Stable tetragonal phase and magnetic properties of Fe-doped HfO_2 nanoparticles

T. S. N. Sales, F. H. M. Cavalcante, B. Bosch-Santos, L. F. D. Pereira, G. A. Cabrera-Pasca, R. S. Freitas, R. N. Saxena, and A. W. Carbonari

Citation: AIP Advances **7**, 056315 (2017); doi: 10.1063/1.4976583
View online: http://dx.doi.org/10.1063/1.4976583
View Table of Contents: http://aip.scitation.org/toc/adv/7/5
Published by the American Institute of Physics

Stable tetragonal phase and magnetic properties of Fe-doped HfO_2 nanoparticles

T. S. N. Sales,[1,a] F. H. M. Cavalcante,[2] B. Bosch-Santos,[1] L. F. D. Pereira,[1] G. A. Cabrera-Pasca,[3] R. S. Freitas,[4] R. N. Saxena,[1] and A. W. Carbonari[1]
[1]*Instituto de Pesquisas Energéticas e Nucleares, University of São Paulo, 05508-000 São Paulo, Brazil*
[2]*Department of Electrical and Computer Engineering of the Colorado State University, Fort Collins, Colorado 80523, USA*
[3]*Faculdade de Ciências Exatas e Tecnologia, Universidade Federal do Pará, 68440000 Abaetetuba, PA, Brazil*
[4]*Instituto de Física, Universidade de São Paulo, CP 66318, 05314970 Sao Paulo, SP, Brazil*

(Presented 2 November 2016; received 23 September 2016; accepted 13 November 2016; published online 10 February 2017)

In this paper, the effect in structural and magnetic properties of iron doping with concentration of 20% in hafnium dioxide (HfO_2) nanoparticles is investigated. HfO_2 is a wide band gap oxide with great potential to be used as high-permittivity gate dielectrics, which can be improved by doping. Nanoparticle samples were prepared by sol-gel chemical method and had their structure, morphology, and magnetic properties, respectively, investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) with electron back scattering diffraction (EBSD), and magnetization measurements. TEM and SEM results show size distribution of particles in the range from 30 nm to 40 nm with small dispersion. Magnetization measurements show the blocking temperature at around 90 K with a strong paramagnetic contribution. XRD results show a major tetragonal phase (94%). [http://dx.doi.org/10.1063/1.4976583]

I. INTRODUCTION

Hafnium oxide (HfO_2), also called hafnia is a wide band gap metal oxide very promising for applications in various fields of science and technology[1,2] because of its physical and chemical properties and good thermal stability. Although HfO_2 has three polymorphs at atmospheric pressure, monoclinic, tetragonal and cubic crystal structure, the only stable phase at room temperature is the monoclinic. Stabilization of tetragonal and cubic phase in ambient conditions can be obtained with doping by different methods of preparation and heat treatment.[3] The tetragonal and cubic phases are predicted to have higher permittivity than the monoclinic phase, being, therefore, important in technological applications such as, CMOS (complementary-metal-oxide-semiconductors) transistors, optical coatings, MEMS (microelectro-mechanical systems), dielectric barriers, and spintronics.[4,5]

For spintronic applications, it is desirable to have a material in which the magnetic metallic ions are diluted in a semiconductor lattice. This can be achieved by doping a non-magnetic semiconductor (e.g., HfO_2) with a transition-metal element (e.g., Fe) allowing the occurrence of a spin polarized current while still exhibiting all of the basic functions of an undoped matrix.[6] To obtain the desired results it is necessary that the dopant atoms must be evenly dissolved in the host lattice and the resulting ferromagnetism indeed originates from the doped matrices.

