



Evolution of the quadrupole hyperfine interaction while milling a Si-HfO₂ blend

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ABSTRACT

As HfO₂ appears as a good candidate to replace SiO₂ in Si complementary metal-oxide-semiconductor devices, a refined knowledge of the possible solid-state reactions between Si and HfO₂ is valuable. Being the Perturbed Angular Correlations technique a very sensitive method to detect small changes in solid state, the goal of this work is to follow the different stages that occur while ball milling a blend Si-HfO₂ by inspecting the hyperfine quadrupole interaction at Hf sites. The characterization is complemented by X-ray diffraction analysis. For comparison, a similar study on pure *m*-HfO₂ is carried out. The results seem to reveal a gradual incorporation of Si in a tetragonal defective phase of hafnia with milling time. In addition, the formation of precursor arrays of the HfSiO₄ structure takes place. After an annealing at 1000 °C an important amount of crystalline hafnion appears.

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1. Introduction

Silicon based complementary metal oxide semiconductor (Si-CMOS) devices consist in a piece of silicon covered by a gate dielectric substance, typically silicon dioxide (SiO₂). As these devices operate with high leakage currents in the nanometric scale, the industry focuses nowadays on the replacement of the SiO₂ gate insulator with new materials, in particular high- κ dielectric oxides. Among these oxides hafnia (HfO₂) appears as a good candidate to substitute SiO₂ due to its hardness and its wide band gap. In spite of its undesirable interfacial phases, namely silicides, silica, and silicates, it has been reported that the mixture of HfO₂ and ZrO₂ with SiO₂ exhibit excellent electrical properties and high thermal stability in direct contact with Si [1,2]. Thus, a refined knowledge of the possible interface reactions between hafnia and silicon is of main interest.

The Perturbed Angular Correlations (PAC) method [3] has proved to be an efficient tool in the investigation of the solid state because it allows the determination of different atomic configurations around special sites (the probe atom sites), hardly resolvable by other techniques. The method briefly consists in an inspection of the angular correlation of the 133–482 keV γ – γ cascade emitted during the ¹⁸¹Hf to ¹⁸¹Ta β -decay. The comparison of the measured angular correlation against that of the isolated probe, known from

the nuclear physics, allows gathering information about the electric field gradients (EFGs) existing in the lattice where the nuclear probes are immersed. The information is drawn from the determination of the so-called quadrupole parameters that describe the EFG at the hafnium lattice site, i.e., its intensity (through the quadrupole frequency ω_Q) and its departure from axial symmetry (through the asymmetry parameter η). In addition, the degree of local disorder due to the presence of impurities or defects in the atomic array can be measured through the distribution width δ of ω_Q . On account of the r^{-3} dependence of the quadrupole interaction, the technique is extremely localized and nonequivalent probe surroundings can be determined.

High-energy mechanical milling is a well-suited method for solid-state processing which has demonstrated its effectiveness for obtaining nanocrystalline sized systems. As milling proceeds, the periodically welding, fracturing and colliding of the particles has the potential to activate different surface processes such as diffusion leading to doping, alloying and new phases formation by means of room temperature solid state reactions [4–6].

PAC technique was previously used to investigate phase transformations in zirconia and hafnia based systems induced by thermal and mechanical processes [7–9] and HfO₂ films grown on silicon substrates [10,11]. In order to contribute with new information about the possible interface reactions between HfO₂ and SiO₂, we carried out recently a Perturbed Angular Correlations study [12]. In that work, the evolution of an equimolar HfO₂ and amorphous SiO₂ powder mixture subjected to high-energy ball milling and annealing treatments was followed by PAC and X-ray diffraction (XRD). As it was expected, mechanical milling produced essentially an augmentation of defects in the hafnium oxide phase which

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was verified by both techniques. In addition, the solid-state reaction that ends up in hafnon (HfSiO_4) formation after annealing the milled blend took place. Due to the amorphous nature of silica, the gradual evolution of the silicon containing phase could not be monitored. Thus it was not possible to discern if the obtained results arose exclusively from the ball milling treatment (structural defects and reduction of particle size) or if the presence of silicon atoms had any influence on them. With the aim of elucidate this point we carried out a study of pure hafnium oxide and a mixture of crystalline silicon and hafnia powders subjected to high energy ball milling. Both systems were studied by PAC and XRD being the first one a control experiment of the damage produced just by mechanical work. Our principal interest is centered in the second system.

