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EFFECT OF SILICON DOPING IN HFO_2 NANOPARTICLES FROM AN ATOMIC VIEW

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ABSTRACT

We have prepared the Hafnium Oxide (HfO_2) nanoparticles (NPs) doped with 5% at. of silicon (Si) using the sol-gel chemical method. Nuclear quadrupole interactions at Hf sites were investigated by perturbed γ–γ angular correlations (PAC) spectroscopy using ^{181}Ta as probe nuclei. This method is based on the hyperfine interactions between the nuclear moments of the probe nuclei with extra-nuclear magnetic fields or electric field gradients (EFGs). In the case of quadrupolar electric interactions, experimental measurements give the quadrupole frequency ν_Q with respective distribution (δ) as well as the asymmetry parameter η of the EFG. The hyperfine parameters were measured within the range from 200°C to 900°C. The structural and morphological characterization of the samples were carried out by X-ray diffraction and scanning electron microscopy (SEM) with electron back scattering diffraction (EBSD). PAC results show a major site fraction of probe nuclei, that was assigned to the monoclinic phase of HfO2, with approximately 60% population, which increases when the temperature of heat treatment increases. The XRD results showed a single phase with the expected monoclinic structure for the as-prepared samples indicating that Si atoms are at substitutional Hf sites.

1. INTRODUCTION

Nanostructured materials have a huge potential for new applications by exploring the significantly different properties when compared to those for bulk [1] that nanoparticles (NPs) and thin film exhibit. NPs can then be applied in areas as different as electrics [2], medicine [3], solar cell [4] and microelectronic circuits [5]. Due to continuing miniaturization in microelectronics, new materials with good electronic, structural and thermal properties are necessary. The hafnium oxide (HfO_2) also called hafnia, due to its physical properties and chemical stability, have attracted considerable attention in the nanostructured form, due to its great potential for applications in microelectronics [6]. Besides being refractory materials with large refractive index (~2.00) [7] it also has high dielectric constant (~25), and high melting point (3085 K) [8-9]. Due to the high dielectric constant and good thermal stability HfO2 can be one an alternative to replace the SiO_2, mainly because of the thickness limitation for SiO_2 to be used as gate oxide layers [8-10]. The properties of HfO_2 nanoparticles can be enhanced if it is doped with another cation [11-14]. Therefore, a detailed investigation of properties of doped HfO_2 is important to understand the physics of these systems and can be achieved only by

atomic scale studies with direct measurements of the local structure and electronic environment [15].

Perturbed Angular Correlation (PAC) technique provides information about the hyperfine interaction between extra nuclear fields and nuclear moments of the probe nuclei at a certain atomic site in the crystalline structure, and consequently allows extracting information about the involved hyperfine parameters as well as characterization of structural and the magnetic transitions of the crystal. PAC is based on the emission of two gamma radiations in a cascade as a result from the decay of the excited states of the probe nucleus ^{181}Hf (^{181}Ta) [16]. However, properties of nanoparticles depend largely on their synthesis procedures. Sol-gel processing is a versatile method, and simple, and entails a low fabrication cost, and low temperatures of the synthetized, and control of the oxide stoichiometry is easy [7-17]. This method allows control of the chemical composition and particle size and it is based on a polymeric precursor that uses citric acid to chelate the cations and together with ethylene glycol reacts with these chelates, forming one a mixture of the ester with water. Heating the mixture leads to polyesterification forming a gel. The powder is obtained after thermal calcination of the gel. Sol-gel is a suitable method to synthesize and doping nanoparticles, because it exhibits homogeneous mixing.

In this work, we have synthesized doped hafnium oxide nanoparticles with 5% Si using a sol-gel method, and reported a local investigation on the temperature dependence of the electric quadrupole interaction of the Si doped HfO_2 nanoparticles measured by PAC technique in the temperature range from 200°C to 900°C. Synthesized samples had their structural and morphological properties investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM) with electron back scattering diffraction (EBSD).

