coating [3–5]. HfO2found promising optical coating applications such as filters, beam splitters, anti-reflection coating, high reflectivity mirrors, etc. [6,7].

METHODOLOGY

Firstly, 1 mol of citric acid (CA) was dissolved in distilled water, followed by the addition of the corresponding amount of $HfCl_4$. After complete dissolution 4 mol of ethylene glycol (EG) was added. This process is carried out at room temperature. Next, the solution was heated at ~90 °C under stirring conditions to remove excess water and to accelerate polyesterification reactions. This treatment produced a viscous material that became a semi-transparent glassy resin upon cooling. In order to obtain the HfO_2 nanocrystals, the resin prepared with these methods were heat-treated in a furnace at 500 and 800 °C in air for 2 h.

Table 1 : For variation of parameters in experimental procedure

Citric Acid Concentartion	$HfCl_4$	Ethylene Glycol Concentration	Annealing Temperature
1 mol	0.1 mol	4 mol	500^{o} C
1 mol	0.1 mol	4 mol	800^{o} C

RESULTS AND DISCUSSION

X-ray diffraction Analysis :

Structural characterization was carried out with help of XRD (D8 ADVANCED Bruker). Figure shows the XRD pattern of sample annealed at 500^{0} C and 800^{0} C synthesized by sol-gel method. The crystal structure, size and orientation of the nanocrystalline HfO_2 were investigated with XRD diffraction pattern. All the diffraction peaks are exactly matches to standard JCPDS (***34-0104)*** data. So it is confirmed that formation of HfO_2 takes place . It is observed that the crystalline nature was obtained for HfO_2 and complete monoclinic phase transformation (reference JCPDS card number: 34-0104). The intensity of the two strong diffraction peaks located at 2θ = 28.47 and 31.84 (Fig. 4) are assigned to the (−111) and (111) planes which reveals that the crystallinity of HfO2 increases with increase in annealing temperature.

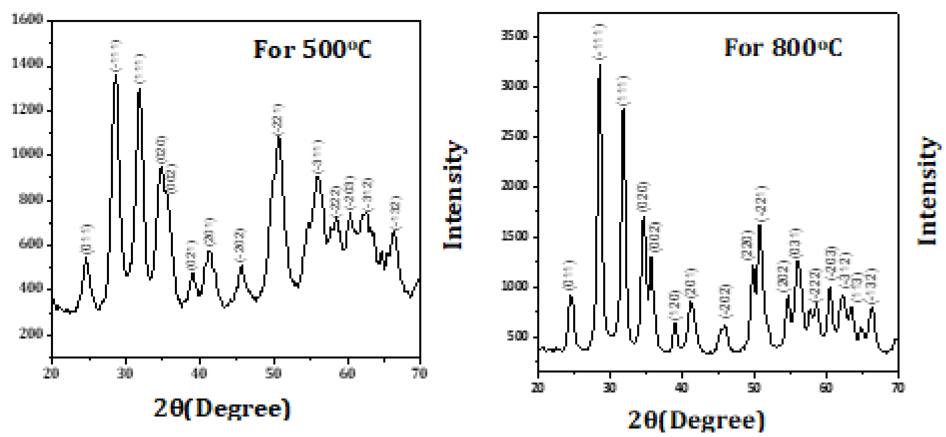

Fig.1 : XRD Pattern of HfO_2 nanocrystals annealed at at 500^{O}C and 800^{O}C

Table 2 : Data for particle size of nanocrystals annealed at 500°C and 800°

θ	*FWHM*	*Size (nm)*	*θ*	*FWHM*	*Size (nm)*
12.28	0.01645	**8.62**	12.28	0.01645	**8.6**
14.25	0.01872	**7.64**	14.27	0.00927	**15.4**
15.91	0.01872	**7.69**	15.91	0.01155	**12**
17.41	0.03027	**4.79**	17.31	0.00715	**15.65**
19.55	0.01715	**8.57**	19.48	0.00702	**20.80**
20.68	0.02331	**6.35**	20.63	0.01645	**21.00**

Optical Analysis :

Optical characterization was carried out with help of UV-VIS absorption spectrometer (JASCO-UV-VIS-NIR spectrometer ; model V-670) . Optical absorption measurements are essential for the understanding of the band gap of material. Figure shows optical absorption spectra of Hafnium Oxide nanocrystals annealed at 500°C and 800°C. Maximum absorption occurred within the UV region from where the absorbance decreased with increase in wavelength. The sudden rise in absorption is observed in UV-region. The absorption spectra shows that for 800°C it is shifted towards the higher wavelength it is due to increase in crystalline size after annealing.