[a]Electronic mail: tatianenas@usp.br

Ferromagnetism was observed in Y-doped HfO_2 nanoparticles[7] and in pure HfO_2 thin films.[8] Moreover, Manory et al.[9] show the control of the structure in cubic and tetragonal phases in thin films and Chain et al.[10] report that the tetragonal phase of the $HfSiO_4$ was produced by solid state reaction of SiO_2 with HfO_2. These prior and other studies show that doped HfO_2 is sensitive to the dopant species and concentration, for example stabilization of tetragonal and cubic phases was obtained by doping with different concentrations up to 25% of Y, Eu and Si.[4,7,10,11]

In the present work, the tetragonal phase of HfO_2 was obtained by doping with Fe at a concentration of 20%. We have synthesized doped hafnium oxide nanoparticles using a sol-gel chemical route. 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 subsequent heating the mixture leads to polyesterification forming a gel. The powder is obtained after thermal calcination of the gel.[3,12] Our samples had their structural and morphological properties investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM), whereas their magnetic properties were investigated by magnetization measurements.

II. EXPERIMENTAL PROCEDURE

The HfO_2 powders doped with Fe were synthesized by sol-gel method, using metallic Hf (99.99% purity), $FeCl_2$ (99.99% purity), citric acid (CA) and ethylene glycol (EG). The reaction was obtained from a stoichiometric mixture of the metal:CA by 1:2 and CA:EG by 40:60 proportions. Metallic Hf was dissolved in hydrofluoric acid (HF) and the $FeCl_2$ was dissolved in deionized water. 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. After that, the temperature was raised to about 100°C until gel formation. The obtained viscous solution was calcined in air at 550°C for 14 hours in order to allow evaporation of the organic material. The resulting nanoparticle powders were then divided into two parts, one part, hereafter named S1, was characterized as it is. The other part (S2) was sealed in an evacuated quartz tube and annealed at 900°C for 12 hours. Both parts were characterized with the same techniques for later comparison. 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.[13] The crystal shape and distribution of nanoparticle samples were characterized with scanning electron microscopy (SEM)with electron back scattering diffraction (EBSD) and transmission electron microscopy (TEM). The magnetic proprieties of samples were carried out in a wide range of temperature using a superconducting quantum interference device (SQUID) (MPMS-XL, Quantum Design).

III. RESULTS AND DISCUSSION

A. Morphology and structure results

Results for TEM image (see Fig. 1) show the morphology of the Fe-doped HfO_2 nanoparticles produced by sol-gel for S1 (after synthesis) and S2 (after further annealing at 900°C) samples. For S2 sample, results show nanoparticles having quasi-spherical morphology with small difference in sizes with an average diameter between 30 nm and 50 nm.

Fig. 2 displays images resulting from the characterization with SEM and EBSD techniques. In S1 sample the image gives a complete picture mapping the spatial correlation of Fe and Hf atoms present in the sample. Small regions with slightly higher concentrations of Fe than Hf were observed indicating some degree of segregation of iron possibly as iron oxide. The image for sample S2, on the other hand, reveals many regions with higher concentrations of Fe with a strong evidence of iron oxide clusters, probably Fe_3O_4 as indicated by magnetic measurements. However, the image also shows that the most part of Fe atoms are almost homogeneously distributed into the HfO_2 phase.

X-ray diffraction (XRD) patterns for S1 and S2 samples of Fe-doped HfO_2 are shown in Fig. 3. The results for sample S1 (after heating at 550°C for 14 h) exhibit a single phase with the diffraction pattern of the monoclinic structure of HfO_2 corresponding to the P21/c space group. Fit based on

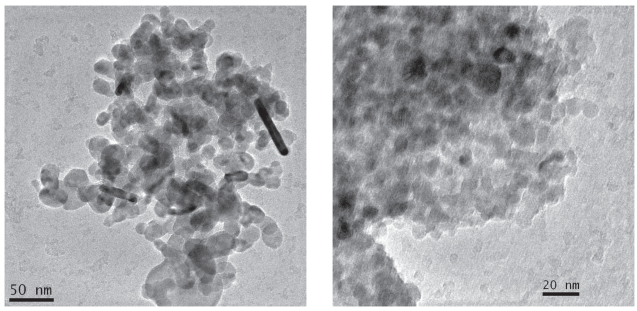

FIG. 1. Transmission electron microscopy (TEM) images for Fe doped HfO_2 for S1 (left) and S2 (right).