2. Experimental

The PAC method is based on the hyperfine interactions of nuclear moments with extra nuclear fields. A detailed description of this method can be found in the literature [13]. The γ - γ 133–482 keV cascade, populated by the β^- decay of ^{181}Hf , was used to measure the quadrupole interaction of the 482 keV ($+5/2$) state of ^{181}Ta . The γ - γ PAC measurements were done using a standard setup with four conical BaF_2 scintillation detectors with a time resolution of 0.6 ns (FWHM). The time differential anisotropy was calculated from the coincidence spectra $N(\theta, t)$, where θ is the angle between detectors and t is the time delay between the two gamma events.

$$R(t) = 2 \frac{N(180^\circ, t) - N(90^\circ, t)}{N(180^\circ, t) + 2N(90^\circ, t)} = A_{22}G_{22}(t) \quad (1)$$

$G_{22}(t)$ is the perturbation function and has the following form for a static quadrupole interaction:

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

The frequencies ω_n are related to the quadrupole frequency $\omega_Q = \pi e Q V_{zz} / 20 h$ by $\omega_n = g_n(\eta) \omega_Q$. The coefficients $g_n(\eta)$ are known functions of the asymmetry parameter $\eta = (V_{xx} - V_{yy}) / V_{zz}$, where V_{kk} ($k=x, y, z$) denotes the principal components of the EFG tensor. The exponential function accounts for a Lorentzian frequency distribution of width δ around ω_Q . We fitted the experimental ratio $R(t)$ by using:

$$R(t) = A_{22} \sum f_i G_{22}^i(t) \quad (3)$$

where f_i is the relative fraction of nuclei that experiences a given perturbation $G_{22}^i(t)$.

^{181}Hf was obtained by activation of ^{180}Hf present in natural metallic hafnium by thermal neutron capture at the CNEA (Comisión Nacional de Energía Atómica, Argentina) RA3 reactor. The radioactive metallic hafnium was dissolved in a HF 4% solution and dropped over HfO_2 powder (98%, Aldrich Chem. Co.). The diffusion of ^{181}Hf into the oxide was assured performing a thermal treatment at 1000°C during 5 h. The obtained radioactive hafnium oxide was mixed with an equimolar amount of crystalline silicon to prepare the Si- HfO_2 blend. High-energy ball milling of 500 mg of the starting material was conducted in a horizontal vibratory mill (Retsch MM2) in air atmosphere at a frequency of 30 Hz. Milling was performed at room temperature for different durations in a stainless steel cylinder (volume 5 cm^3) using one 3 g ball made of the same material keeping the ball to powder mass ratio at about 6 throughout the experiment.

Non-radioactive equimolar mixtures of silicon and hafnia were prepared and treated in the same way to perform complementary X-ray diffraction analyses. These measurements were carried out in a Phillips X'pert PW 1710 diffractometer using $\text{Cu-K}\alpha$ radiation in the range $20^\circ \leq 2\theta \leq 80^\circ$ with steps of 0.05° every 2 s.

XRD and PAC measurements were performed on the sample after selected milling times. A final result was obtained by annealing the mixture at 1000°C for 2 h after the last milling step.

Equivalent PAC and XRD measurements were carried out on pure HfO_2 as control experiments.

3. Results and discussion

XRD patterns from the blend Si- HfO_2 at different milling times are shown in Fig. 1. Diagrams clearly show, as milling proceeds, the attenuation and broadening of the peaks from monoclinic hafnia ($m\text{-HfO}_2$) and crystalline silicon. In particular, the latter peak disappears after 5 h of mechanical treatment. In addition, the appearance of a second defective phase is evident around $2\theta = 30^\circ$. This phase can be associated with the tetragonal structure of hafnia ($t\text{-HfO}_2$)