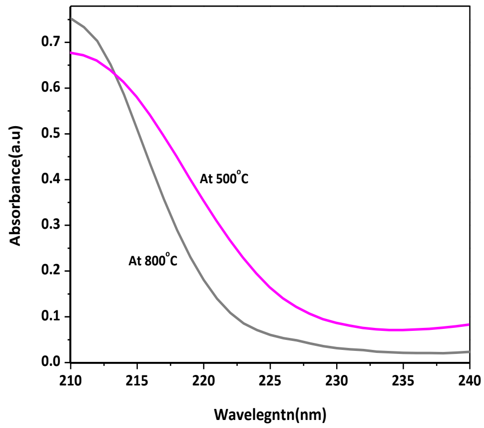

Fig 2: Tauc's plot for HfO_2 nanocrystals annealed at at 500°C and 800°C

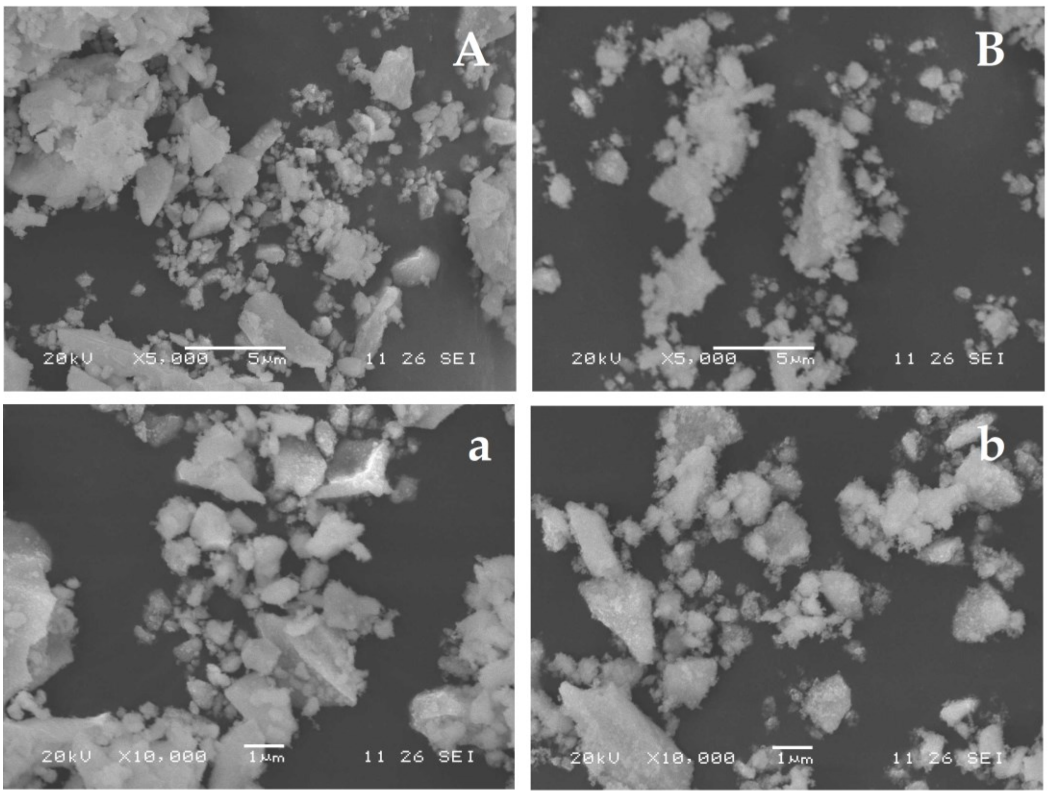

Fig 3 : A & B SEM images of HfO_2 nanocrystals annealed at 500°C and 800°C . **a &** b are corresponding magnified images

The monoclinic HfO_2 structure is reported as an indirect band gap material (9,10,11).The band gap can be obtained from the extrapolation of the straight-line portion of $(\alpha h\nu)^{1/n}$ vs. hv plot . The band gap energy E_g of nanocrystalline HfO_2 was calculated using n=2 and extrapolating the linear portion of curve or tail as shown in fig. The band gap value calculated from Tauc's plot are 5.48 eV and 5 eV for sample annealed at 500°C and 800°C. The obtained result indicating an E_g lower than the reported in the literature (12,13). Comparing the band gap of both samples, it is seen that increase in annealing temperature which predicts a decrease in the width of band hence a decrease in the value of band gap energy Eg. This is due to increase in particle size with increase in annealing temperature .In our study, the band gap value of HfO_2 decreases with increase in the crystalline size . The value of the band gap for our sample is in good agreement with the literature values for HfO_2 nanoparticles obtained by many techniques.

CONCLUSION

- Nanocrystalline HfO_2 can be successfully synthesized by sol-gel method
- XRD confirms the formation of monoclinic structure of Hafnium Oxide (HfO_2).
- After increase in annealing temperature crystallinity of particles increases.
- The average crystalline size was estimated around 7.27 nm and 15.57 nm for nanocrystals annealed at 500°C and 800°C respectively.

- Optical spectra for Hafnium Oxide material shows the Maximum absorption occurred within the UV region.
- The band gap value calculated from Tauc's plot are 5.48eV and 5 eV for both annealed at 500°C and 800°C.
- From band gap of both samples it is observed that band gap energy decreases with increase in annealing temperature. This is due to increase in particle size with increase in annealing temperature.

Conflicts of interest: The authors stated that no conflicts of interest.

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