2. EXPERIMENTAL PROCEDURE

2.1. Sample preparation

The preparation of HfO_2 NPs doped with Si were synthesizes by sol-gel method, using metallic Hf (99.99 % purity), metallic silicon (99.99 % purity), citric acid and ethylene glycol were taken in stoichiometric proportion to produce initial colloid. The reaction was obtained from mixture of the metal:citric acid by 1:2 and citric acid:ethylene glycol by 40:60 proportions. Metallic Hf was dissolved in hydrofluoric acid (HF) and the metallic Si was dissolved in nitric acid (HNO_3). Both solutions were mixed in a single becker with citric acid under magnetic stirring, heated at 60°C and followed by addition of ethylene glycol. The resulting solution was continuously mixed with magnetic-stirring during 24h at room temperature for homogenization. The sol was heated to ~ 100°C until gel aggregation. After that, the solution was calcined in air at 550°C for 14 hours in order to stimulate the evaporation of organic material. The resulting NPs powder was characterized by XDR, and SEM, and parameters nuclear by PAC. For PAC measurements it is necessary the incorporation of probe nuclei by the samples. This was obtained by the irradiation the sample with neutrons in the IEA-R1 reactor with a neutron flux around 4.0 10^{13} n/cm²-s for a period of 30 minutes since ^{180}Hf

isotopes presenting in the samples capture neutrons and form the radioisotope 181Hf which decays to the probe nuclei ^{181}Ta.

2.2. Characterization techniques

The crystal structure of samples was investigated by X-ray diffraction (XRD) with the resulting patterns being analyzed with the Rietveld refinement method through Rietica software. The crystal shape and distribution of nanoparticle samples were characterized with scanning electron microscopy (SEM) with electron back scattering diffraction (EBSD), and parameters unclears by PAC.

2.2.1. Spectroscopy PAC

The PAC measurements were carried out using a conventional fast-slow coincidence set-up using four conical BaF_2 detectors scintillators Fig.1 with a time resolution of 0.6 ns. Measurements were taken in the temperature range of 200°C–900°C using ^{181}Ta as probe nuclei with samples sealed in an evacuated quartz tube positioned in a compact furnace. The gamma cascade of 133-482 keV, populated in the β^- decay of ^{181}Hf, was used to measure the quadrupole interaction of the 482 keV ($5/2^+$) state of ^{181}Ta. The analysis of the experimental perturbation function R(t) contains information about the probe by the fitted hyperfine interaction parameters, shown in equation 1.

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

Where A_{22} is the angular correlation coefficient, f_i are the site fractions occupied by probe nuclei. The perturbation factor $G_{22}(t)$ of correlation function contains detailed information about the hyperfine interaction. In the case of an electric quadrupole interaction, measurements of $G_{22}(t)$ alloy to determine the quadrupole frequency, $\nu_Q = eQVzz/h$ and the asymmetry parameter, $\eta = (Vxx - Vyy)/Vzz$, where ν_Q is quadrupole moment of the 482 keV state and Vxx, Vyy, and Vzz are the components of the electric field gradient at the probe nuclei sites.

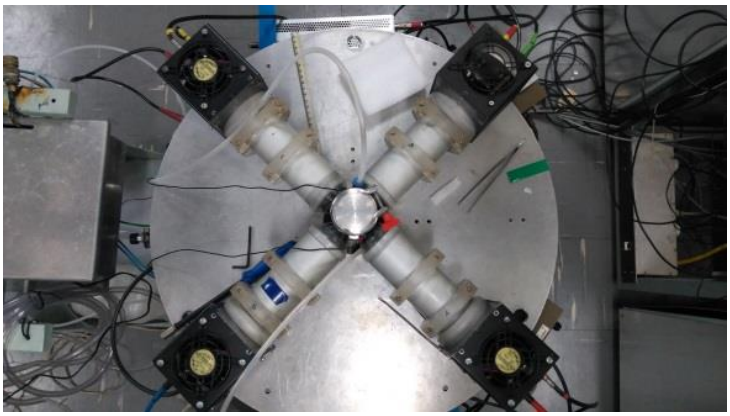

Figure 1: Spectrometer

3. RESULTS AND DISSCUSION

Fig. 2 displays images resulting from the characterization with SEM and EBSD techniques. The results show an agglomeration of particles that adhere together and grow with triangular orientation, as can be seen 2.left. This shape is a result of the synthesis method. The right side of Fig. 2.rith shows a complete picture mapping of the spatial correlation of Si and Hf atoms present in the sample.

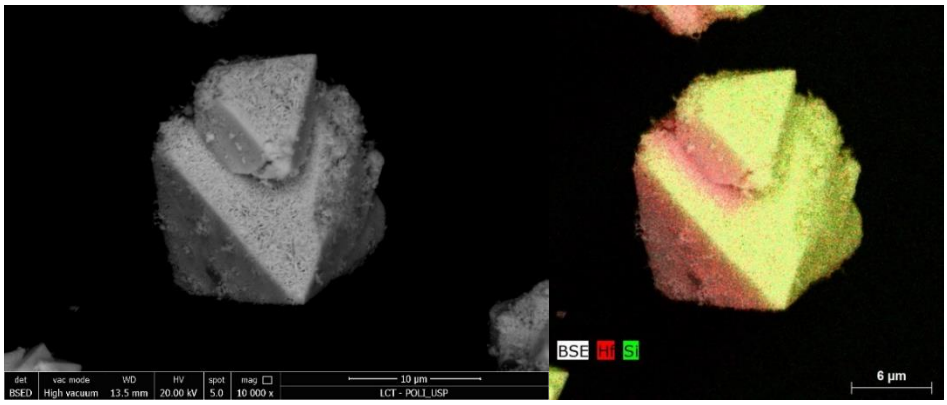

Figure 2: Scanning electron microscopy show the growth (left) and electron backscattering diffraction showing the spatial distribution of Si and Hf doped (right).

