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PAC study in the HfO_2–SiO_2 system

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ABSTRACT

A high-*k* HfO_2/SiO_2 gate stack is taking the place of SiO_2 as a gate dielectric in field effect transistors. This fact makes the study of the solid-state reaction between these oxides very important. Nanostructure characterization of a high-energy ball milled and post-annealed equimolar HfO_2 and amorphous SiO_2 powder mixture has been carried out by perturbed angular correlations (PAC) technique. The study was complemented with X-ray diffraction and positron annihilation lifetime spectroscopy (PALS). The experimental results revealed that the ball milling of equimolar mixtures increases the defects concentration in hafnium oxide. No solid-state reaction occurred even after 8 h of milling. The formation of $HfSiO_4$ (hafnon) was observed in the milled blends annealed at high temperatures.The PAC results of the milled samples are compared with those obtained for pure *m*-ZrO_2 subjected to high-energy ball milling and with reported microstructure data for the system ZrO_2–SiO_2.

1. Introduction

The nanotechnological interest in reducing the dimensions of Si complementary metal–oxide–semiconductor devices has led to a need of replacing the SiO_2 gate insulator with high-*k* dielectric oxides, in order to maintain a smaller leakage current without loosing the gate properties. Among many candidates, HfO_2 and its alloys with SiO_2 have attracted the attention due to their high permittivity and thermodynamic stability concerning solid-state reactions with Si substrate. With the aim of studying in the near future the reactions between both oxides at the interface of thin films, we began to investigate a more simple system: the binary oxide blend SiO_2–HfO_2. With this objective, perturbed angular correlations (PAC) and positron lifetime studies (PALS) of the solid state reactions between both oxides mixed by ball milling have been performed.

High-energy ball milling is a useful tool for solid-state powder processing that involves repeated welding, fracturing, and re-welding of particles. It enables powder particles to be always in contact with atomically clean surfaces minimizing the diffusion distance. The technique has been widely used to synthesize a variety of equilibrium and non-equilibrium alloy phases without posterior annealing [1] and to reduce the critical temperature of solid state-reactions [2].

High-energy ball milling on binary oxide blends containing hafnium oxide can give different results depending on the chemical nature of the other oxide and relative amounts between them. In particular, the damage produced in HfO_2 depends on the hardness of the other oxide.

The purpose of the present work is to study the solid-state reaction between the mentioned oxides using equimolar binary blends subjected to high-energy ball milling followed by thermal treatments under air.

Although it is well known that the formation of $HfSiO_4$ (hafnon) occurs after a long high temperature annealing of the blend HfO_2–SiO_2 [3], the behavior of these oxides subjected to milling followed by annealing treatments has not been studied. A few reports exist on a similar system containing Zr, a well-known surrogate for hafnium. In particular, it has been reported the synthesis of nanocrystalline $ZrSiO_4$ (zircon) [4] from equimolar blends of ZrO_2 and amorphous SiO_2 by ball milling and subsequent annealing.

We carried out these studies using the perturbed angular correlations (PAC) method and complementary techniques, such as X-ray diffraction and positron annihilation lifetime spectroscopy (PALS). This last method is highly sensitive to vacancy-like defects in solids. The measurement of the positron lifetime gives information on the type and quantity of defects.

The PAC method is a powerful tool for the determination of the electric field gradients (EFG) at atomic sites in solids. In this way it is possible to characterize different compounds and phases. The method requires a radioactive probe with special properties. In the present study, the probe ^{181}Ta was introduced by doping the starting material HfO_2 with radioactive ^{181}Hf that decays to the

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mentioned probe by β emission. Preliminary results are presented in this paper.

2. Materials and methods

PAC gives information of the electric field gradients (EFG) at atomic sites in solids allowing the determination of the atomic configuration around them. The method requires a radioactive probe with special nuclear properties located at the site where the EFG is to be measured: the isotopes must decay through the emission of two gamma rays in cascade. The technique is based on the existence of an angular correlation between these gamma rays. If the nucleus interacts with its surroundings during the decay, the angular correlation is perturbed. In the case of quadrupole electric interaction, the experimental measurement gives the values of the two components that characterize the EFG tensor: the quadrupole frequency ω_Q and the EFG asymmetry parameter η. The width δ of the possible distribution of frequencies around the mean value of ω_Q is also obtained. A detailed description of this method can be found in the literature [5].