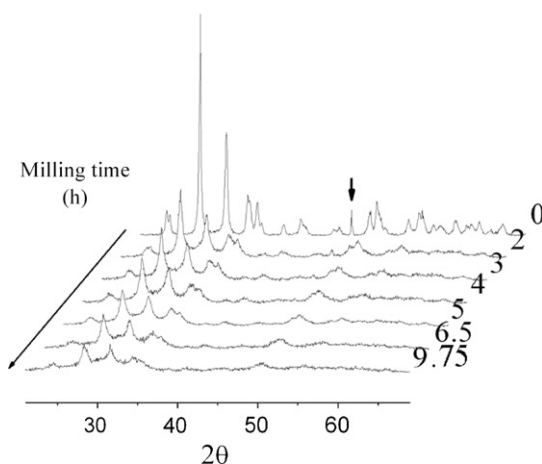


Fig. 1. XRD patterns of the Si- HfO_2 blend determined after different milling times. In the unmilled blend, the arrow points to a characteristic reflection of crystalline silicon while the rest of the peaks correspond to monoclinic hafnia.

where the main diffraction peak is expected exactly at the mentioned angle [14]. A similar behavior was observed in milled $m\text{-ZrO}_2$ (compound quite similar to $m\text{-HfO}_2$) where a defective tetragonal phase was evident at $2\theta = 30.3^\circ$ [7]. One of the parameters that tend to stabilize the tetragonal over the monoclinic form is the contribution of the surface energy which increases with the diminution of the crystallites size produced by ball milling [14,15]. Another cause of stabilization would be the presence of aliovalent impurities. The iron contamination of the samples, coming from the milling cylinders, was estimated to be less than 3 at.% by Mössbauer Spectroscopy. This small amount of Fe^{3+} could contribute partially to the stabilization of the tetragonal phase and will not affect the hyperfine interactions of the ^{181}Ta probes except for its contribution to the frequencies distribution δ , as it will be discussed below.

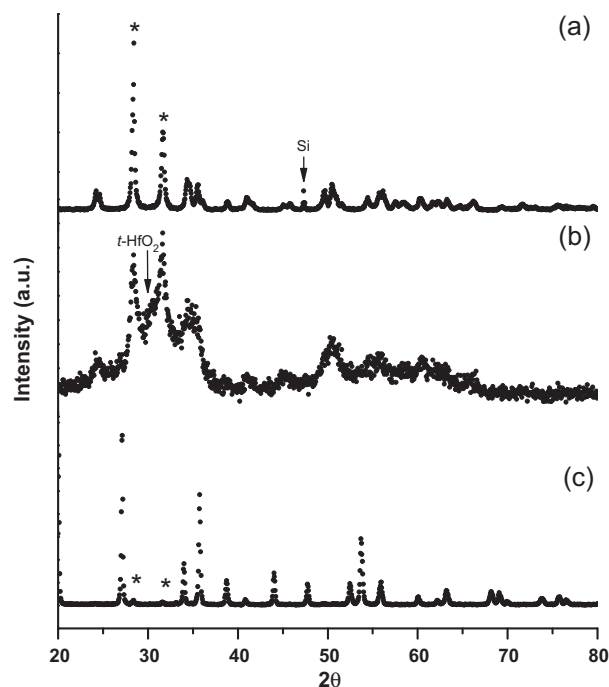


Fig. 2. Comparison between the diffractograms of the starting blend (a), the 9 h 45 min milled sample (b) and the annealed sample (c). Symbols indicate the major peaks of $m\text{-HfO}_2$ (*). The arrow points to characteristic reflections of crystalline silicon and $t\text{-HfO}_2$ in (a) and (b) respectively. In (c), the peaks without symbols correspond to HfSiO_4 .