Figure 3 shows the X-ray diffraction patterns for HfO2 doped with 5% Si. The results for samples after annealing at 550°C for 14 h exhibit a single phase with the monoclinic structure of HfO2 corresponding to the P21/c space group. Results obtained for the lattice parameters of the sample by a fit based on Rietveld method are shown in table 1. The values are consistent with those found in the literature for pure HfO2, which shows that the expected monoclinic phase was achieved.

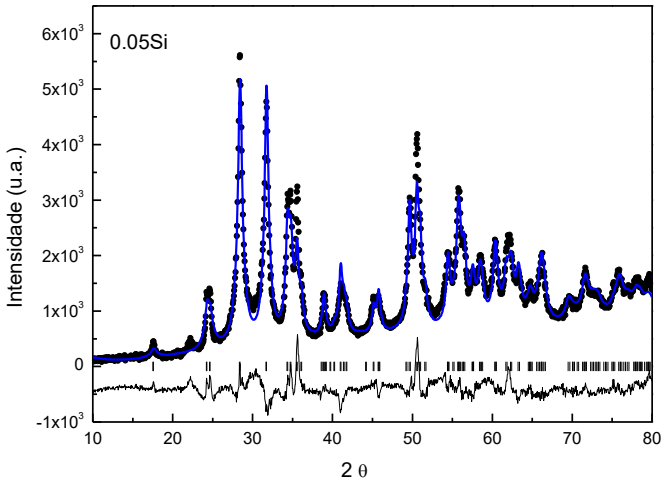

Figure 3: X-ray powder diffraction pattern along with Rietveld refinement (solid curve) for HfO2 doped with 5%Si.

Table 1: Lattice parameters obtained from the fit of the XRD patterns shown in figure 3 using the Rietica software. Values are given in angstroms.

Si concentration	a	b	c	Volume
Literature (0%)[15]	5,1187(4)	5,1693(1)	5,2970(4)	138,36
5%	5,1216(1)	5,1655(1)	5,2934(1)	140.04

From the results in Table 1, one can observe a slight variation in the crystalline parameters, probably due to the introduction of dopant atoms.

Figure 2 displays the spin rotation spectra ($-A_{22}G_{22}(t)$) along with the fit of the theoretical perturbation function $G_{22}(t)$ that describes the electric quadrupole interaction. Spectra were acquired at temperature ranges of 200°C–900°C for HfO_2 sample doped with concentrations of 5% Si.

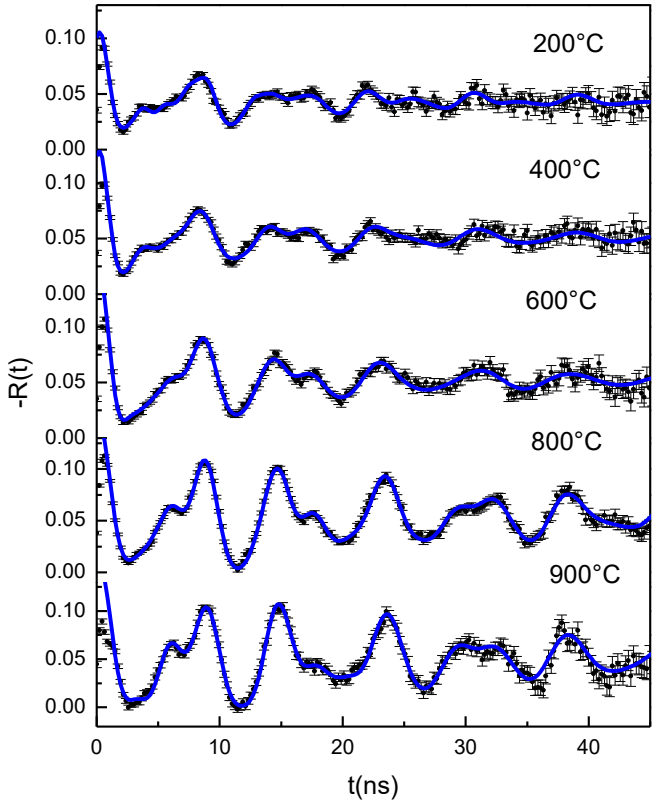

Figure 4: Pac spectra for (111Ta) probe in Hf doped with 5%Si at different temperatures. The solid lines are the least square fit of the theoretical function to the experimental data.