The samples consisted in equimolar blends of HfO_2 (Aldrich Chem. Co. 98%) and SiO_2 (Johnson Matthey Alfa Products Spec-pure). The hafnium oxide was activated by thermal neutron capture at the CNEA (Comisión Nacional de Energía Atómica) reactor. The radioactive isotopes ^{181}Hf were produced by the nuclear reaction ^{180}Hf (n, γ) ^{181}Hf. The β^- decay of ^{181}Hf ($T_{1/2}$ = 42 d) gives place to the PAC probe ^{181}Ta. The mixed oxides were ball milled in a horizontal vibratory mill (Retsch MM2) in air at a frequency of 30 Hz. The ball to powder mass ratio was about 6. The oxides blends were milled during 2, 4, 6 or 8 h (denoted hereinafter B_2, B_4, B_6 and B_8) and pelleted. After measuring the hyperfine interactions on the milled blends, subsequent spectra were obtained after annealing them for 30 min at increasing temperatures covering the 500–1200 °C thermal range. All the PAC measurements were carried out at room temperature.

Samples without activity were prepared in the same way for X-ray diffraction (XRD) analysis and PALS studies.

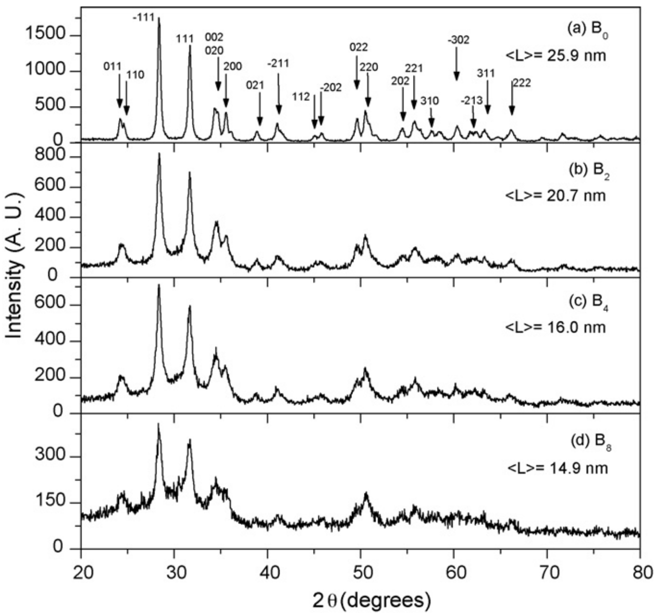

Fig. 1. XRD patterns for (a) the unmilled blend, (b) B_2 (c) B_4 and (d) B_8. The major peaks of monoclinic hafnium oxide are indexed. It is shown, for each case, the average grain size $\langle L \rangle$ extracted from the fitting of the XRD pattern (in all the cases the statistical error is 0.5 nm).

3. Results and discussion

The X-ray powder patterns recorded from the unmilled (B_0) homogenous mixture and patterns obtained for the ball milled powder mixtures are shown in Fig. 1. The diffractogram of the unmilled mixture seemingly contains only the reflections of the monoclinic phase of hafnium oxide (m-HfO_2). Reflections of SiO_2 do not appear due to the amorphous nature of the starting material. It is evident from the figure that in the course of ball milling, the peak broadening has increased. This broadening results from the refinement of grain size (from 25.9 nm in the starting material to 14.9 nm in the 8 h milled sample) and the augment of internal strain. It is also evident that there is no trace of the formation of $HfSiO_4$ even after 8 h of ball milling. This clearly indicates that hafnon cannot be prepared just by ball milling equimolar blends of HfO_2 and SiO_2. The broad diffuse halo signals that appear especially in samples B_4 and B_8 could correspond to a Hf–Si–O amorphous phase.