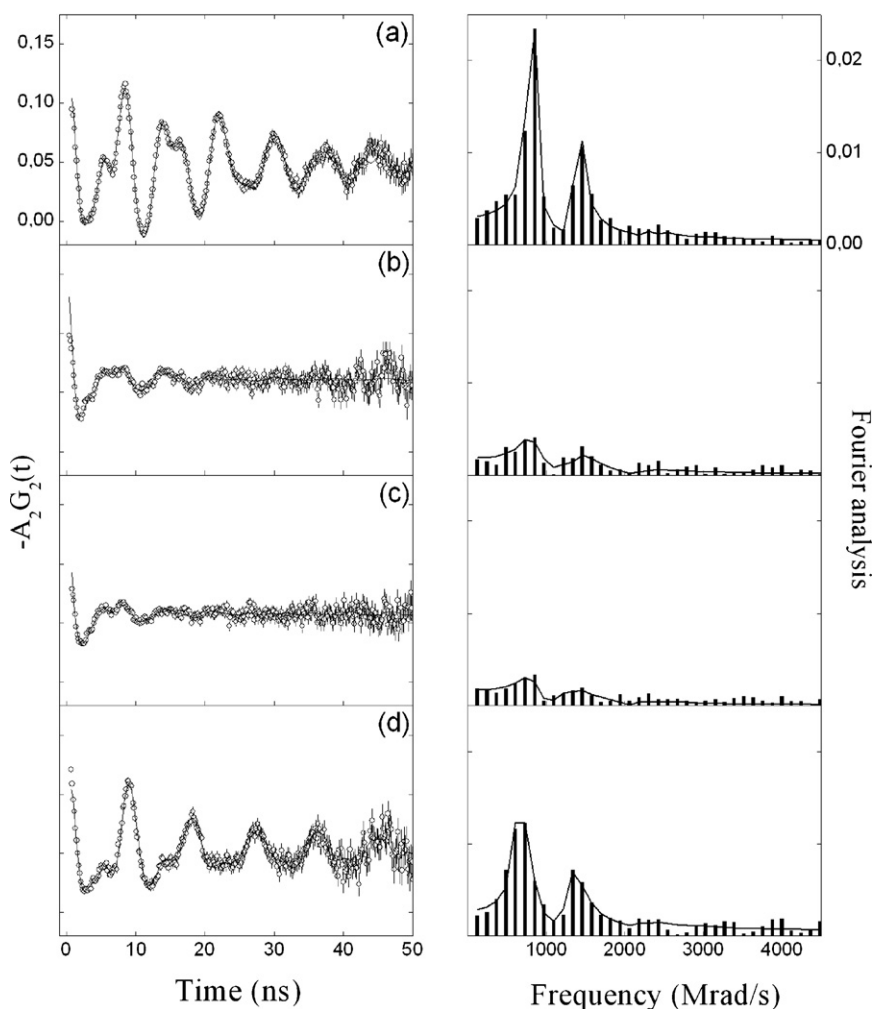


Fig. 3. Spin rotation curves and their corresponding Fourier analyses determined for the Si-HfO₂ blend: (a) starting material, (b) 4 h milled and (c) 9 h 45 m milled sample. The result after annealing the 9 h 45 m milled blend at 1000 °C during 2 h is shown in (d).

Similar diffractograms, except from the presence of the peak associated with silicon, were obtained in the control experiment involving only pure hafnium oxide. In this way the XRD patterns from Si-HfO₂ and from pure HfO₂ are essentially the same for milling times longer than 6 h.

In Fig. 2(a) and (b) the XRD patterns of the unmilled and the 9 h 45 min milled Si-HfO₂ mixture are shown in order to facilitate the comparison between the starting material and the result from the last milling step. In the latter (Fig. 2b) the complete disappearance of crystalline silicon, the broadening of the monoclinic hafnia peaks and the presence of an incipient peak corresponding to *t*-HfO₂ at $2\theta = 30.1$ are evident.

The noticeable modification of the diffractogram from the annealed sample, displayed in Fig. 2(c), undoubtedly reveals that the annealing produced a solid state reaction to give place to a formation of a new compound. The same compound, identified as HfSiO₄, was obtained in our previous work [12] after anneal at 1000 °C for 2 h a milled SiO₂-HfO₂. Indeed, the diffractogram displayed in Fig. 2(c) evidences, after the thermal treatment, the presence of a majority phase of HfSiO₄ that coexists with small traces of *m*-HfO₂. The existence of small amounts of hafnon after the last milling step (Fig. 2b) cannot be excluded.

