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PAC study of HfO_2 nanofilms grown on Si substrates

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ABSTRACT

Thin oxide films (100 nm) grown on silicon (1 0 0) substrates were characterized by Perturbed Angular Correlation (PAC). Three samples were analyzed: (a) prepared by electron beam evaporation; (b) prepared by atomic-layer chemical vapor deposition method, with H_2O and $HfCl_4$ as precursors; (c) prepared by metal organic chemical vapor deposition with tetrakis-diethyl-aminohafnium and O_2 as precursors. The radioactive ^{181}Ta isotopes used as PAC probes appeared in the samples after the β-decay of ^{181}Hf. These isotopes were introduced, in the cases of samples prepared by chemical vapor deposition, by ion implantation. In the case of samples prepared by electron beam evaporation, the PAC isotopes ^{181}Hf were produced by neutron activation of the film by the reaction ^{180}Hf(n,γ)^{181}Hf. PAC measurements were carried out at room temperature after annealing at different temperatures from 773 K up to 1273 K in air. The PAC technique allows to determine the electric field gradient at the probe sites. In this way, the crystallization of the hafnium oxide films was monitored, characterizing at a nanoscopic level the atomic surrounding of the probes.

1. Introduction

HfO_2 is recognized as one of the best dielectric material for present next generation of complementary metal-oxide semiconductor devices, due to its high thermodynamic stability on silicon and high permittivity compared to other dielectrics (k > 20–25) [1]. Specifically, the interest is to replace SiO_2 as gate dielectric in the semiconductor devices, keeping the dielectric thickness in the nanometer range. For this reason many complex methods were used during the last decade to obtain nanostructured thin films of HfO_2 on silicon [2]. We have studied thin films, prepared by some of these methods, by means of the Perturbed Angular Correlation (PAC) technique. This technique allows to determine the electric field gradient (EFG) at probe sites. In this way, the crystallization of the hafnium oxide films was monitored, characterizing at a nanoscopic level the atomic surrounding of the probes. Measurements were carried out at room temperature after annealing under air at different temperatures up to 1273 K.

2. Experimental

2.1. Sample preparation

We got samples deposited on to (1 0 0) Si by three methods.

Sample "a" was prepared depositing hafnium by electron beam evaporation (EBE), the silicon substrate was kept at 573 K during the procedure [3]. Sample "b" was prepared by atomic layer deposition (ALD). This method provides the growth of ultrathin HfO_2 films with acceptable conformality, density and dielectric properties [4]. ALD proceeds via alternate exposure of the substrate surface to evaporated metal and oxygen precursors and the solid film forms as a result of successive surface reactions between monolayers of precursor molecules alternately adsorbed. In the present case were used Cl_4Hf and water as precursors. The substrate was kept at 573 K during deposition.

Sample "c" was prepared by metal organic chemical vapor deposition (MOCVD). This method is similar to ALD, but an organic metal precursor is used. The process involves the molecular deposition and the pyrolysis of the precursor. In our case tetrakis-diethyl-aminohafnium and O_2 were used as precursor. The substrate was kept at 758 K during deposition.

Details of the preparation of the samples "b" and "c" are given in Ref. [5].

2.2. ^{181}Hf/^{181}Ta Perturbed Angular Correlation measurements

In the case of sample "a", the PAC isotopes ^{181}Hf were produced by neutron activation of the film in the reactor of CNEA (Comisión Nacional de Energía Atómica, Argentina) by the reaction ^{180}Hf(n,γ)^{181}Hf. The radioactive ^{181}Ta isotopes used as PAC probes appeared in the samples after the β-decay of ^{181}Hf. In the cases of samples "b" and "c", the isotopes were introduced by ion implantation. The implantation was carried out at the H-ISKP (Helmholtz Institut für Strahlen und Kernphysik der Universität Bonn) using ions with an energy of 160 keV.