The results of the hyperfine interaction parameters obtained by best fit to the experimental data obtained in the temperature ranges of 200°C–900°C are shown in table 2.

Table 2: Temperature dependence of hyperfine parameters for Si-doped HfO_2

HfO_2	ν_Q (MHz)	η	Fraction (%)
200	785 (9)	0.30 (3)	16 (4)
	1163 (7)	0.59 (2)	22 (3)
	874 (12)	0.21 (3)	62 (3)
400	775 (3)	0.33 (1)	32 (4)
	971(23)	1.00	25 (5)
	928 (17)	0	43 (5)
600	748 (3)	0.39 (1)	42 (4)
	886 (8)	1.00	6 (1)
	888 (9)	0	52 (5)
800	733 (1)	0.42 (1)	63 (7)
	878 (5)	1.00	9 (1)
	509 (3)	1.00	27 (2)
900	727 (1)	0.44 (1)	71 (6)
	318 (9)	1.00	3 (1)
	496 (5)	1.00	26 (1)

All the spectra measured at different temperatures for Si-doped HfO_2 were fitted with a model considering probe nuclei occupying three site fractions.

The values of the quadrupole frequency and the asymmetry parameter obtained for one of these fractions correspond to those expected for the quadrupole interactions of ^{181}Ta in the monoclinic phase of hafnium oxide: $\nu_Q \approx 750$ MHz and $\eta \approx 0.36$, initially with population of 16% at 200 ^oC that increases to 71% at 900 ^oC becoming majority, as reported in reference 15. This result is an indication that the local structure around probe nuclei becomes more regular and the crystallinity of samples increases. The decrease in ν_Q and the increase in η with the increase of temperature, reaching the values of $\nu_Q = 727$ MHz and $\eta = 0.44$ at 900 ^oC (the usual values are $\nu_Q = 790$ MHz and $\eta = 0.35$-0.38) can be ascribed to the presence of Si atoms in the crystal lattice of the HfO_2. This distortion is probably an indication of the change in electronic and structural arrangement around the ^{181}Ta probe nuclei caused by the addition of Si dopants that have ionic radius different from that of Hf.

The second fraction site characterized initially by a large ν_Q that drops fast when temperature increases and large η can be assigned to probe nuclei at surface region. The population of this fraction shows a decrease due to the heat treatment causing the grain to increase in size diminishing the surface area by volume ratio [18-19].

The third site is also from the ^{181}Ta probe substituting Hf, this site may be related with a transition to a tetragonal structure in range of the temperature 400°C at 600°C. This can be verified by $\eta = 0$ which is the result a tetragonal structure, i.e. without distortion. As show

reference by 20, the doping HfO2 with another cation such as Si can induce the tetragonal phase.

4. CONCLUSION

The initial conclusion we could extract from the results is that the PAC technique is capable to study the doping in oxides and can be a powerful tool to investigate the characteristics of a particular atomic site and its surroundings. The results of HfO_2 showed that the sol-gel method for nanoparticle preparation is appropriate. Besides, of the producing in quality doped samples with the expected structure. Moreover, the introduction of the dopant in the HfO_2 sample causes a slight perturbation in the crystal lattice.

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REFERENCES

1. B. Aslibeiki, P. Kameli, M. H. Ehsani, "MnFe2O4 bulk, nanoparticles and film: A comparative study of structural and magnetic properties", *Ceramics International,* **42,** pp. 12789-12795 (2016).
2. Z. J. Wanga, T. Kumagai, H. Kokawa, J. Tsuaur, M. Ichiki, R. Maeda, "Crystalline phases, microstructures and electrical properties of hafnium oxide films deposited by sol–gel method" *Journal of Crystal Growth*, **281**, pp. 452–457 (2005).
3. M. Chen, N. Hanagata, T. Ikoma, J. Huang, K. Li, C. Lin, F. Lin, "Hafnium-doped hydroxyapatite nanoparticles with ionizing radiation for lung cancer treatment", *Acta Biomaterialia*, **37**, pp. 165–173(2016).
4. M. M. Shabat, D. M. El-Amassi, D. M. Schaadt, "Design and analysis of multilayer waveguides containing nanoparticles for solar cells", *Solar Energy*, **137**, pp. 409-412 (2016).
5. H. Wang, J. Guo, J. Li, J. Wei, "Fabrication of bimetallic nanoparticles/multi-walled carbon nanotubes composites for microelectronic circuits" *Carbon*, **49**, pp.779-786 (2011).
6. C. Mannequin, A. Delamoreanu, L. Latu-Romain, V. Jousseaume, H. Grampeix, S. David, C. Rabot, A. Zenasni, C. Vallee, P. Gonon, "Graphene-HfO2-based resistive RAM memories", *Microelectronic Engineering,* **161**, pp. 82-86 (2016).
7. M. Zaharescu, V.S. Teodorescu, M. Gartner, M.G. Blanchin, A. Barau, M. Anastasescu, "Correlation between the method of preparation and the properties of the sol–gel HfO2 thin films", *Journal of Non-Crystalline Solids*, **354**, pp 409–415 (2008).
8. J.H. Choi, Y. Mao, J.P. Chang, "Development of hafnium based high-k materials-A review", *Materials Science and Engineering,* **72**, pp. 97–136 (2011).

