Hyperfine Interact (2010) 198:41–45
DOI 10.1007/s10751-010-0250-z

Characterization of nanostructured HfO_2 films using Perturbed Angular Correlation (PAC) technique

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Published online: 19 December 2010
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Abstract The hyperfine field at ^{181}Ta lattice sites in nanostructured HfO_2 thin films was studied by the Perturbed Angular Correlation (PAC) technique. Thin oxide films were deposited by Electron Beam Evaporation on a silicon substrate. The thickness of the films was ∼100 nm and ∼250 nm. Radioactive ^{181}Hf nuclei were produced by neutron activation of the film samples in the Brazilian Research Reactor (IPEN IEA-R1) by the reaction ^{180}Hf(n,γ)^{181}Hf. PAC measurements were carried out after annealing at 1473 K. The PAC technique allows the determination of the electric field gradient (EFG) at the probe sites.

Keywords HfO_2 · PAC spectroscopy · Electric field gradient · Thin film

1 Introduction

In the last three decades mainly SiO_2 was used as a gate dielectric in the silicon based CMOS (complementary-metal-oxide-semiconductors) technology, and since integrated circuits are getting continuously smaller, the use of SiO_2 is facing its technological limits. High-k materials substituting SiO_2 are currently under intense investigation to face the down-scaling process in the CMOS technology. The basic

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idea is to find a material with a higher dielectric constant k than that of SiO_2, which is compatible with the present Si technology. Hafnium dioxide (HfO_2) has high chemical stability, excellent dielectric properties ($k \simeq 23$) and mechanical hardness [1]. Even though significant effort has been dedicated to the investigation of Hf based gate dielectric material systems, key issues like bulk and interface oxygen diffusion, as well as charge trapping [2], still lack a complete understanding when the goal is a long-term operation of HfO_2 based devices. Those studies are not focused only on potential applications but they are also concerned with fundamental physics problems [3]. Crucial insight in the physics of these systems can be achieved only by atomic scale studies with direct measurements of the local structure and electronic environment. 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 ^{181}Ta as probe nuclei. The EFG reflects the charge distribution surrounding the probe nucleus. Since the magnitude of the signal decreases rapidly with the increase of the distance between the charges and the probe nucleus, the EFG measurements provide unique information on the local arrangement into the grains and at interfaces of nanostructured materials and thin films.

2 Experimental procedure

The thin oxide films were deposited by electron beam evaporation process on a silicon substrate. The thickness of the films was about 100 and 250 nm. The ^{181}Hf activity was produced by neutron activation of the thin film in the Brazilian Research Reactor (IPEN IEA-R1) by the reaction ^{180}Hf(n,γ)^{181}Hf. The PAC measurements were performed with the thin film at room temperature in air. After annealing at 1473 K in air, new measurements were performed.

The PAC method is based on the hyperfine interaction of nuclear moments with extra nuclear magnetic fields or EFG's. In the case of electric quadrupole interaction, the experimental measurement gives the quadrupole frequency ν_Q with respective distribution δ as well as the EFG asymmetry parameter η. A detailed description of this method can be found in [2, 4]. Results of previous PAC works in HfO_2 can be found in the literature [5]. 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 $A_{22} = -0.288$ [4]. The $\gamma - \gamma$ PAC measurements were done 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 W(θ, t), where θ is the angle between detectors and t is the time delay between events, the time differential anisotropy follows.

$$R(t) = 2\frac{W(180^\circ, t) - W(90^\circ, t)}{W(180^\circ, t) + 2W(90^\circ, t)} \sim A_{22}G_{22}(t)$$

For a static quadrupole interaction, the perturbation function has the form

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

The frequencies ω_n are related to the quadrupole frequency $\nu_Q = eQV_{zz}/h$ by $\omega_n = g_n(\eta)\nu_Q$. The coefficients $g_n(\eta)$ are known functions of the asymmetry parame-

