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Perturbed angular correlation study of a nanostructured HfO_2 film

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Abstract The hyperfine field at ^{181}Ta lattice sites in a nanostructured HfO_2 thin film was studied by the perturbed angular correlation (PAC) technique. The thin oxide film was deposited by pulsed laser ablation on a silicon substrate kept at 673 K. The thickness was about 25 nm. The radioactive ^{181}Hf ions were produced by neutron activation of the very thin film in the Portuguese research reactor by the reaction ^{180}Hf(n,γ)^{181}Hf. PAC measurements were carried out at room temperature after annealing at different temperatures up to 1,473 K in air. The PAC technique allows determining the electric field gradient at the ^{181}Ta probe sites. The ^{181}Ta isotopes appear in the sample as disintegration product of ^{181}Hf.

Keywords Thin films · Hyperfine interactions · Silicon · Hafnium oxide

1 Introduction

Hafnium Oxide (HfO_2) has been studied in the last years due to its high dielectric constant $k \approx 23$ and interesting physics properties [1] that lead to use HfO_2 as a good candidate to replace SiO_2 in microelectronics. The increasing miniaturization of the semiconductor devices and the need to avoid tunneling currents for a decreased

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insulating layer thickness promotes the replacement of SiO_2 by HfO_2 [2]. Therefore, it would be interesting to perform research using a very sensitive local technique in order to search for structural changes and the point defects behavior, getting a better understanding of the properties at the interface between the HfO_2 layer and the Si substrate. This work reports a preliminary study of the HfO_2 thin film by means of the Perturbed Angular Correlation (PAC) technique. PAC is a powerful tool to study the EFG using the ^{181}Ta as a nuclear probe. The presence of hafnium in the film assures the possibility of using ^{181}Ta as probe.

2 Experimental procedure

The thin oxide film was deposited by pulsed laser ablation on a silicon substrate kept at 673 K. The film thickness was about 25 nm. The ^{181}Hf activity was produced by neutron activation of the thin film in the Portuguese Research Reactor by the reaction ^{180}Hf(n, γ)^{181}Hf using a neutron flux of 2×10^{13} n cm^{-2} s^{-1} for 60 h. The PAC measurements were performed with the thin film at room temperature in air. After annealing at different temperatures in air, new measurements were performed. 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 quadrupolar electric interaction, the experimental measurement gives the quadrupolar 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 [3]. Results of previous PAC works in HfO_2 can be found in the literature [4]. 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 $A_{22} = -0.288$ [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 (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

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

was calculated. $G_{22}(t)$ is the perturbation function which describes the time modulation of the angular correlation, f_i are the fractions of the probes used to fit the data.

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

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

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. In the case of single crystals, the coefficients S_{2n} depend on

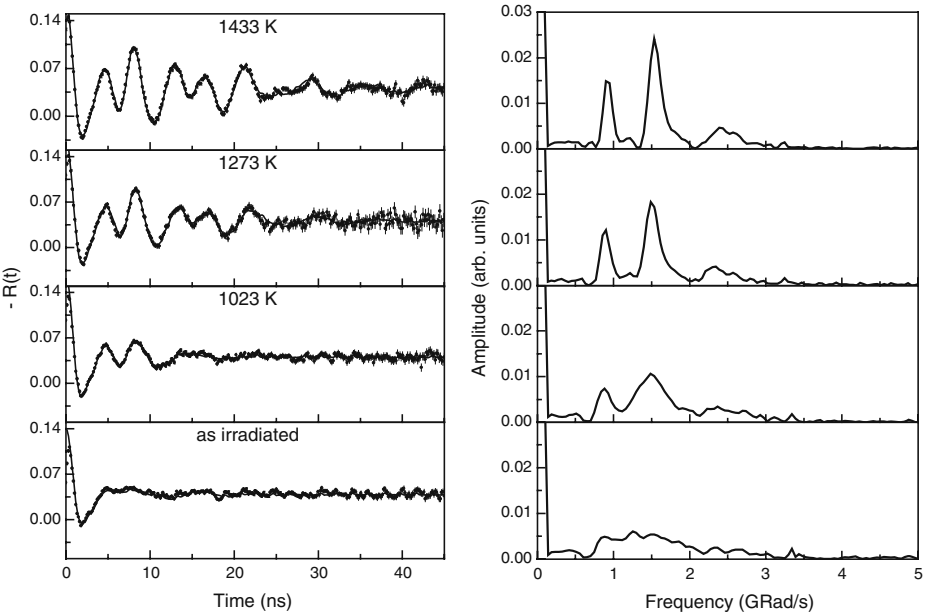

Fig. 1 Perturbed $R(t)$ functions (*left*) with corresponding frequency spectra (*right*) for ^{181}Ta probe nuclei in HfO_2 thin film measured after annealing at the indicated temperatures. *Solid lines* are the least squares fit of the theoretical function to the experimental data. The normal to the surface of the thin film was in the detectors plane at 45° with the detectors (orientation: 90°, 45°, 90°, −45°)