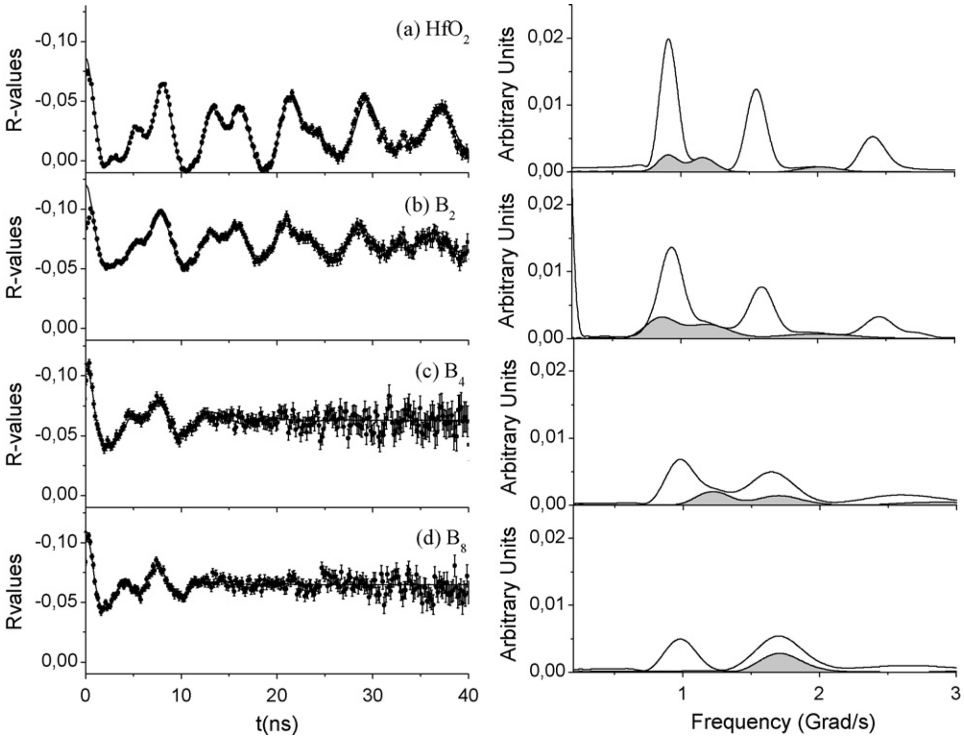

Fig. 2. PAC spectra and their Fourier transforms. A shadowed area indicates the contribution of I_2 to the transform. (a) Hafnium oxide, (b) B_2, (c) B_4 and (d) B_8.

PAC spectra and their fitting curves for hafnium oxide (starting material) and selected milled samples are shown in Fig. 2. All these spectra were fitted assuming the existence of two quadrupole interactions. A well-defined interaction, hereinafter denoted as I_1, corresponding to m-HfO_2 ($\omega_Q = 128$ Mrad/s, $\eta = 0.34$) [6] is obtained for the starting material and gives account of the three major peaks of the Fourier transform (FT). The shadowed area in the FT shows the contribution of another interaction I_2 that can be associated with a defective phase.

Although I_1 and I_2 are present in the milled blends spectra (Fig. 2b–d), it is observed that, as the milling time increases, the hyperfine parameters of I_2 change and its relative fraction f_2 increases. In particular, it can be observed a significant change in I_2 after the 4 h milling treatment. After the final milling, I_2 can be associated with amorphous regions that could include silicon atoms. In this way, the material would become an aggregate of nanocomposites of m-HfO_2 and amorphous Hf–Si–O phases. The assumption of the formation of a Hf–Si–O amorphous phase is founded on the analysis of previous PAC results in ball milled pure ZrO_2 [7]. Due to the structural similarity between ZrO_2 and HfO_2 and the chemical similarity between the cations, the hyperfine interactions that experience the hafnium probes in ZrO_2 are the same that those measured in HfO_2 starting material in the present work. It has been shown that the ball milling of zirconia only leads to phase transformations (from m-ZrO_2 to t-ZrO_2) but not to the appearance of an interaction similar to that we have labelled I_2 in the milled samples. This would indicate the presence of both cations in the amorphous phases.