Rietveld method yields lattice parameters a = 5.1186(6) Å, b = 5.1641(5) Å, and c = 5.2924(6) Å. Because there is no evidence of any iron oxide peaks we can conclude that the majority of Fe atoms are replacing Hf at cationic sites.

As for the sample S2 (annealed for 12 h at 900°C in evacuated quartz tube), XRD results reveal a major phase (94 %) with the space group symmetry I41/*amd* and lattice parameters a = b = 6.5699(1) Å and c = 5.9649(1) Å. Same space group with similar lattice parameters was identified in samples of $HfSiO_4$ (hafnium orthosilicate).[14] This space group show the tetragonal structure when the Hf-O bond in the first coordination are represented by HfO_8 group.

X-ray diffraction results for sample S2 strongly indicate the possibility of incorporation of SiO_2 to Fe-doped HfO_2 nanoparticles from the quartz tube during annealing, although the temperature for the reaction of HfO_2 with SiO_2 to form $HfSiO_4$ is higher than that used during annealing. XRD results then show the formation of tetragonal structure with a fraction of 94% and the monoclinic structure (fraction of 6%) from HfO_2.[15] In addition, XRD results do not show peaks corresponding to the iron oxides Fe_3O_4 or Fe_2O_3.

If the accidental incorporation of SiO_2 really occurred, it is an important evidence that the tetragonal structure was well stabilized with doping of Fe (20%) plus a smaller concentration of Si from SiO_2. This result would be also more interesting if we take into account that small concentrations of Si (up to 8.5%) doping in HfO_2 thin films do not lead to the hafnium orthosilicate type structure.[16] This structure was only obtained by a stoichiometric mix of SiO_2 and HfO_2 with solid state reactions after long time mixing followed by high temperature annealing or high pressure.[10,11]

B. Magnetic measurements

In order to verify the formation of iron oxides as well as to characterize the magnetic properties of Fe-doped HfO_2 samples, magnetic measurement were carried out in a wide range of temperature (2-300K) and applied field using a superconducting quantum interference device (SQUID) (MPMS-XL) magnetometer.

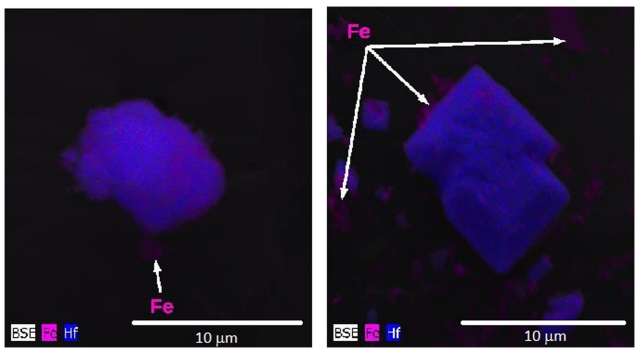

FIG. 2. Electron back scattering diffraction (EBSD)images showing the spatial distribution of Fe and Hf in Fe doped HfO_2 for S1 (left) and S2 (right).

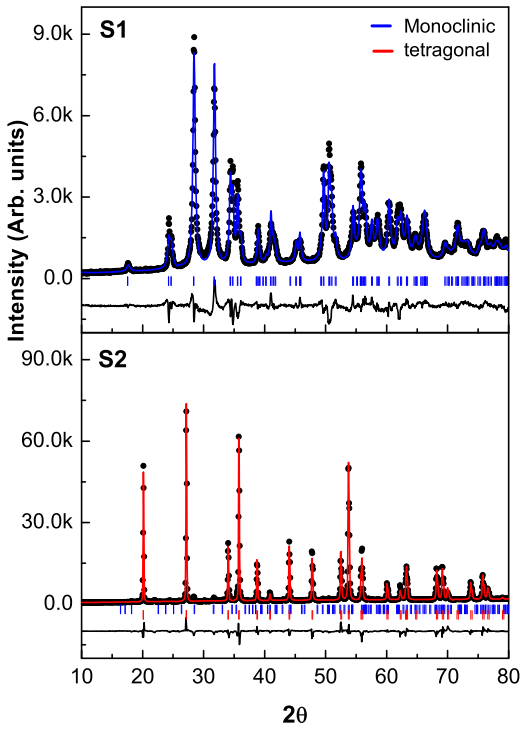

FIG. 3. X-ray powder diffraction pattern along with Rietveld refinement (solid curves) for S1 (top) and S2 (bottom) samples.

