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Short Communication

SYNTHESIS, STRUCTURAL AND MORPHOLOGICAL CHARACTERIZATION OF HAFNIUM OXIDE NANOPARTICLES

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ABSTRACT

Hafnium oxide nanoparticles were successfully synthesized using hydrothermal method and were characterized by XRD, SEM, HRTEM and Raman spectral techniques. Analysis on XRD and Raman showed the existence of pure HfO_2 nanoparticles in the monoclinic phase. From XRD analysis, the average crystallite size of HfO_2 was found to be 26.31, 28.47 and 31.11 nm with respect to varies temperatures viz., 140,160 and 180°C respectively. The SEM and HRTEM images of the HfO_2 shown that the nanoparticles were appeared as seed like shape of the surface.

Keywords: HfO2, Hydrothermal method, XRD, SEM and HRTEM Techniques

1. INTRODUCTION

The nanoparticles inspired the researchers to develop simple and cost-effective techniques for the development of nanostructure of materials of technological significance. Due to their favorable solid-state and electrochemical properties, the first and third row transition metal oxides tend to be particularly cathode materials were attractive in electrochemical energy storage systems. Most transition metal oxide nanoparticles state with the aspect of their low size, rich abundance, low toxicity and diverse oxidation states [1-3].

The interesting properties make HfO_2 is one of the most effective refractory materials. HfO_2 materials are very promising for improved resolution in immersion lithography, because of their high refractive index. Despite of its strong oxidation properties, the benefits of HfO_2 NPs have been extended to medical applications, such as radiotherapy [4-6].

Hafnium oxide NPs were synthesized by using the hydrothermal, solvothermal microwave and precipitation methods [7, 8]. Considering the importance and potent applications of HfO_2, in this research paper we report the hydrothermal synthesis and the characterization of HfO_2 NPs. The as-prepared HfO_2 NPs were characterized by X-ray diffraction, Raman analytics, scanning electron microscope and high-resolution transmission electron microscopy techniques.

2. MATERIAL AND METHODS

Materials

All the chemicals used in this experiment is analytical quality reagent and they are used without any further step of refining. Hafnium tetrachloride ($HfCl_4$) is brought from sigma Aldrich.

2.1. Synthesis of HfO_2 NPs

The HfO_2 nanoparticles were synthesized by hydrothermal route. The precursor was first prepared by dissolving 0.160 g of $HfCl_4$ into 30 ml of distilled water to form the solution for hafnium hydroxide chloride ($Hf(OH)_2Cl_2$). The aqueous solution of NaOH (3.0 M, 30 ml) had been added drop wise to the above solution, causing the reaction with ($Hf(OH)_2Cl_2$) to form hafnium hydroxide ($Hf(OH)_4$). After that the solution was shifted into a Teflon-lined autoclave and was heated at 140°C, 160°C and 180°C for 24 h and the respective products were alternatively purified with ethanol and water. The resultant precipitate was completely dried at 60°C for 12 h.

3. RESULTS AND DISCUSSION

3.1. XRD analysis

XRD patterns of the pure HfO_2 obtained with different temperatures (140,160 and 180°C) are shown in Fig. 1. In the XRD pattern, it observed that the major diffraction peaks are centered at 2θ = 17.33°, 24.30°, 28.11°, 31.44°, 34.14°, 35.40°, 37.78°, 40.95°, 45.55°, 49.69°, 50.48°, 54.45°, 55.40°, 56.50°, 60.15°

and 62.05° corresponding to the (100), (110), (-111), (111), (200), (020), (021), (121), (112), (022), (220), (300), (221), (130), (131) and (113) planes of HfO_2 respectively. The diffraction peaks are matched to the monoclinic structure of HfO_2 (JCPDS 06-0318). As the temperature decreases, the diffraction peaks become sharper and narrower, indicating the high crystalline nature, as well as the formation of large particles due to the mechanism of grain production. The average crystalline size was calculated as per the following equation:

$$D = n\lambda/\beta\cos\theta$$

Where 'D' is the average crystalline size, 'n' is the scherrer constant (0.9), 'λ' is the incoming X-ray wavelength of Cu-K_α (1.54 Å), 'β' is the full width half maximum and 'θ' is the diffraction angle. The average crystallite size was found to be 26.31, 28.47 and 31.11 nm corresponds to the HfO_2 with the specific temperatures of 140,160 and 180°C respectively.