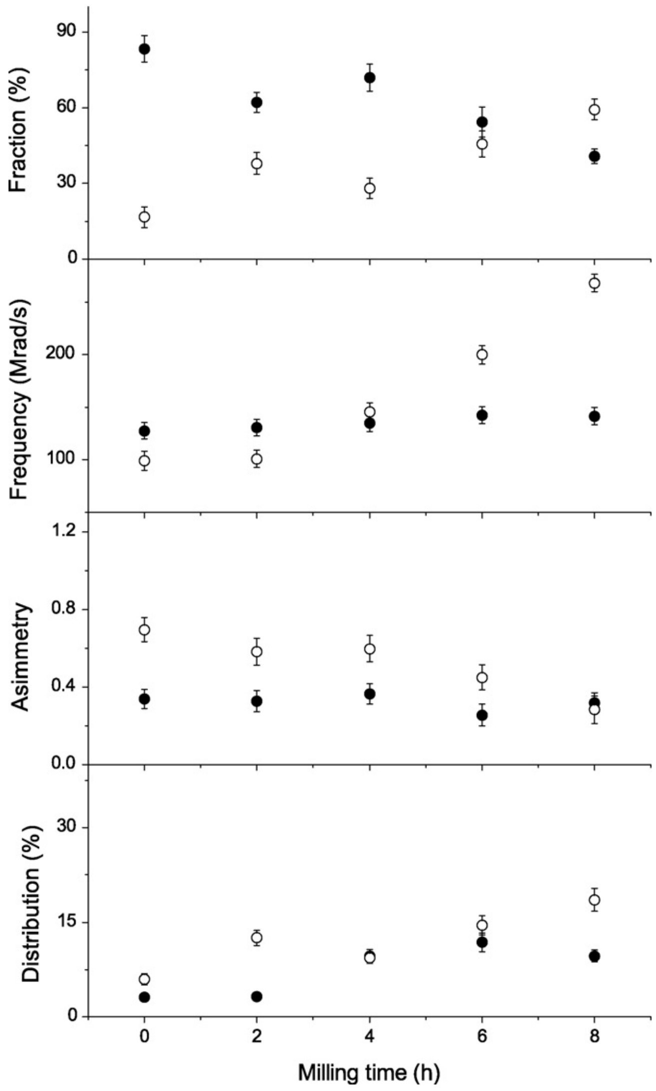

Fig. 3. Evolution of the PAC parameters of the blend as a function of milling time. (●) m-HfO_2 and (○) defective phase.