The two γ-rays emitted in cascade from the excited state of ^{181}Ta, populated from the β-decay of ^{181}Hf in the sample, were detected by a planar setup of four BaF_2 detectors arranged in 90° geometry. The coincidence-counting rate, after discounting accidental counts, can be written as:

$$W(\theta, t) = W_0 \left[\exp\left(-\frac{t}{\tau}\right)\right] \left[1 + \sum_k A_{kk} G_{kk}(t) P_k(\cos\theta)\right] \quad (1)$$

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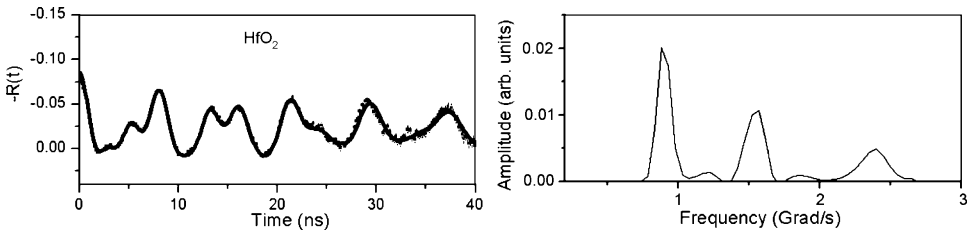

Fig. 1. Typical PAC results obtained with a powder sample of polycrystalline HfO_2 (bulk). The striped area indicates the contribution of I_1 and the shadowed area indicates the contribution of I_2 to the transform. This transform shows the frequencies ω_1, ω_2 and ω_3 associated with each contribution (see Eq. (3)).

where W_0 is a constant which will be eliminated in the data treatment, τ is the mean lifetime of the intermediate state of the probe nucleus, A_{kk} are the angular correlation coefficients, G_{kk} are the perturbation factors, $P_k(\cos\theta)$ are Legendre polynomials and θ is the angle between the detectors. Since only A_{22} term is relevant for the case of ^{181}Ta, taking measurements at 90° and 180°, the perturbation factor is extracted by determining the ratio:

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

If the perturbation is caused by a static EFG acting on the probe nucleus of quadrupole moment Q and the EFG tensor is described by its main component V_{zz} and the asymmetry parameter η, the perturbation factor is

$$G_{22}(t) = \sigma_{20} + \sum_{n=1}^{3} \sigma_{2n} \cos(\omega_n t) \cdot \exp(-\delta\omega_n t) \quad (3)$$

The coefficients σ_{2n} and frequencies ω_n are known functions of the asymmetry parameter η and quadrupole frequency $\omega_Q = eQV_{zz}\pi/2h$. The effect of a Lorentzian frequency distribution of width δ around ω_Q is taken into account by the exponential of Eq. (3).

To consider the possibility of several phases, a superposition of perturbation factors weighted with their relative fractions f_i was assumed. This linear combination, convoluted with the time revolution of the equipment, was fitted to the experimental data.

3. Results and discussion

Typical PAC results are shown in Fig. 1. These results were obtained using a powder sample of polycrystalline HfO_2 (bulk). They are displayed for further comparison with those obtained with the films. This spectrum was fitted assuming the existence of two fractions of probes in the oxide which undergo quadrupole interactions I_1 and I_2. The corresponding hyperfine parameters are:

I_1	$f_1 = 83(2)\%$	$\omega_{Q1} = 127.7(2)$ Mrad/s	$\eta_1 = 0.34(1)$	$\delta_1 = 3.1(1)\%$
I_2	$f_2 = 17(1)\%$	$\omega_{Q2} = 99.4(9)$ Mrad/s	$\eta_2 = 0.70(3)$	$\delta_2 = 6.0(9)\%$

The interaction I_1, with a very well defined frequency, corresponds to the monoclinic phase of hafnium oxide. It gives account of the three major peaks in the Fourier transform. The contribution I_2 corresponds to another phase of hafnium oxide. It is probably the cubic phase stabilized by a small amount of impurities [6]. The characteristic hyperfine parameters for this phase have been reported for different aliovalent impurities and typical values are in the following ranges: $\omega_Q = 90$–100 Mrad/s, $\eta_1 = 0.75$–1 and $\delta_1 = 5$–15% [7–9]. This phase contains many oxygen vacancies, which produce a nonzero EFG at the probe site.

