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Characterization of nanostructured HfO_2 films using RBS and PAC

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ABSTRACT

The hyperfine field at ^{181}Ta lattice sites in a nanostructured HfO_2 thin film doped with Fe was studied using Rutherford Backscattering Spectrometry and Perturbed Angular Correlation techniques. The 409 nm Hf film was deposited by Electron Beam Evaporation on a silicon substrate. The radioactive ^{181}Hf ions were produced by neutron activation of the nanofilm in the Brazilian Research Reactor (IPEN IEA-R1) by the reaction ^{180}Hf(n,γ)^{181}Hf. These studies provided an excellent opportunity to obtain unique information regarding local arrangement of the grains, structure, phase transformations of nanoparticles and interfaces of nanostructured materials and the thin film.

1. Introduction

Nowadays high-tech industry addresses efforts on development of thin films and nanoparticles research. They play a key role in areas such as microelectronics, surface engineering, systems engineering, optical and magnetic, and electrochemical. Moreover, investigation on nano-structured systems such as nanoparticles and thin films is a sensitive test for fundamental properties of condensed matter at extremely small environments. In recent years, the silicon based microelectronics industry has made a great progress in the performance of electronic devices, currently called (CMOS Complementary Metal-Oxide Semiconductor), where oxides perform a key role, as well as in magneto-electronics or spintronics. A particular case is of nano-scale films such as hafnium oxide (HfO_2) that has received increased attention since the advent of Intel's patent where the SiO_2 was replaced by HfO_2 as gate dielectric material to continue the down-scaling of CMOS transistors [1,2]. There are, however challenges to be overcome in the production of thin layers of HfO_2 to obtain systems which are free of defects or in which defect or dopant concentrations are introduced in a controlled manner. In addition, the smaller are the systems the more important and difficult is the control of their electronic properties since the concentration of defects and dopants and the interface and surface area to volume ratio in these systems are inversely proportional to the film thickness. The high-tech companies are highly interested on scientific findings about the behavior of observable defects in phenomena such as electrical conductivity, charge dispersion and ferromagnetism. However, these results can only be acquired by using experimental techniques highly specialized. The Perturbed Angular Correlation (PAC), a powerful tool to sample local environments on the scale of a few atomic lengths monitoring microscopic regions, are among them. The investigation of hyperfine interactions in monoclinic HfO_2 thin films by means of the PAC technique is possible by measuring the electric field gradient (EFG) using the ^{181}Ta as probe nuclei. The EFG reflects the charge distribution surround the probe nucleus. Since the magnitude of the signal decreases rapidly with increasing distance between the charges, and the probe nucleus, these measurements provide unique information on the local arrangement in the grains and interfaces of nanostructured materials and thin films.

1.1. Sample Preparation

The thin metallic film was deposited by Electron Beam Evaporation on a pure silicon substrate at room temperature in a vacuum system with an operating pressure of about 10^{-9} mbar. This guarantees *ab initio* the thin film production with a minimum contamination of oxygen, O, and other impurities such as carbon, C, or nitrogen N. The thickness of the film was 409 ± 0.2 nm, measured during the evaporation process with a Quartz Cristal balance and confirmed by Atomic Force Microscopy, AFM, and the Rutherford Backscattering Spectrometry, RBS, measurements. The initial target was commercial 99.9% pure metallic Hf. RBS studies were performed with a 1 mm diameter collimated beam of $^4He^+$ ions. The ^{181}Hf activity was produced by neutron activation of the thin film in the Brazilian Research Reactor (IPEN IEA – R1) by the nuclear reaction ^{180}Hf(n,γ)^{181}Hf. The PAC measurements were conducted at ambient temperature after sample annealing treatment at

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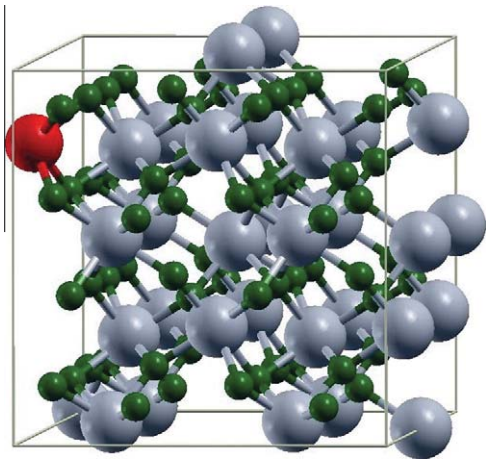

Fig. 1. Unit cell of the monoclinic HfO_2, green circles represent O atoms and gray circles represent Hf atoms. The impurity of Ta is located at substitutional Hf-sites.

