Journal of Alloys and Compounds 536S (2012) S50–S54

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Evolution of the quadrupole hyperfine interaction while milling a Si-HfO_2 blend

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ARTICLE INFO

Article history:
Received 27 June 2011
Received in revised form 9 February 2012
Accepted 13 February 2012
Available online 24 February 2012

Keywords:
Oxide materials
Mechanical alloying
Hyperfine interactions
Perturbed Angular Correlations, PAC

ABSTRACT

As HfO_2 appears as a good candidate to replace SiO_2 in Si complementary metal-oxide-semiconductor devices, a refined knowledge of the possible solid-state reactions between Si and HfO_2 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-HfO_2 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-HfO_2 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 $HfSiO_4$ structure takes place. After an annealing at 1000 °C an important amount of crystalline hafnon appears.

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 (SiO_2). As these devices operate with high leakage currents in the nanometric scale, the industry focuses nowadays on the replacement of the SiO_2 gate insulator with new materials, in particular high-κ dielectric oxides. Among these oxides hafnia (HfO_2) appears as a good candidate to substitute SiO_2 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 HfO_2 and ZrO_2 with SiO_2 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 ^{181}Hf to ^{181}Ta 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 HfO_2 films grown on silicon substrates [10,11]. In order to contribute with new information about the possible interface reactions between HfO_2 and SiO_2, we carried out recently a Perturbed Angular Correlations study [12]. In that work, the evolution of an equimolar HfO_2 and amorphous SiO_2 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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doi:10.1016/j.jallcom.2012.02.082

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 $\omega_Q = \pi eQV_{zz}/20\,h$ 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 Cu-K_α radiation in the range $20^\circ \le 2\theta \le 80^\circ$ 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-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-HfO_2)

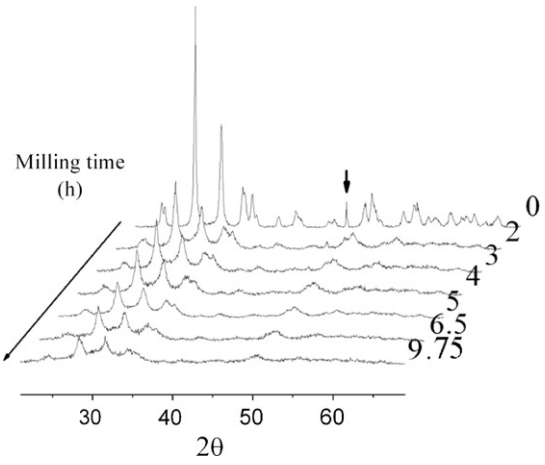

Fig. 1. XRD patterns of the Si-HfO_2 blend determined after different milling times. In the unmilled blend, the arrow points to a characteristic reflection of crystalline silicon while the rest of the peaks correspond to monoclinic hafnia.

where the main diffraction peak is expected exactly at the mentioned angle [14]. A similar behavior was observed in milled m-ZrO_2 (compound quite similar to m-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 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.

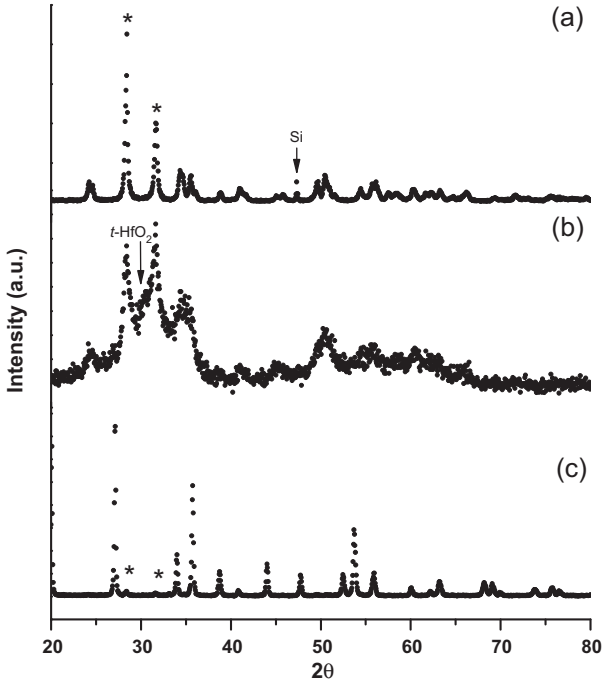

Fig. 2. Comparison between the diffractograms of the starting blend (a), the 9 h 45 min milled sample (b) and the annealed sample (c). Symbols indicate the major peaks of m-HfO_2 (*). The arrow points to characteristic reflections of crystalline silicon and t-HfO_2 in (a) and (b) respectively. In (c), the peaks without symbols correspond to $HfSiO_4$.