Fig. 4 shows the zero field cooling (ZFC) and field cooling (FC) measurements as a function of temperature obtained with an applied magnetic field H = 100 Oe for the two samples S1 and S2. Two peaks were observed at low temperatures in ZFC curve for the sample S1, which suggests the presence of magnetic nanoparticles of different phases. These two peaks observed at around 45 K and 84 K suggest two different blocking temperatures corresponding to two different average-size group of magnetic nanoparticles distributed in the sample S1 (possibly iron oxides as suggested by TEM images). A careful visual inspection in the temperature dependence of ZFC shows a quite smooth jump around 258 K (see inset in Fig. 4) that is a signature corresponding to the Morin transition due to the presence of α-Fe_2O_3. FC magnetic curve reveals a strong paramagnetic contribution.

The ZFC-FC curves for S2 sample (after annealing in evacuated quartz tube)are also shown in Fig. 4. These curves reveal a transition around 120 K which is characteristic of the Verwey transition indicating the presence of the magnetite Fe_3O_4. Due to the high magnetic moment of magnetite it is not possible to observed any magnetic contribution from other magnetic phases neither a possible blocking temperature characteristic of nanoparticles with ferromagnetic behaviour.

IV. SUMMARY

In conclusion our results suggest that sample S1 is formed by HfO_2 homogeneously doped with Fe atoms, which are at substitutional cationic sites in the monoclinic structure with a strong paramagnetic behavior. Results also show the presence of very small amount of magnetic impurities (probably iron oxides) phases in S1 sample. Results for sample S2 show an amazing stabilization of tetragonal structure with a fraction of 94 % with the probable presence of Fe_3O_4, not detected by XRD measurements but from magnetic measurements. Although the formation of Fe clusters is evident in both samples (very small fraction in S1), it was possible to obtain a stable tetragonal phase as clearly shown by x-rays diffraction patterns. We can suggest that this stable phase was only possible due of the presence of iron with a small accidental presence of Si atoms incorporated during the annealing in quartz tube. Further investigation on HfO_2 simultaneously doped with Fe and Si, as suggested by the results reported in this paper, is necessary to study the influence of concentration of

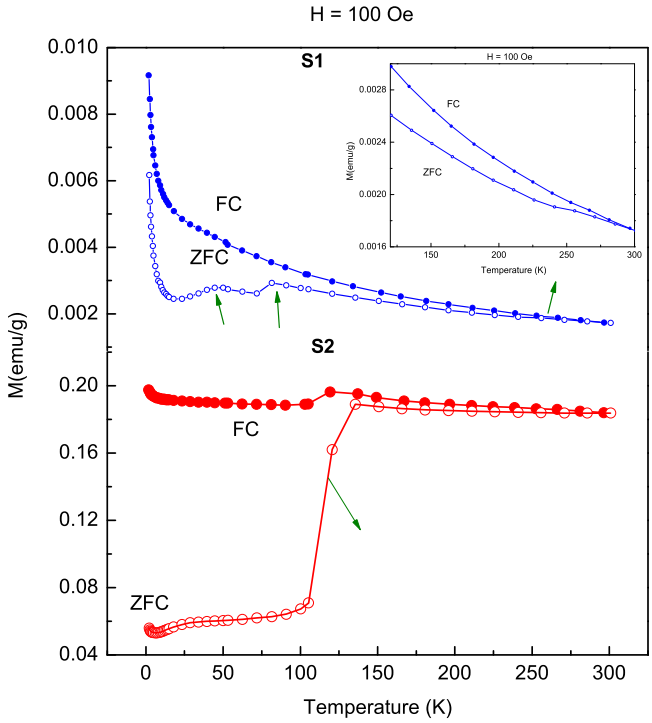

FIG. 4. Temperature dependence of the ZFC and FC obtained with an applied magnetic field of H = 100 Oe for S1 (top) and S2 (bottom) samples. The inset displays the ZFC and FC curves in the range from 150 K to 300 K. The arrows indicate the presence of peaks in the curves.