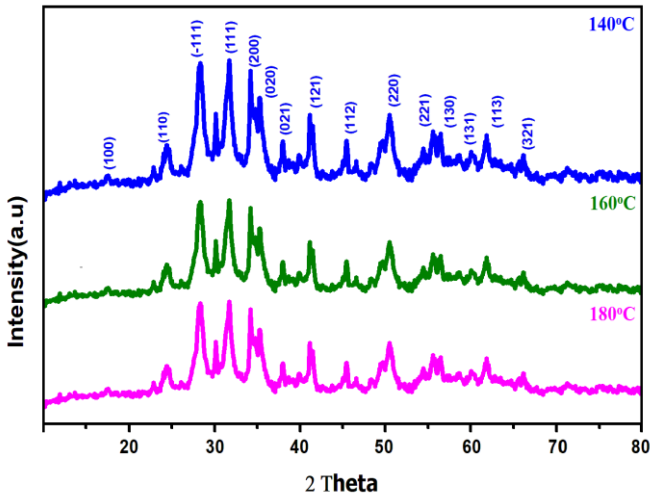

Fig. 1: XRD patterns for HfO_2 nanoparticles

3.2. Raman spectra for HFO_2 NPS

The Raman spectrum of HfO_2 NPs prepared using hydrothermal process is reproduced in Fig. 2. The Raman shifts are mainly due to the heavier metal atom vibrations (Hf-Hf vibrations) and the lighter non-metal ion vibrations of Hf –O or O-O [9]. The peaks observed at 113, 133, 149, 252, 381, 479, 576 and 671 cm^{-1} can be assigned to the A_g modes. The remaining peaks located at 165, 241, 324, 331, 498, 547, 633 and 777 cm^{-1} correspond to the monoclinic HfO_2 B_g modes. The Raman bands observed are in strong agreement with the theoretical values of monoclinic HfO_2 [10].

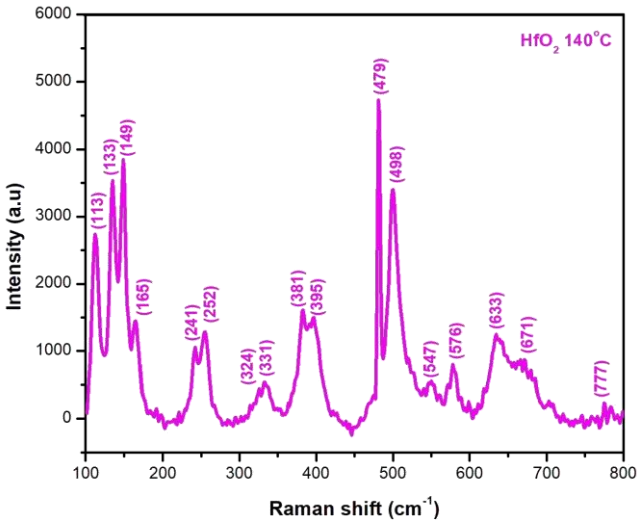

Fig. 2: Raman spectrum of as prepared HfO_2

3.3. Morphological analysis

Fig.3 shows the SEM image of HfO_2 sample. The primitive HfO_2 has a seeds particle agglomerated to sponge like shapes. The HRTEM images of the sample are shown in Fig. 4. The TEM result concluded the agglomerations of large number of seed like shapes (Fig. 4a) and the corresponding electron diffraction pattern (Fig. 4b) for the selected area revealed the existence of ring nature due to the poly-crystalline nature of the crystallites. As shown in Fig. 4c, the fringe patterns represent well crystalline nature of the HfO_2 NPs. The observed distance of the interlayer is about 0.20 nm corresponds to the plane (112), which can be matched with XRD results.