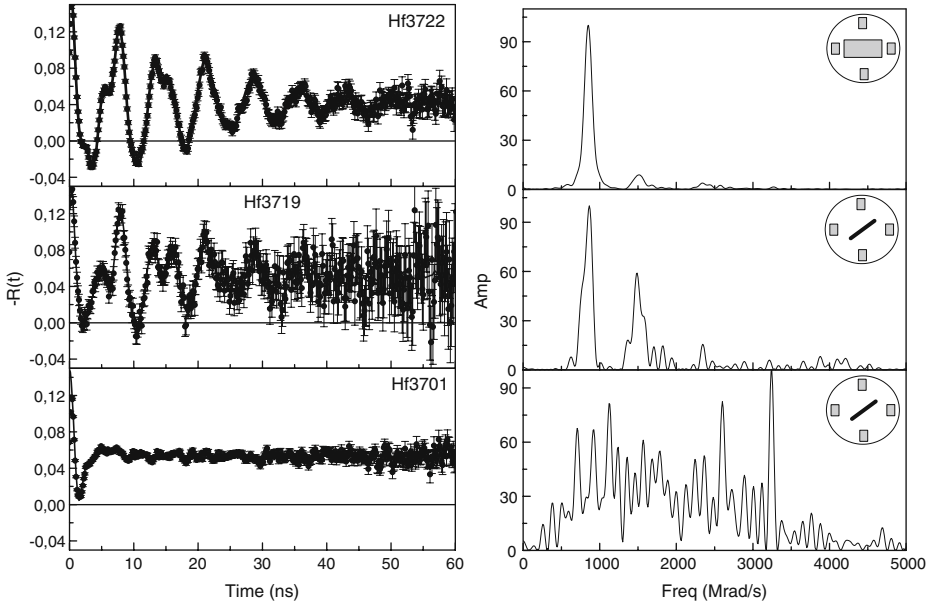

Fig. 1 Time differential anisotropy (*left*) with corresponding frequency spectra (*right*) for ^{181}Ta probe nuclei in a HfO_2 thin film measured as irradiated (Hf3701, 100 nm) and after annealing at 1473 K. *Solid lines* are the least squares fit of the theoretical function to the experimental data. The crystal orientation relative to the positions of the detectors are shown in the *circles*

ter $\eta = (V_{xx} - V_{yy})/V_{zz}$, 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. In the case of single crystals, the coefficients S_{2n} of the frequencies ω_n depend on both η and the angles between the emission direction of the γ-rays and the principal axes of the EFG tensor, which are defined by the position of the single-crystal relative to the detectors. Details of this dependence can be found elsewhere [4].

3 Results and discussion

Typical PAC results for the 100 and 250 nm thin films are shown in the Figs. 1 and 2. The left side shows the measured time differential anisotropy function R(t) fitted to the experimental perturbation function $G_{22}(t)$ and is derived from a least square fit procedure. On the right side, the Fourier analysis of R(t) are displayed. The results for the measurements as irradiated and after annealing in air for one hour at 1473 K are shown. In order to confirm the single-crystal nanostructure of the film, measurements have been performed at different orientations of the silicon substrate. The orientations of the crystallographic axes, with respect to the detectors (grey squares), are shown in the circles, and specified by the angles given in the figures.

Figure 1 clearly shows that the electric quadrupole frequencies measured after irradiation of the sample are in the range from 500 to 3,300 Mrad/s and have a