Characteristic PAC spectra for the Si-HfO₂ blend obtained after selected milling times and for the annealed sample are shown in Fig. 3. In Fig. 3a, the spectrum from the unmilled blend is shown. Despite the starting material consists in two components, namely

silicon and hafnia, the PAC spectrum corresponds only to *m*-HfO₂ owing to the fact that the ¹⁸¹Hf isotopes were introduced in this phase. In consequence, the obtained results can be fitted with the typical *m*-HfO₂ hyperfine parameters [16]:

$$f_1 = 100\% \quad w_{Q1} = 125_1 \text{ Mrad/s} \quad \eta_1 = 0.36_1 \quad \delta_1 = 3_1\%$$

The evolution of the PAC spectra as milling proceeds (displayed in Fig. 3b and c) shows a diminution of the monoclinic phase of hafnia in benefit of the appearance of new phases, in agreement with the XRD. The observed high distribution δ of the characteristic frequencies is related to the nanoscopic disorder (structural defects, impurities, surface effects) in the vicinity of the probe atoms. The PAC spectrum from the annealed sample evidences a dramatic change of the sample after the thermal treatment, in concordance with XRD. This result is well fitted with two predominant fractions: a fraction of probes in the monoclinic phase (characterized by the parameters given above) and a fraction in HfSiO₄ through its characteristic quadrupole interaction:

$$w_Q = 115_1 \text{ Mrad/s} \quad \eta = 0.09_1 \quad \delta = 4_1\%$$

These parameters are in agreement with those reported in the literature [12,17,18].

In order to fit the PAC spectra following to the milling treatments, it was used up to three components. The fitted hyperfine parameters for the Si-HfO₂ blend are shown in Fig. 4. As we already

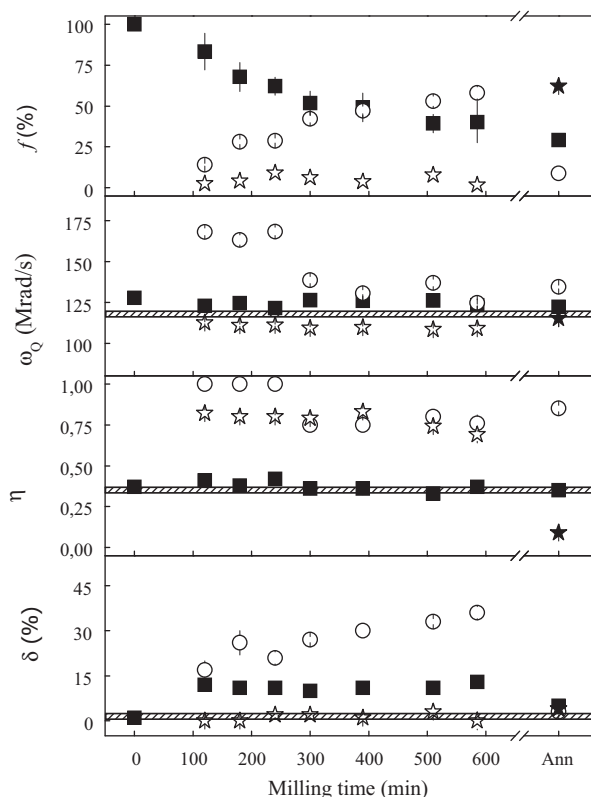


Fig. 4. Quadrupole parameters determined for different milling times of the Si-HfO₂ blend and for the annealed sample. Dashed regions represent the quadrupole parameters corresponding to *m*-HfO₂, free of defects [16].

mention, the milling treatment results in the diminution of the monoclinic phase of hafnia in benefit of the appearance of new phases. The two phases accompanying the monoclinic phase (full squares) must include silicon atoms as it can be infer from the comparison with the results of milled pure hafnia shown in Fig. 5. Therefore, before discussing the Si-HfO₂ results, we will analyze the results of this control experiment. Mechanical milling of pure hafnia results in a monotone diminution of the monoclinic phase in benefit of a new phase (open triangles) whose characteristic parameters remain practically constant with the milling treatments. In addition, the quadrupole parameters of the monoclinic phase progressively deviate from the values of the *m*-HfO₂ free of defects.

The new phase, which appears at expenses of the monoclinic one, can be associated with a tetragonal phase of hafnia since similar quadrupole frequencies were observed in stabilized tetragonal forms of ZrO₂ [7]. The presence of this tetragonal phase is in agreement with the XRD results.