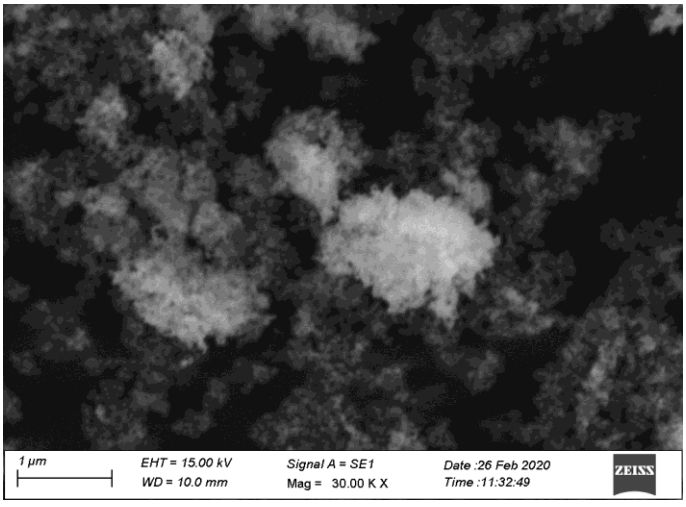

Fig. 3: Surface morphology of HfO_2

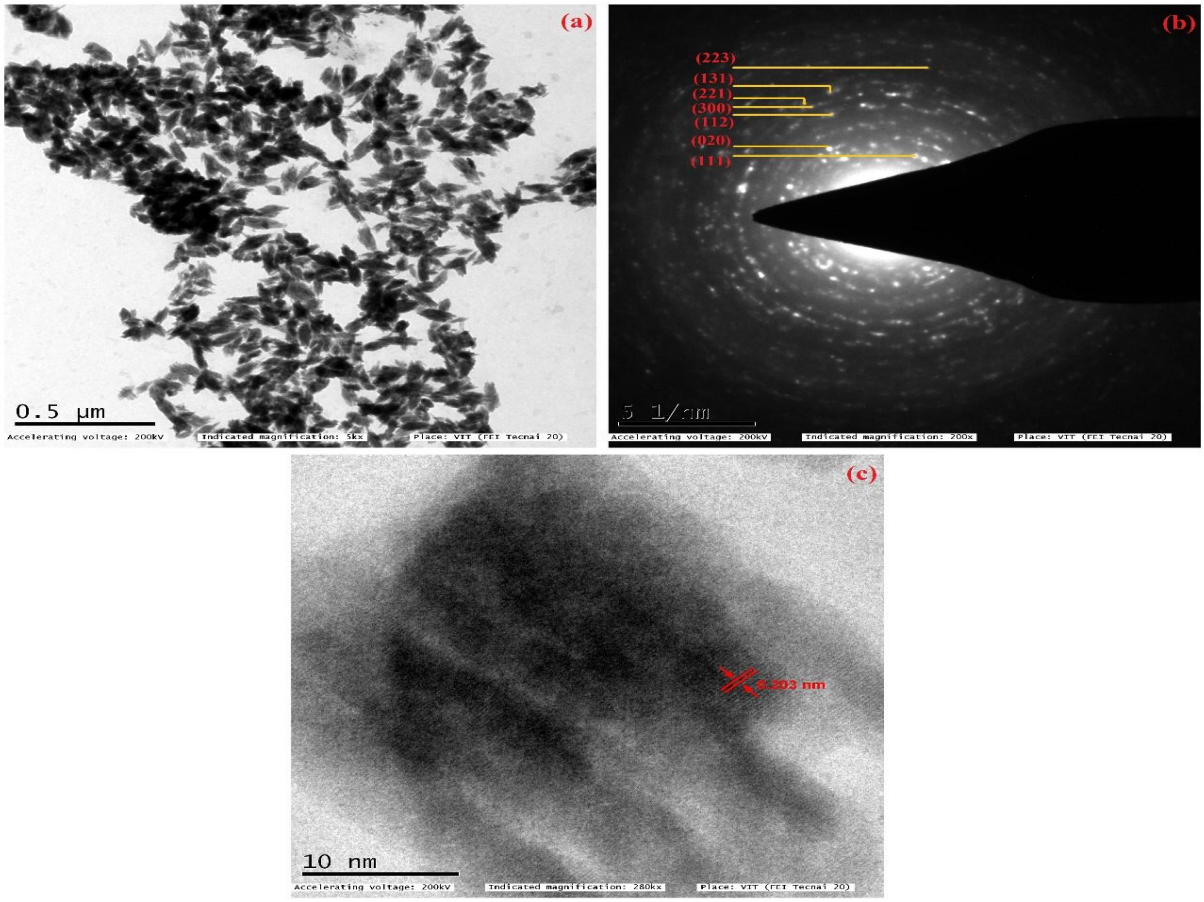

Fig. 4: HRTEM images of (a) HfO_2 (b) SAED pattern of HfO_2 and (c) high resolution image of HfO_2

4. CONCLUSION

In summary, HfO_2 NPs were successfully synthesized using hydrothermal method. The XRD analysis verified that the HfO_2 nanoparticles showed a pure monoclinic phase and were well matched with JCPDS card No. 06-0318. The effect of temperature is effectively influenced the size of the HfO_2 nanomaterials. The Raman shift of the bands are mainly due to the vibration of heavier metal atoms and the peak observed could be assigned to the monoclinic HfO_2 A_g and B_g modes. The Raman bands that were observed are very well agreed with the theoretical monoclinic HfO_2. HRTEM and SEM morphology indicated that the HfO_2 is observed as the seed like particles.

5. REFERENCES

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