both η and the angles between the emission direction of the γ-rays and the principal axes of the EFG tensor. Details of this dependence can be found elsewhere [3].

The different crystal orientations relative to the four detectors are defined in the following way: Z is the axis normal to the detector plane and X and Y are along the lines which join opposite detectors. The spectra taken at different substrate orientations are labeled with the polar coordinates (Θ_2, Φ_2) and (Θ_3, Φ_3) of two crystallographic vectors $\mathbf{e_2}$ and $\mathbf{e_3}$, with respect to the laboratory system XYZ already defined. $\mathbf{e_2}$ was taken along the direction (010), and $\mathbf{e_3}$ was taken along the (100) axis. The angle Φ_i is undefined whenever $\Theta_i = 0$; these cases have been labeled with the letter u.

3 Results and discussion

Figure 1, left side, shows the measured anisotropy function $R(t)$ adjusted with the perturbation function $G_{22}(t)$ that describes the experimental data and is derived by the least square fit procedure. The results are shown for the measurement as irradiated and after annealing in air for one hour at the temperatures indicated in the figure. The orientation of the silicon crystal substrate during the measurements was such that the normal to the surface of the film was in the detectors plane, forming angles of 45° with the lines joining opposite detectors. On the right side of Fig. 1 the result of the Fourier analyses is displayed. It is clearly is shown that the amplitudes

Table 1 Best fit parameters for the spectra shown in Fig. 1

Temp. annealing (K)	ν_Q (MHz)	η	δ (%)	Fraction (%)
1,433	815 (1)	0.38 (1)	5.34 (8)	80
	972 (7)	0.48 (2)	7.62 (6)	20
1,273	792 (1)	0.36 (1)	7.03 (1)	80
	974 (7)	0.45 (2)	7.30 (4)	20
1,023	778 (4)	0.36 (1)	14.45 (3)	80
	904 (14)	0.79 (3)	11.11 (1)	20
As irradiated	778 (3)	0.39 (1)	19.68 (3)	49
	1257 (4)	0.25 (3)	31.50 (1)	51

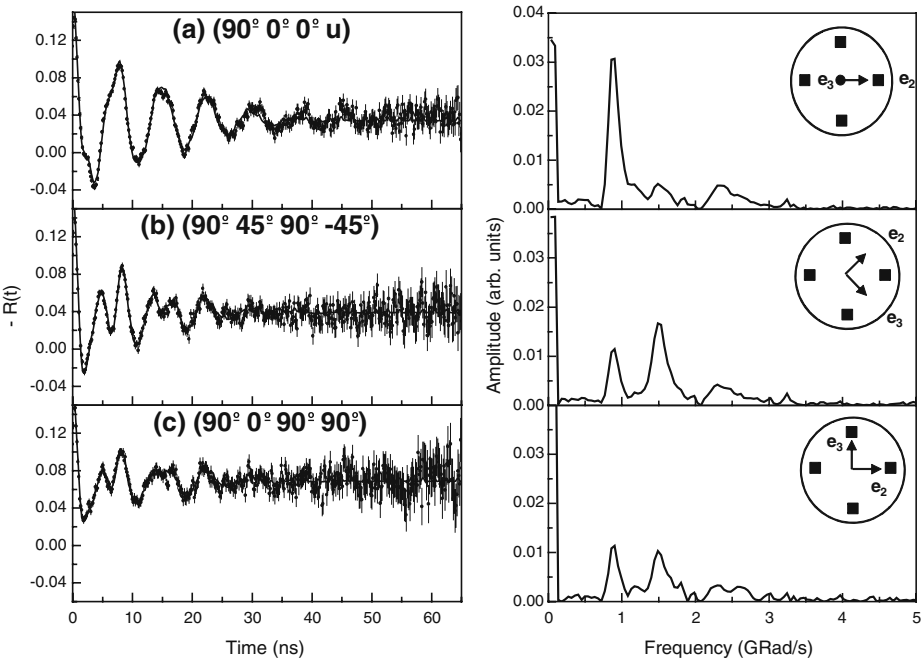

Fig. 2 $R(t)$-functions taken at different crystal orientations. The substrate crystalline orientation is defined by the positions of the vectors $\mathbf{e_2}$ and $\mathbf{e_3}$ relative to the detectors

of the three sharp frequencies ω_1, ω_2 and ω_3 increase with increasing temperature of annealing.