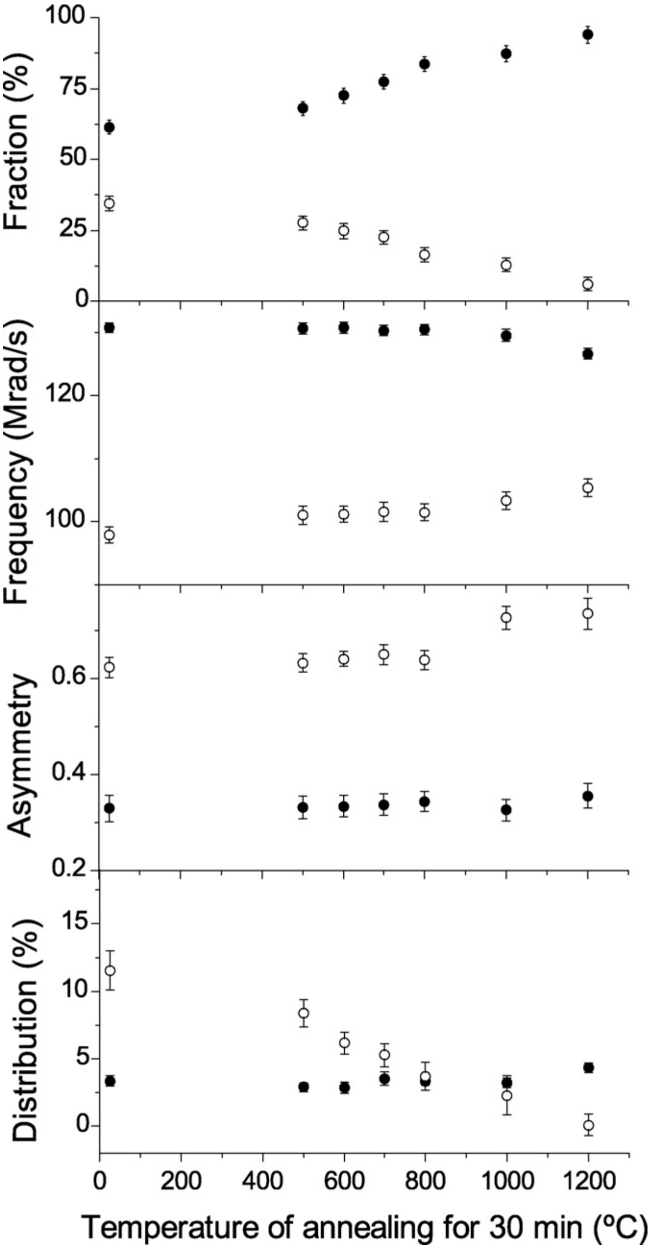

Fig. 4. Evolution of the PAC parameters of B_2 as a function of annealing temperature. (●) m-HfO_2 and (○) defective phase.

Regarding the evolution of the PAC parameters with the milling time (shown in Fig. 3) only I_2 presents relevant changes. Defective phase transformations are revealed by an increase in δ_2 and especially by a notable augment in the frequency ω_2.

The evolution of PAC parameters of B_2 as a function of temperature is plotted in Fig. 4. The interaction associated to m-HfO_2 becomes unique with the annealing treatments due to the gradual recovery of the defects and crystallization of the amorphous regions. This process includes the segregation of minority atoms from the amorphous phases. Similar behaviour was observed with the other milled samples.

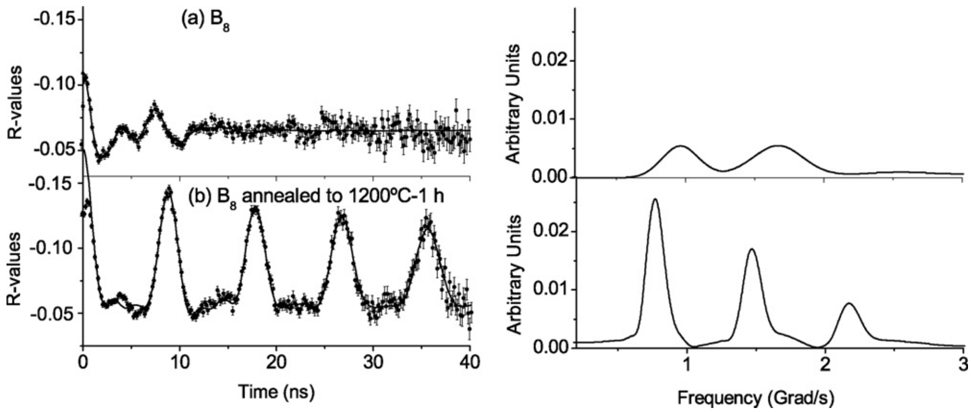

Fig. 5. PAC spectra and Fourier transforms for (a) B_8 and (b) B_8 annealed to 1200 °C for 1 h.

Although it has been reported the synthesis of $ZrSiO_4$ (zircon) from an equimolar blend of ZrO_2–SiO_2 subjected to ball milling treatment for 5 min and post-annealed to 1200 °C during 1 h [4], no trace of $HfSiO_4$ was found after the annealing to the same temperature. This apparent discrepancy between these analog systems is probably due to the characteristics of the thermal treatment. In our case we arrived gradually to the final temperature while in the experiments on Zr-based blends the heating was done directly to 1200 °C. The gradual heating probably avoids the solid-state reaction due to the segregation of minority cations from amorphous phases and the increase of particle size of the starting materials.

