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$_2$.

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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 losing 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...
mentioned probe by $\beta$ 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 $\omega_Q$ and the EFG asymmetry parameter $\eta$. The width $\Delta$ of the possible distribution of frequencies around the mean value of $\omega_Q$ 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,$\gamma$) $^{181}$Hf. The $\beta^-$ decay of $^{181}$Hf ($T_{1/2} = 42$ d) gives place to the PAC probe $^{181}$Ta. The $\beta^-$ 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 $^\circ$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.

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. 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).](image1)

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$_8$. 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).
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.

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 $\delta_2$ and especially by a notable augment in the frequency $\omega_2$.

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.
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:

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

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 $\tau_i$ of intensity $f_i$. No source correction was done. The two main components, $\tau_1$ of 175 ps and $\tau_2$ of 375 ps do not depend on the milling time. The value of $\tau_3$ is 1700 ps for B$_2$ and it decreases to 1450 ps for B$_8$.

The first lifetime component $\tau_1$ 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 $\tau_2$, it includes positron annihilation in the kapton radioactive cover material and in certain vacancy-like defects. The long-lived lifetime, $\tau_3$ 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 anneal-

![Fig. 5. PAC spectra and Fourier transforms for (a) B$_8$ and (b) B$_8$ annealed to 1200 °C for 1 h.](image)

![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.](image)

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

This work was partially supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CICPBA), Argentina.
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