Concerning the phases which appear when milling the Si-HfO₂ blend, one interaction becomes predominant with milling time (open circles in Fig. 4). This phase can be assigned to the stabilization of defective *t*-HfO₂ including silicon. This last statement is based on the observed differences in the defective *t*-HfO₂ hyperfine parameters of the two studied systems. It is interesting to note the abrupt modification of the frequency and asymmetry parameter of this interaction observed for milling times over 4 h in coincidence with the disappearance of the silicon signal in the diffractograms (Fig. 1). From this point, the fraction and characteristic quadrupole parameters of this phase remain constant except for a monotone increase in the distribution δ as milling progresses.

The other new phase (open stars), characterized by a well defined and with small amplitude interaction, remains constant

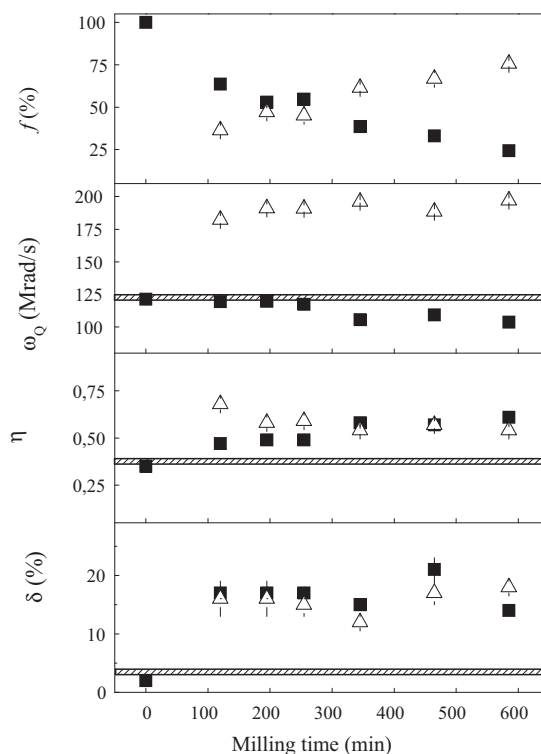


Fig. 5. Quadrupole parameters determined for the control experiment of milled HfO₂. Dashed regions represent the quadrupole parameters corresponding to *m*-HfO₂, free of defects [16].

along the whole milling procedure. A simple calculation, based on the point charge model, reveals that a vacancy in hafnium eight fold coordination in crystalline hafnion results in highly asymmetric interactions. In this way, this Si-Hf-O compound having a similar frequency to HfSiO₄ but with a higher asymmetry parameter can be ascribed to a defective hafnion phase. It is worth mentioning that after the annealing treatment the content of *m*-HfO₂ in the blend remains without major modifications and that crystalline HfSiO₄ appears at the expense of these new silicon containing phases.

Although it is clear that the majority phase results from the incorporation of Si atoms in the hafnium oxide matrix, the origin of the minority Si-Hf-O phase requires a more detailed analysis. The possibility of formation of this phase as a result of the doping of the Si matrix with hafnium or the incorporation of Si in the oxide matrix will be discussed. Experiments of ball milling of binary blends containing hafnia have been reported [19–21]. The doping with Hf atoms of the second component has been observed in the cases of binary blends containing Fe₂O₃, Cr₂O₃ [19] and Tm₂O₃ [20]. As an important difference with the present case, in these experiments the amount of HfO₂ was chosen to keep a concentration of Hf impurities up to 3 at.% respects to the total cation content. Moreover this fact made impossible the appearance of hafnia phases doped with the second cation. Regarding the minority Si-Hf-O phase that appears in the present equimolar blends, we consider improbable that it could arise from the incorporation of Hf in the Si matrix. The solid solubility of Hf in Si has not been determined, but is likely to be very small [22]. In addition, the fact that Hf is tightly bound to oxygen in the starting material and the difference of electronegativity between Si and Hf make the incorporation of Si in the Hf matrix a more reliable origin for this minority phase.

On the other hand, in the milling of the Si-HfO₂ blend, there is not a significant change in the quadrupole parameters

of remnant *m*-HfO₂, indicating that the presence of silicon diminishes the mechanical damage on the monoclinic phase. Moreover the absence of silicon in the control experiment results in a higher reduction of the monoclinic phase at longer milling times, having the remaining part of monoclinic hafnia parameters which differ from the characteristic values of the *m*-HfO₂ free of defects.