For this reason, and in order to produce a solid-state reaction, a direct thermal annealing to 1200 °C during 1 h was carried out to fresh samples B_2 and B_8. In Fig. 5 the spectra and the fitting curves obtained for B_8 before and after the thermal treatment are shown. A dramatic change in the characteristic of the interactions is observed in Fig. 5b. The spectrum for the annealed sample was fitted assuming the existence of a predominant interaction characterized by the following hyperfine parameters:

$$I_1: \quad f_1 = 61.7(2.2)\%, \quad \omega_{Q1} = 117.6(0.3)\,\text{Mrad/s}, \quad \eta_1 = 0.05(0.02), \quad \delta_1 = 2.8(0.2)\%$$

According to the literature this main component can be associated with the formation of $HfSiO_4$ (hafnon) [3,8]. The rest of the probes are in defective phases with unknown stoichiometry.

Diffraction patterns of fresh non-radioactive samples B_2 and B_8 directly annealed at 1000 °C during 2 h are displayed in Fig. 6. The thermal treatment resulted in the recrystallization of HfO_2 in B_2 and the production of a solid-state reaction in B_8 giving place to $HfSiO_4$.

PALS characterizations were made on the milled samples and in B_2 after annealed at 1000 °C during 2 h. The positron lifetime spectra were decomposed into three exponential decays, each one characterized by a positron lifetime τ_i of intensity f_i. No source correction was done. The two main components, τ_1 of 175 ps and τ_2 of 375 ps do not depend on the milling time. The value of τ_3 is 1700 ps for B_2 and it decreases to 1450 ps for B_8.

The first lifetime component τ_1 could be associated with positron annihilation in the bulk of the material. A value of 194 ps has been reported in cubic 9YSZ ball milled ceramic [10]. Regarding τ_2, it includes positron annihilation in the kapton radioactive cover material and in certain vacancy-like defects. The long-lived lifetime, τ_3 is assigned to the annihilation in air spaces between the powder particles. The decrease of this component with the milling time is due to the size reduction of the spaces. All the intensities remain constant with the milling treatments. The thermal annealing in B_2 results in the decrease of f_2 in benefit of f_1 due to the disappearance of defects that contributed to the second component.

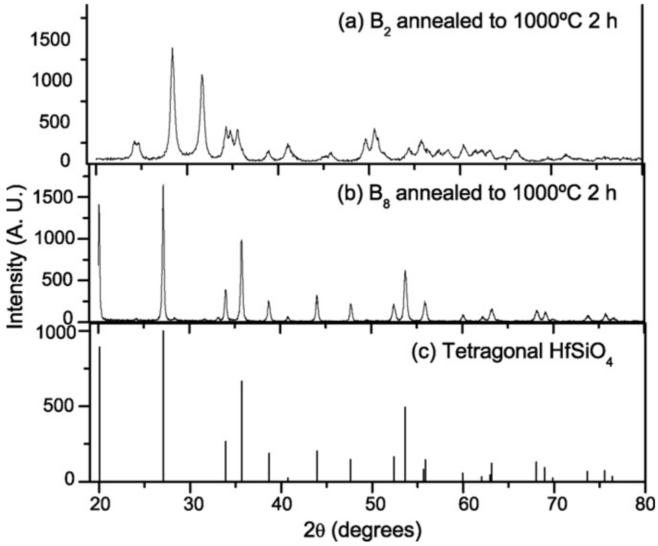

Fig. 6. XRD patterns for (a) B_2 annealed at 1000 °C for 2 h and (b) B_8 annealed at 1000 °C for 2 h. In (c) the main peaks of tetragonal $HfSiO_4$ [9] are shown.

4. Conclusions

Experiments show that ball milling on the blends results in the formation of nanocomposites of *m*-HfO_2, and amorphous Hf–Si–O phases. The serial annealing treatments remove the defects and lead to the crystallization of hafnium oxide from the amorphous phase. This process includes the segregation of minority cations from the different phases.

The formation of hafnon occurs for adequate milling times followed by annealing at high temperature. This compound does not appear after the gradual thermal treatments.

Similar experiments on ball milled pure *m*-HfO_2 and ZrO_2–SiO_2 equimolar blends will be performed to elucidate the nature of the defective phase.

Acknowledgements

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