The spectra obtained with the samples "as prepared" are shown in Fig. 2. The spectrum 2a, corresponding to the sample prepared by EBE, was fitted with the following interactions:

I_1	$f_1 = 79(5)\%$	$\omega_{Q1} = 175(5)$ Mrad/s	$\eta_1 = 0.71(4)$	$\delta_1 = 31(2)\%$
I_2	$f_2 = 15(4)\%$	$\omega_{Q2} = 316(3)$ Mrad/s	$\eta_2 = 0.48(5)$	$\delta_2 = 4(1)\%$
I_3	$f_3 = 6(1)\%$	$\omega_{Q3} = 433(1)$ Mrad/s	$\eta_3 = 0$	$\delta_3 = 0\%$

I_1 corresponds to probes in an amorphous phase. These probes are subjected to a broad distribution of EFGs. The frequency distribu-

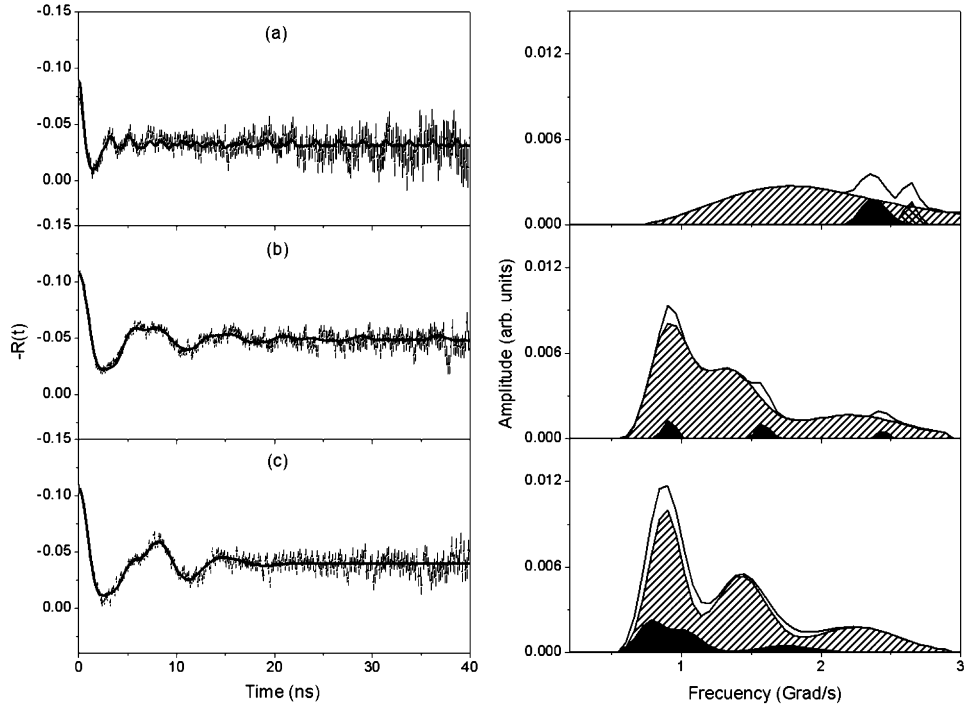

Fig. 2. PAC spectra and their Fourier transforms, for samples a–c. The striped area indicates the contribution of I_1, the shadowed area indicates the contribution I_2 and crossed area indicates the contribution of I_3 to the transform.