In Table 1 are shown the relevant parameters of the best least square fit to the experimental data. We realize that the best fit is obtained with two frequencies corresponding to two different fractions characterized by different η and δ.

In order to confirm the single crystalline structure of the film, measurements have been performed for different orientations of the silicon substrate after annealing at 1,233 K. Results are displayed in Fig. 2. The orientations of the crystallographic axes $\mathbf{e_2}$ and $\mathbf{e_3}$ of the Si substrate, with respect to the detectors (black squares), are shown in the circles, and specified by the angles given in the figures.

The Fourier analyses of the spectra displayed in Fig. 2a show the signature of the almost single crystal with an EFG essentially normal to the plane of the sample: only

Table 2 Best fit parameters for the spectra obtained for measurements after annealing at 1,233 K

Orientation	ν_Q (MHz)	η	δ (%)	Fraction (%)
90° 0° 0° u°	738 (3)	0.38 (1)	7.94 (9)	80
	937 (6)	0.51 (1)	7.17 (6)	20
90° 45° 90–45°	789 (1)	0.36 (1)	7.54 (1)	80
	966 (8)	0.47 (2)	7.65 (5)	20
90° 0° 90° 90°	789 (2)	0.36 (1)	7.63 (3)	80
	944 (10)	0.51 (3)	8.03 (1)	20

The angle Φ_i is undefined whenever $\Theta_i = 0$; these cases have been labeled with the letter u

Table 3 S_{2n} parameters for both interactions fitted to the spectra obtained after annealing at 1,233 K

Orientation	S_{20}	S_{21}	S_{22}	S_{20}
90° 0° 0° u°	0.19 (2)	0.50 (3)	0.12 (4)	0.18 (4)
90° 45° 90–45°	0.23 (3)	0.21 (3)	0.39 (4)	0.17 (4)
90° 0° 90° 90°	0.45 (5)	0.19 (4)	0.23 (5)	0.13 (4)

The angle Φ_i is undefined whenever $\Theta_i = 0$; these cases have been labeled with the letter u

ω_1 is seen. The spectrum shown in Fig. 2b reproduces the same orientations that the data in Fig. 1. The increase in the S_{20} in the spectrum Fig. 2c confirms than the principal axis of the EFG is essentially along e_3. The parameters of the least square fits are shown in Tables 2 and 3.

From the data shown in Fig. 1 we conclude that only after annealing at very high temperatures we can see a very well-resolved electric quadrupole interaction. In the spectra as irradiated, we observe a broad frequency distribution. This EFG distribution can be due to structural defects, very small nanocrystals or amorphous material. The time zero anisotropy A_{22} does not show any dependency with increased annealing temperature as observed in the measurements with HfO_2 powder samples [4]. The values of the quadrupole frequency and the asymmetry parameter obtained after annealing at 1,433 K correspond to the ones expected for the quadrupole interactions of ^{181}Ta in the monoclinic phase of hafnium oxide: $\nu_Q = 815$ MHz and $\eta = 0.38$ [4–7].

4 Conclusions

The main conclusion from the measurements shown in Figs. 1 and 2 are that after the irradiation of the film, it appears as amorphous, plenty of structural defects or consisting in very small nanocrystals. With increasing annealing temperature the film adopt a single crystalline structure displaying a preferred orientation with the main EFG axis essentially perpendicular to the surface of the substrate. As is clearly seen in the Fig. 2 the frequencies ω_2 and ω_3 almost disappear for the measurement with the surface of the film in the plane of the detectors. The ω_2 frequency is dominant if the film is measured in the geometry of the measurements shown in Fig. 1. A second conclusion is that we distinguish two fractions of probe atoms, one of 80% that can be associated to ^{181}Ta in monoclinic Hafnium oxide. The other fraction of 20% corresponds to the ^{181}Ta probes in a region of the film with a different crystalline structure, probably near to the interface.

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