1473 K, ensuring the oxidation process of the Hf thin film. A detailed description of this method can be found in [3]. The γ–γ PAC measurements were done using a standard set up with four conical BaF_2 detector scintillators with a time resolution of 0.6 ns [4].

The PAC method is based on the hyperfine interaction of nuclear moments of the probe with extra nuclear magnetic fields or electric field gradients (EFGs). In the case of quadrupolar electric interaction, the experimental measurement gives the quadrupolar frequency ν_Q with respective distribution δ as well as the asymmetry parameter η of EFG. A detailed description of this method can be found elsewhere [4]. Results of previous PAC measurements in HfO_2 can be found in the literature [5,6]. The γ–γ 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, with an anisotropy coefficient $A_{22} = -0.288$. The γ–γ PAC measurements have been carried out using a standard set up with four conical BaF_2 detector scintillators with a time resolution of 0.6 ns (FWHM). From the coincidence spectra $N(\theta, t)$, where θ is the angle between detectors and t is the time delay between events, the time differential anisotropy.

$$R(t) = 2\frac{N(180^{deg}, t) - N(90^{deg}, t)}{N(180^{deg}, t) + 2N(90^{deg}, t)} = A_{22}G_{22}(t) = \sum f_1 G^i_{22}(t) \qquad (1)$$

has been calculated. $G_{22}(t)$ is the perturbation function which describes the time modulation of the angular correlation perturbed

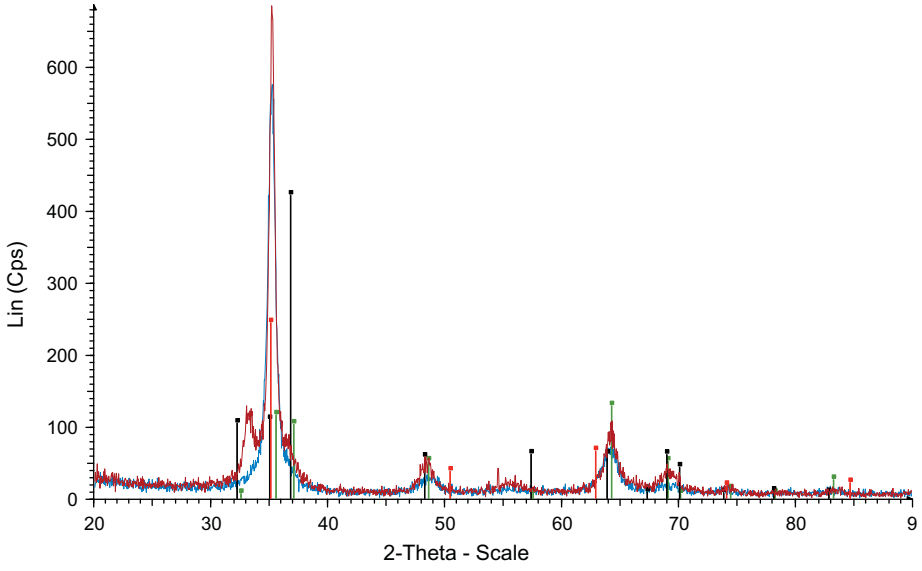

Fig. 2. Room temperature Hf film XRD spectra. Identification of the main peaks: Hf on channels 35, 51 and 84; $Hf_{0.43}Zr_{0.57}$ on channels 37, 48, 61 and 70.