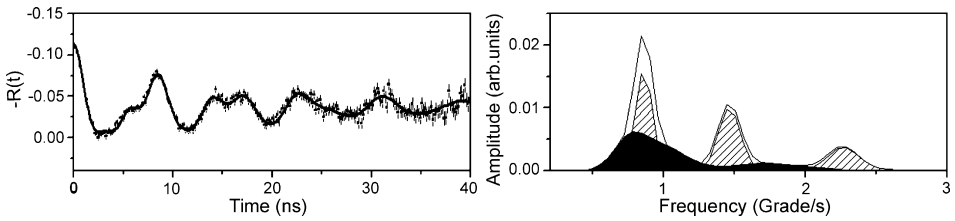

Fig. 3. PAC spectrum obtained with sample c after annealing at 773 K. The striped area indicates the contribution of I_1 and shadowed area indicates the contribution of I_2 to the transform.

tion is centered at a value much higher that the average values of the hafnium oxide frequencies. As the hafnium evaporation was carried out in an ultra-high vacuum chamber, not much oxidation is expected at this stage. The interactions I_2 and I_3 can be associated with nanocrystals of well defined composition as indicated by the reduced value of δ_2 and δ_3. The last interaction was assumed to be axially symmetric ($\eta = 0$) because the high value of the quadrupole frequency does not allow to determine η. The contribution of each interaction to the Fourier transform is shown in Fig. 2.

The spectrum 2b, corresponding to the sample prepared by ALD, was fitted with the following interactions:

I_1	$f_1 = 95(5)\%$	$\omega_{Q1} = 111(1)$ Mrad/s	$\eta_1 = 0.53(1)$	$\delta_1 = 16(1)\%$
I_2	$f_2 = 5(1)\%$	$\omega_{Q2} = 130(1)$ Mrad/s	$\eta_2 = 0.32(3)$	$\delta_2 = 1.0(1)\%$

In this case, the hyperfine parameters of the interaction I_2 keep correspondence with the parameters associated with the monoclinic phase of hafnium oxide. In the Fourier transform it is possible to identify the three peaks corresponding to this interaction and to observe that they appear practically where the characteristic values for bulk material are expected. In the case of interaction I_1, the distribution of the EFGs is higher than expected for a well crystallized material, indicating that the film has many defects. These defects have been, at least partially, introduced during the ion implantation. This interaction can be associated with a defective monoclinic phase of hafnium oxide.

The spectrum 2c (sample prepared by MOCVD) was fitted with the following interactions:

I_1	$f_1 = 85(5)\%$	$\omega_{Q1} = 118(1)$ Mrad/s	$\eta_1 = 0.42(1)$	$\delta_1 = 13(1)\%$
I_2	$f_2 = 15(4)\%$	$\omega_{Q2} = 87(2)$ Mrad/s	$\eta_2 = 0.65(1)$	$\delta_2 = 12(1)\%$

Here, the hyperfine parameters of the predominant interaction are close to those of the monoclinic phase of hafnium oxide. Again, the distribution of the EFGs is higher than expected for a well crystallized material, indicating that the phases have defects. Like the previous case, defects have been introduced partially during the ion implantation. The second interaction can be assigned to another defective phase of hafnium oxide. We will assume it is the defective cubic phase.

To study the removal of defects and crystallization, the samples were annealed. The thermal treatments had duration of 30 min and were carried out at intervals of 100 °C, beginning at 773 K. The spectrum obtained with sample "c", after annealing at this temperature is shown in Fig. 3. It can be fitted with the following interactions:

I_1	$f_1 = 59(3)\%$	$\omega_{Q1} = 120(1)$ Mrad/s	$\eta_1 = 0.34(1)$	$\delta_1 = 4.5(2)\%$
I_2	$f_2 = 41(2.0)\%$	$\omega_{Q2} = 85(1)$ Mrad/s	$\eta_2 = 0.65(3)$	$\delta_2 = 16(2)\%$

I_1 is associated with probes in polycrystalline monoclinic hafnium oxide. The interaction I_2 corresponds to probes in the defective cubic phase of hafnium oxide. The subsequent annealing treatments, in the case of this sample, do not produce significant