Si on the structural properties of Fe-doped HfO_2. We also propose a detailed investigation of the role of iron in Fe-doped HfO_2 because it can be a promising material with possible magnetic and electric proprieties useful to technological application as reported in the literature which shows that a small amount of ferromagnetic impurity phase, such as γ -Fe_2O_3 or Fe_3O_4, present in the grain boundary of nanocrystals of oxides such as $BiFeO_3$, change the magnetic and electric properties of the host compound.[17]

ACKNOWLEDGMENTS

Partial financial support for this research was provided by Fundação de Amparo a Pessquisa do Estado de São Paulo (FAPESP). The authors thankfully acknowledge the financial support provide by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq). LFDP acknowledge the financial support provide by CAPES and ELETRONUCLEAR.

[1] X. Zhao and D. Vanderbilt, Phys. Rev. B **65**, 233106 (2002).
[2] Z. J. Wang, T. Kumagai, H. Kokawa, J. Tsuaur, M. Ichiki, and R. Maeda, J. of Crystal Growth **281**, 452 (2005).
[3] J. Wang, H. P. Li, and R. Steven, J. Mater. Sci. **27**, 5397 (1992).
[4] M. Villanueva-Ibanez, C. Le Luyer, O. Marty, and J. Mugnier, Optical Materials **24**, 51 (2003).
[5] T. Nishide, S. Honda, M. Matsuura, and M. Ide, Thin Solid Films **371**, 61 (2000).
[6] F. Pan, C. Song, X. J. Liu, Y. C. Yang, and F. Zeng, Mater. Sci. Eng. R **62**, 1 (2008).
[7] Z. D. Dohčević-Mitrović, N. Paunović, B. Matović, P. Osiceanu, R. Scurtu, S. Aškrabić, and M. Radović, Ceramics International **41**, 6970 (2015).
[8] M. Venkatesan, C. B. Fitzgerald, and J. M. D. Coey, Nature **430**, 630 (2004).
[9] R. R. Manory, T. Mori, I. Shimizu, and S. Miyake, J. Vac. Sci. Technol. A **20**, 549 (2002).
[10] C. Y. Chain, L. C. Damonte, S. Ferrari, E. Munoz, C. Rodríguez Torres, and A. F. Pasquevich, J. of Alloys and Compounds **495**, 527 (2010).
[11] B. Manoun, R. T. Downs, and S. K. Saxena, American Mineralogist **91**, 1888 (2006).
[12] M. P. Pechini, U.S. Patent no. 3330697 (11 July 1967).
[13] J. Howard and B. A. Hunter, Australian Nuclear Science and Technology Orgonization Lucas Heights Research Laboratories A Computer Program for Rietveld Analysis of X-Ray and Neutron Powder Diffraction Patterns - RIETICA. Australia, N. S. W. (1997).

[14] J. Varghese, T. Joseph, K. P. Surendran, T. P. D. Rajana, and M. T. Sebastian, Dalton Trans. **44**, 5146 (2015).
[15] H. Putz, *MATCH Phase Identification From Powder Diffraction Data*. Bonn, Germany (2016).
[16] E. Yurchuk, J. Müller, S. Knebel, J. Sundqvist, A. P. Graham, T. Melde, U. Schroder, and T. Mikolajick, Thin Solid Films **533**, 88 (2012).
[17] P. K. Siwach, J. Singh, H. K. Singh, G. D. Varma, and O. N. Srivastava, J. Appl. Phys. **105**, 07D916 (2009).