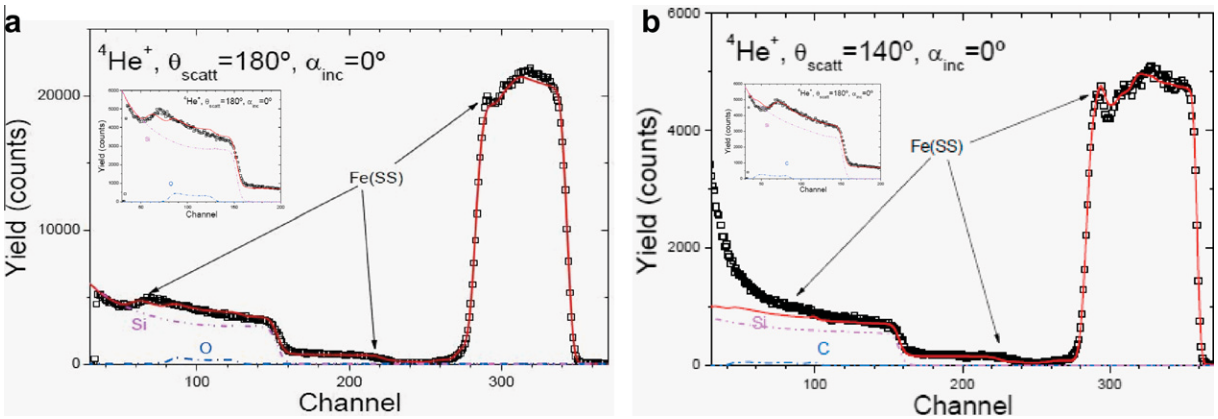

Fig. 3. RBS spectrum for a 409 nm thick Hf film deposited on a silicon substrate ((□): data; (–): simulation). The data were analyzed with the IBA DataFurnace NDF v9.2g [7] indicating the Fe presence at the surface, beginning and end of the Si layer, and throughout the Hf film (channels 240 and 260).

by the hyperfine interaction and f_i are the fractional site populations of probe nuclei used to fit the data. For a static quadrupole interaction, the perturbation function has the form

$$G_{22}(t) = \sum_{n=0}^{3} S_{2n} e^{-\delta\omega_n t} cos(\omega_n t) \quad (2)$$

The frequencies ω_n are related to the quadrupole frequency $\nu_Q = eQV_{zz}/\hbar$ by $\omega_n = g_n(\eta)\nu_Q$. The coefficients $g_n(\eta)$ are known functions of the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, where V_{kk} ($k = x,y,z$) denote the principal components of the EFG tensor. The exponential function accounts for a lorentzian frequency distribution δ around ω_n. Fig. 1 show the monoclinic HfO_2 structure.

2. Results

Room temperature X-ray diffraction measurements (XRD) were carried out with a Bruker-AXS D8-Discover diffractometer using Cu $K_{\alpha 1,2}$ radiation lines, collimated with a parabolic mirror and a nickel filter; the width of the beam was about 0.6 mm. The scan measurements were done in two-theta grazing geometry on the film before annealing. According to the database ICDD PDF-2 from 2006, the X-ray diffraction spectrum shown in Fig. 2 clearly indicates the presence of cubic Hf and $Hf_{1-x}Zr_x$ phases.

The RBS experiments were carried out at the 3.1 MeV Van de Graaff accelerator at ITN, Portugal. The characterization of the metallic film, before annealing treatment, was performed using a 2 MeV ^{4}He ions in the RBS chamber. The detectors were set at 140° (standard detector) and 180° (annular detector) and the angles of incidence were 0° and 25°. The data were analyzed with the IBA DataFurnace NDF v9.2g [7]. The RBS data were collected in different spots on the sample and compared. No significant difference was observed in the data collected from different points on the sample surface. The data presented in Fig. 3 (a) and (b) visibly indicates the presence of Fe in a surface peak, as well as with fairly high concentration in a well-defined layer of the Si substrate, and with smaller concentration in the Hf film. The fitting-route accounted for the small Zr natural content in the Hf, around 3–4% with respect to the Hf concentration. The best fit was achieved by introducing a light impurity, with concentration around 50 at.%. Two sets of fits were analyzed, one where oxygen, O, is the light element, shown in Fig. 3 and respective inserts, and another where carbon, C, is the light element. The results seem to indicate that the Hf concentration decreases with depth; first there is a layer (about half the film) with around 50 at.% Hf, then this decreases towards the interface with the Si. In the fits, more of the light elements were introduced to compensate for the lower Hf amount; however, some degree of mixing with the Si substrate cannot be excluded. From the results at the low energy region, displayed in the inserts of Fig. 4, it can be assumed that there is no O in the film surface and volume, at least not in the amount required (50 at.%) to reproduce the Hf yield, but instead C should be present, mainly in the Si substrate. The depth profile is shown in the Fig. 4 for the case of C presence.

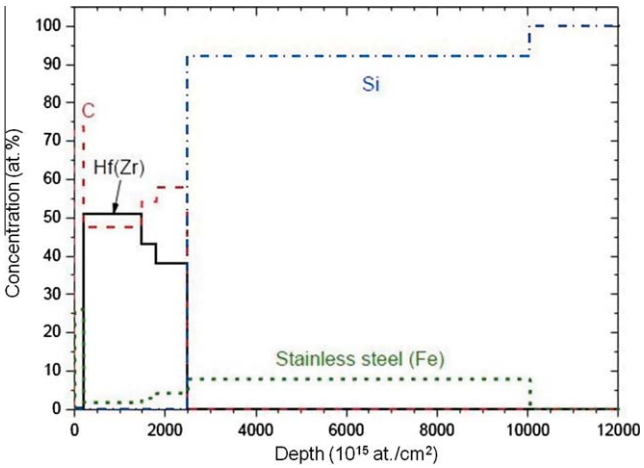

Fig. 4. RBS spectrum for HfO_2 film. The data were analyzed with the IBA DataFurnace NDF v9.2g [7].