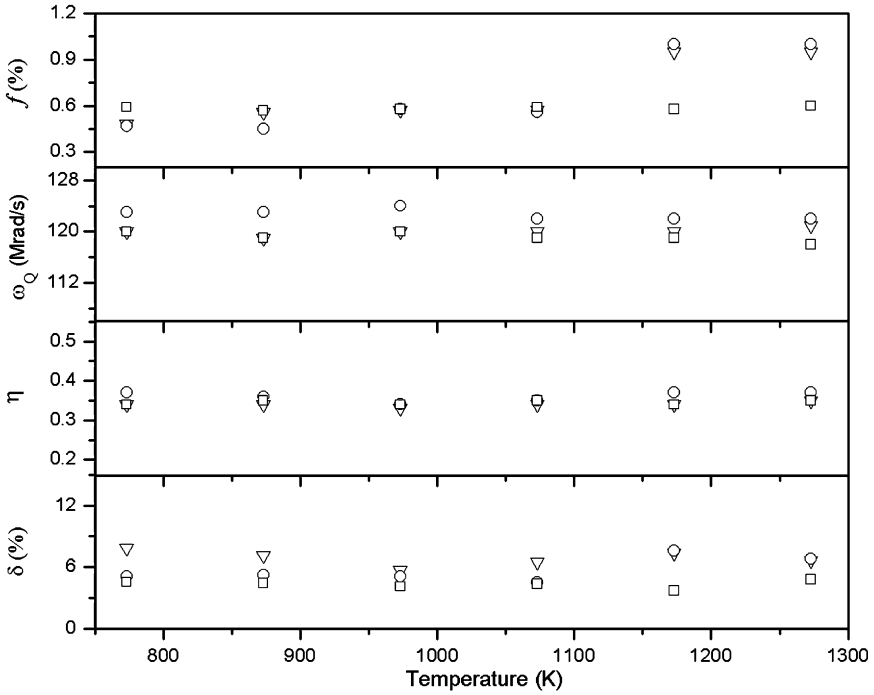

Fig. 4. Evolution of the PAC parameters of I_1 as a function of annealing temperature for the three samples. (▽) EBE, (◯) ALD and (□) MOCVD.

changes in the hyperfine parameters as is shown in Fig. 4 (only for interaction I_1), where these values are displayed as a function of the annealing temperature. This indicates that the first annealing at 773 K is the most important. In the cases of samples "b" and "c", the implantation produced radiation damage. This is the reason for the change of sample "c" with the first annealing. This sample was grown with the substrate at 758 K, and thus the removed defects with the annealing at 773 K were introduced during the implantation. The spectra kept this appearance until the last treatment, carried out at 1273 K. The quadrupole frequency remains in all the cases a little below the value corresponding to bulk monoclinic hafnium oxide. The frequency distribution width δ decreases but remains higher than the value expected for bulk material, indicating the contributions of probes near to the interfaces of the film.

In the case of samples "a" and "b", after annealing at 773 K, the interactions I_1 and I_2 are also present in similar proportions, but in these cases, annealing at temperature higher than 1073 K produce the removal of I_2 in benefit of I_1.

The coefficients σ_{2n}, in Eq. (3), depend on the Euler angles given orientation of the principal axes of the electric field gradient tensor respect to the laboratory frame. In the present study all the spectra were fitted assuming polycrystalline samples without any preferential orientation. After the annealing at 1273 K, PAC measurements were carried out for different substrate orientations, without to see any difference in the spectra. All this indicate that the films were polycrystalline. These results contrast with those of similar PAC experiments carried out on hafnium thin films of 25 nm of thickness prepared by Pulsed Laser Ablation [10].

4. Conclusions

The films have grown amorphous or plenty of defects depending on the method of preparation. In all cases a high degree of crystallinity is achieved with annealing at 773 K. The films consist essentially of the monoclinic phase of hafnium oxide and of a defective phase with similar characteristics in all the cases. Whereas the defective phase is removed by annealing at temperature higher that 1073 K in the case of samples prepared by EBE and ALD, it remains in the case of the sample prepared by MOCVD. In the three cases, after annealing at the highest temperature (1273 K) the width of the frequency distribution remains larger than the expected value for bulk material, indicating the contribution of probes near to the interfaces of the films.

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