9. J. Gao, G. He, B. Deng, D.Q. Xiao, M. Liu, P. Jin, C.Y. Zheng, Z.Q. Sun, "Microstructure, wettability, optical and electrical properties of HfO2 thin films: Effect of oxygen partial pressure", *Journal of Alloys and Compounds*, **662**, pp. 339-347(2016).
10. J. Robertson, R. M. Wallace, "High-K materials and metal gates for CMOS applications", *Materials Science and Engineering*, **88**, pp. 1-41(2015).
11. R. Ma, M. Liu, G. He, M. Fang, G. Shang, J. Zhang, X. Chen, J. Gao, G. Fei, L. Zhang, "Effects of rapid thermal annealing on interfacial and electrical properties of Gd-doped HfO2 high-k gate dielectrics", *Journal of Alloys and Compounds*, **646**, pp. 310-314 (2015).
12. S. Gálvez-Barboza, L.A. González, B. A. Puente-Urbina, E. M. Saucedo-Salazar, L.A. García-Cerda, "Preparation and characterization of Ce-doped HfO2 nanoparticles", *Journal of Alloys and Compounds*, **643**, pp. 62–66 (2015).
13. Yu-Fen. Zhang, H. Ren, Zhi-Tao. Hou, "First-principles calculations of electronic and optical properties of F, C-codoped cubic HfO2" *Journal of Magnetism and Magnetic Materials*, **375**, pp. 61-64 (2015).
14. Z. D. Dohčević-Mitrović, N. Paunović, B. Matović, P. Osiceanuc, R. Scurtuc, S. Aškrabić, M. Radović, "Structural dependent room-temperature ferromagnetism in yttrium doped HfO2 nanoparticles", *Ceramics International*, **41**, pp. 6970–6977 (2015).
15. F.H.M. Cavalcante, M.R. Gomes, A.W. Carbonari, L.F.D. Pereira, D.A. Rossetto, M.S. Costa, E. Alves, N.P. Barradas, N. Franco, L.M. Redondo, A.M.L. Lopes, J.C. Soares, "Characterization of nanostructured HfO2 films using RBS and PAC", *Nuclear Instruments and Methods in Physics Research*, **273**, pp. 195–198 (2012).
16. V.N. Ivanovski, B. Cekic, A. Umicevic, T. Barudzija, G. Schumacher, I. Ma - darevic, V. Koteski, "Site preference of Hf dopant in Ni3Al alloys: A perturbed angular correlation study" *Journal of Alloys and Compounds,* **622**, pp. 541–547 (2015).
17. R. Ramos-González, L.A. García-Cerda, M.A. Quevedo-López, "Study of the surface modification with oleic acid of nanosized HfO2 synthesized by the polymerized complex derived sol–gel method", *Applied Surface Science,* **258**, pp. 6034-6039 (2012).
18. A. B. Umicevic, B. Đ. Cekic, J. N. Belosevi-Cavor, V. J. Koteski, B. Papendorf, R. Riedel, E. Ionescu, "Evolution of the local structure at Hf sites in SiHfOC upon ceramization of a hafnium-alkoxide-modified polysilsesquioxane: A perturbed angular correlation study", *Journal of the European Ceramic Society*, **35**, pp. 29–35 (2015).
19. M. Uhrmacher, "Can PAC measurements be used to investigate defects in nano-structures?", *Defect and Diffusion Forum*, **311**, pp. 105-133 (2011).
20. C-K. Lee, E. Cho, H-S. Lee, C. S. Hwang, S. Han, "First-principles study on doping and phase stability of HfO2" *Phys. Rev. B, **78**,* 012102 (2008).