4. Conclusions

A global analysis of the experiments shows that the milling of silicon and hafnia produces the diminution of the monoclinic phase of hafnia in benefit of the appearance of new phases, both containing silicon atoms, as it can be inferred from the results of the control experiment. The majority of these phases seems to arise from a gradual incorporation of Si in a defective tetragonal phase of hafnia whereas a second minority well defined Si-Hf-O is also observed. Moreover, the presence of these silicon containing phases tend to diminish the mechanical damage on the remnant *m*-HfO₂ as milling progresses.

The formation of important amounts of crystalline HfSiO₄ is observed after anneal the milled silicon and hafnia blend at 1000 °C, at the expense of the silicon containing phases.

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References

- [1] G.D. Wilk, R.M. Wallace, J.M. Anthony, *J. Appl. Phys.* 89 (2001) 5243–5275.
- [2] G.D. Wilk, R.M. Wallace, J.M. Anthony, *J. Appl. Phys.* 87 (2000) 484–492.
- [3] H. Frauenfelder, R.M. Steffen, in: K. Siegbahn (Ed.), *Alpha-, Beta- and Gamma-ray Spectroscopy*, vol. 2, North Holland Publishing Co., Amsterdam, 1965.
- [4] C. Suryanarayana, *Prog. Mater. Sci.* 46 (2001) 1–184.
- [5] H.J. Fecht, *Nanostruct. Mater.* 6 (1995) 33–42.
- [6] Y. Chen, T. Hwang, M. Marsh, J.S. Williams, *Metall. Mater. Trans. A* 28 (5) (1997) 1115–1121.
- [7] A. Scian, E. Aglietti, M.C. Caracoche, P.C. Rivas, A.F. Pasquevich, A.R. Lopez García, J. Desimoni, P.C. Rivas, M.C. Caracoche, *J. Am. Ceram. Soc.* 77 (6) (1994) 1525–1530.
- [8] S. Koićki, M. Manasijević, B. Cekić, *Hyperfine Interact.* 14 (1983) 105–110.
- [9] M.C. Caracoche, M.T. Dova, A.R. López García, *J. Mater. Res.* 5 (9) (1990) 1940–1947.
- [10] A.F. Pasquevich, F.H.M. Cavalcante, J.C. Soares, *Hyperfine Interact.* 179 (2007) 67–72.
- [11] R.A. Quille, A.F. Pasquevich, *J. Alloys Compd.* 495 (2010) 634–637.
- [12] C.Y. Chain, L.C. Damonte, S. Ferrari, E. Muñoz, C. Rodríguez Torres, A.F. Pasquevich, *J. Alloys Compd.* 495 (2010) 527–531.
- [13] G. Schatz, A. Weidinger, *Nucl. Condens. Matter Phys.*, John Wiley & Sons, Chichester, 1996.
- [14] M. Forker, P. de la Presa, W. Hoffbauer, S. Schlabach, M. Bruns, D.V. Szabó, *Phys. Rev. B* 77 (2008) 054108–054111.
- [15] S. Schlabach, D.V. Szabó, D. Vollath, P. de la Presa, M. Forker, *J. Appl. Phys.* 100 (2006) 024305.
- [16] A. Ayala, R. Alonso, A. Lopez García, *Phys. Rev. B* 50 (6) (1994) 3547–3552.
- [17] H. Jaeger, S.P. McBride, *Hyperfine Interact.* 177 (2007) 51–56.
- [18] A. Vasquez, J.D. Rogers, A. Maciel, E.R. Fraga, *Rev. Bras. Fis.* 3 (1973) 311–315.
- [19] C.Y. Chain, R.A. Quille, A.F. Pasquevich, *Anales AFA* 21 (2009) 131–134.
- [20] E.L. Muñoz, G.N. Darriba, A.G. Bibiloni, L.A. Errico, M. Renteria, *J. Alloys Compd.* 495 (2010) 532–536.
- [21] C.Y. Chain, R.A. Quille, A.F. Pasquevich, *J. Alloys Compd.* 495 (2010) 524–526.
- [22] A.B. Gokhale, G.J. Abbaschian, in: T.B. Massalski, W.W. Scott Jr. (Eds.), *Binary Alloy Phase Diagrams*, vol. 3, 2nd ed., ASM International, USA, 1996.