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Perturbed angular correlation technique applied for studies of formation hafnon structures of $HfSiO_4$ at different temperatures

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1. Introduction

The idea of substituting high-k metal oxides with ceramic gate dielectrics has sparked interest, especially concerning Hf/Zr-based composites. Hafnium ($HfSiO_4$) and zirconium ($ZrSiO_4$) silicates, for hafnium Also known as hafnon, renowned for their advanced properties such as thermal and chemical stability, have shown potential in various applications, including environmental barrier coatings and matrices for storing radioactive waste [1]. Moreover, they exhibit significant resistance to water vapor corrosion [2]. Additionally, these materials possess a high dielectric constant, making them primary candidates to serve as gate dielectrics [3].The formation of tetragonal-phase $HfSiO_4$ ($ZrSiO_4$) involves blending precursor oxides HfO_2 (ZrO_2) and SiO_2 in equimolecular proportions. Traditionally, tetragonal phase formation occurs in the temperature range of 1400 – 1500°C. In this study, however, we introduce an alternative method for synthesizing hafnon-like structures at significantly lower temperatures ($T \sim 900$°C). Understanding the roles of Si in the reaction of HfO2 powder with the quartz requires a multielement study of composite particles, as well as high-accuracy detection of element concentrations. We have investigated the effect of the HfO2 with Si by measuring hyperfine interactions at ^{181}Ta probe nuclei on Hf sites using the perturbed γ–γ angular correlations (PAC) spectroscopy. The structural analysis was carried out by X-ray diffraction (XRD) technique.

2. Methodology

2.1 Sample preparation

The preparation of HfO_2 nanoparticles was conducted using the sol-gel method, chosen for its cost-effectiveness and the ease with which particle size can be controlled. Resulting in a powder that was annealed at 700 °C and 900 °C in a quartz tube under vacuum for 14 hours.

2.2 X-ray diffraction characterization (XRD)

X-ray diffraction (XRD) analysis was utilized to investigate the phase composition of the synthesized and annealed samples. The measurements were conducted using a Bruker D8 Advance 3kW diffractometer at the Multiuser X-ray Diffraction Laboratory (IPEN-CNEN, Brazil). The obtained XRD patterns were subsequently refined using Rietica software.

2.3 Perturbed γ–γ angular correlations (PAC)

The PAC method is based on the hyperfine interaction of nuclear moments with extra nuclear magnetic fields or electric field gradients (EFGs). In the case of electric quadrupolar interaction (Q), the experimental measurement gives the quadrupolar frequency (ν_Q) with respective distribution δ as well as the asymmetry parameter (η).This method needs a probe nuclear decay with γ-γ cascade with a half-life of nanoseconds a detailed description of this method can be found in literature [4] For Hf compounds, the ^{181}Hf → ^{181}Ta probe activity was generated through neutron activation. The ratio of these coincidence spectra provides the spin-rotation function R(t) described in the equation 1.

$$R(t)=A_{22}G_{22}(t)=\sum f_i G_{22}^{i}(t) \qquad (1)$$

The $G_{22}(t)$ is the perturbation function which describes the time modulation of the angular correlation, the term G_{22} provides the hyperfine parameters of the structure.

3. Results and Discussion

Figure 1 shows the diffractogram the powder after 550 °C calcination and after annealed 700 °C at 900 °C in a quartz tube for 14h. The diffractograms clearly reflect structural evolution; the nucleation of hafnon ($HfSiO_4$) phase in the samples annealed in quartz is accompanied by a strong suppression of the monoclinic phase of hafnia (m-HfO_2)

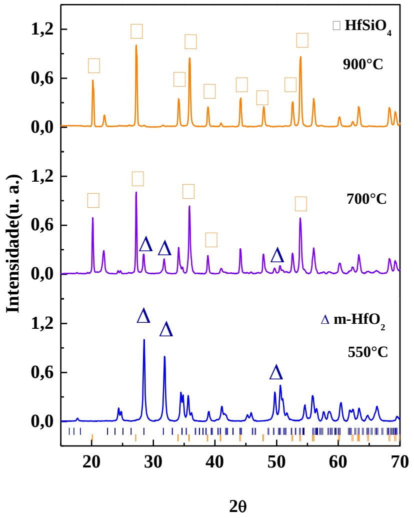

Figure 1: XRD patterns of HfO2 after 550 °C calcination, 14h annealing at 700 °C and 900 °C in direct contact with quartz.

The PAC spectra were fitted with thee sites at temperatures ranging from 200 °C - 900 °C. As illustrated in Figure 1, the introduction of Si into the crystalline structure of HfO2 occurs at 700 °C, leading to alterations in its structure. This phenomenon is also evident in the PAC spectra as show in figure 2, where the structural transition is observed at 900 °C, with a major fraction (~65%) exhibiting a well-defined ν_Q, indicating a tetragonal structure and showing η = 0.

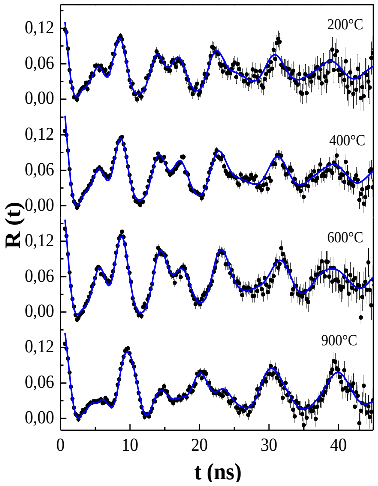

Figure 2: Spin-rotation spectra measured whit ^{181}Ta probe nuclei and the measurements were carried out in a temperature range of 200°C – 900 °C.

4. Conclusions

A sol-gel methodology employed for hafnium oxide production is favorable for hafnon formation, given that the particles are in the nanometer range. The temperature used for hafnon production is typically around 1400°C, whereas our methodology allows for a lower temperature of 900°C. Due to the nanoparticle's contact with the quartz wall, composed of silicon (Si), Si atoms seamlessly integrate into the crystalline structure of HfO_2 with minimal formation energy. To comprehend the hafnon formation process, it will be necessary to analyze other characterization techniques such as transmission electron microscopy (TEM).

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