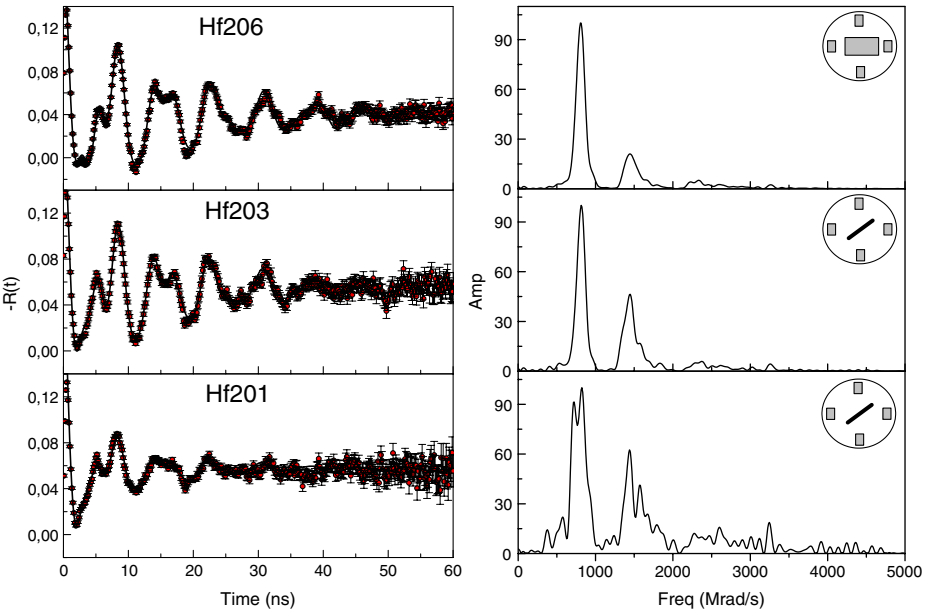

Fig. 2 Time differential anisotropy (*left*) with corresponding frequency spectra (*right*) for ^{181}Ta probe nuclei in a HfO_2 thin film measured as irradiated (Hf201, 250 nm) and after annealing at 1473 k. *Solid lines* are the least squares fit of the theoretical function to the experimental data. The crystal orientation relative to the positions of the detectors are shown in the *circles*

Table 1 Best fit parameters for the spectra

Sample	ν_Q (MHz)	η	δ (%)
Hf3701	814 (4)	0.37 (1)	14.82 (1)
Hf3719	796 (3)	0.35 (1)	3.89 (2)
Hf3722	793 (1)	0.37 (1)	4.71 (3)
Hf201	771 (3)	0.36 (1)	11.41 (2)
Hf203	766 (2)	0.35 (1)	5.55 (4)
Hf206	759 (3)	0.35 (1)	5.32 (2)

quite broad distribution. However, after annealing the distribution decreased and, consequently the frequencies are well defined it was possible to clearly see the crystallographic orientation of the films relative to the detectors. It was observed that the amplitude of the frequency ω_2 almost vanishes when the position of the samples change from face perpendicular to that with face parallel to the plane of the detectors. This difference is a clear indication that the sample is a single-crystal. In Table 1 the relevant hyperfine parameters obtained from the best least square fit to the experimental data are presented.

From the data shown in Figs. 1 and 2 we can see that after annealing at very high temperatures we have a very well-resolved electric quadrupole interaction. In the spectra as irradiated, we have a frequency distribution and the Fourier analysis shows a high frequency that vanishes with annealing. The time zero anisotropy A_{22} does not show any dependency on annealing temperature as observed in the measurements with HfO_2 powder samples [5]. The values of the well defined quadrupole frequency correspond to that expected for the quadrupole interaction of ^{181}Ta in the monoclinic phase of hafnium dioxide, [5–7]: $\nu_Q = 815$ MHz and $\eta = 0.38$.

4 Conclusions

The most striking result of the present study is that after the irradiation of the HfO_2 thin films are no more amorphous but nanostructured. The dimensions of the nanocrystals are initially very small and they grow with increasing annealing temperature. The EFG parameters measured at room temperature are in perfect agreement with the literature [5–7]. As is clearly seen in the Figs. 1 and 2 the frequencies ω_2 and ω_3 almost disappear for the measurements in which the orientation of the films is that with the surface of the film parallel to the plane of the detectors and showed that the film has a single crystalline structure with a preferred orientation regarding the main EFG axis which is essentially perpendicular to the surface of the substrate.

Acknowledgements FHMC thankfully acknowledge the support provided by Centro de Física Nuclear da Universidade de Lisboa (CFNUL) and ISEL in the form of research fellowships. MSC acknowledges the financial support from CAPES. AWC and RNS thankfully acknowledge the support provided by CNPq in the form of research fellowships.

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