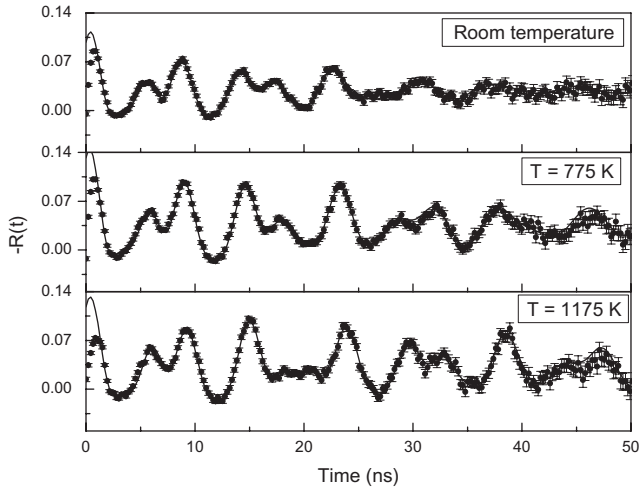

Fig. 5. Perturbation functions $R(t)$ for ^{181}Ta probe nuclei in HfO_2 thin film measured by PAC at indicated temperatures. Solid lines in $R(t)$ plots are the least squares fit of the theoretical function to the experimental data.

Table 1
Hyperfine parameters from the fitted PAC spectra.

Temp (K)	NiQ (MHz)	η	δ	Fraction (%)
273	776(2)	0.38	0.046	74
	819(1)	0.41	0.039	26
775	746(1)	0.41	0.031	74
	846(8)	0.41	0.043	26
1175	728(1)	0.45	0.022	75
	812(9)	0.41	0.052	25

Fig. 5 shows typical experimental spectra for HfO_2 samples measured by PAC at room temperature after annealing at 1473 K (which oxidizes the metallic film) and subsequently measured at temperatures of 775 and 1175 K (see details in Ref. [5]). R(t) functions were fitted with the perturbation function $G_{22}(t)$ of Eq. (2) which describes the evolution of the hyperfine interactions in HfO_2 thin films. Results show that the probe nuclei experience two distinct quadrupole frequencies as shown in Table 1. The values of ν_{Q1} and η_1 correspond to that expected for the quadrupole interaction of ^{181}Ta in the monoclinic phase of hafnium oxide (ν_Q = 815 MHz and η = 0.38) [5]. The quadrupole frequency ν_{Q1} is therefore interpreted as the probe nuclei ^{181}Ta occupying the defect-free sites in the monoclinic HfO_2. The second frequency ν_{Q2} indicates defect configuration around the probe nuclei. In the case of thinner film, our preliminary results indicate that the annealing of the sample can induces dislocation of oxygen and or silicon diffusion throughout the interface hafnium-silicon creating regions with oxygen deficiency or silicon impurity or both. The fitted values of the hyperfine parameters obtained from PAC spectra are given in the table 1.

3. Conclusion

PAC measurements of nuclear electric QIs have been combined with RBS and X-ray shows that is a powerful tool to investigate

structure, phase transformations of nanoparticles. From the X-ray we have concluded that HfO_2 powder crystallize in the monoclinic phase. The Fe doped Hf metallic film with single crystalline quality was grown on Si (0 0 1) substrates by electron beam evaporation. The maximum concentration of Fe homogeneously distributed in the film is 0.04 at.%. The oxidation progression was successfully achieved by annealing treatment of the Hf thin metallic film. The QI of the nuclei ^{181}Ta on metal sites of HfO_2 thin films has been determined by PAC spectroscopy. The results shown in Fig. 5 measured indicates that HfO_2 film show a preferential orientation with the main axis perpendicular to the surface of the film after annealing. PAC technique has shown to be a very powerful tool to provide microscopic information on a nanoscale. Further PAC measurements of HfO_2 thin films with different thicknesses and dopant concentration, performed in different atmospheres and as a function temperature, are under progress.

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