

## Stabilization of the cubic phase of $\text{HfO}_2$ by Y addition in films grown by metal organic chemical vapor deposition

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Addition of yttrium in  $\text{HfO}_2$  thin films prepared on silicon by metal organic chemical vapor deposition is investigated in a wide compositional range (2.0–99.5 at. %). The cubic structure of  $\text{HfO}_2$  is stabilized for 6.5 at. %. The permittivity is maximum for yttrium content of 6.5–10 at. %; in this range, the effective permittivity, which results from the contribution of both the cubic phase and silicate phase, is of 22. These films exhibit low leakage current density ( $5 \times 10^{-7}$  A/cm<sup>2</sup> at –1 V for a 6.4 nm film). The cubic phase is stable upon postdeposition high temperature annealing at 900 °C under  $\text{NH}_3$ . © 2006 American Institute of Physics. [DOI: 10.1063/1.2216102]

High dielectric permittivity oxides have been the focus of intensive researches directed towards finding a replacement for  $\text{SiO}_2$  as a gate dielectric in complementary metal-oxide-semiconductor (CMOS) devices.<sup>1,2</sup> Among the possible candidates,  $\text{HfO}_2$  is one of the most attractive due to its medium dielectric permittivity, high band gap, and reasonable band gap offsets with silicon.<sup>2–4</sup> Another important feature is its thermal stability with silicon at temperatures up to 1100 °C.<sup>5</sup> Zhao and Vanderbilt<sup>6</sup> have theoretically predicted that  $\text{HfO}_2$  exhibits a higher permittivity ( $\kappa$ ) in the cubic ( $\kappa \sim 29$ ) or in the tetragonal ( $\kappa \sim 70$ ) structures than in the monoclinic one ( $\kappa \sim 16$ –18), which is the stable thermodynamic phase at room temperature. It is therefore desirable to prepare  $\text{HfO}_2$  in the cubic or tetragonal forms. However, at atmospheric pressure, these structures are stable at high temperatures (the monoclinic to tetragonal and tetragonal to cubic transformations occur at, respectively,  $\sim 1700$  and  $\sim 2700$  °C).<sup>7,8</sup>  $\text{HfO}_2$  is isomorphous of  $\text{ZrO}_2$  with a similar structure.<sup>9</sup> For  $\text{ZrO}_2$ , it is well known that the cubic phase can be stabilized by adding oxides such as  $\text{MgO}$ ,  $\text{CeO}_2$ , or  $\text{Y}_2\text{O}_3$ . The cubic  $\text{HfO}_2$  structure is a fluorite-type structure<sup>8</sup> and  $\text{Y}_2\text{O}_3$  crystallizes in a cubic-centered structure ( $\text{Fl}_2\text{O}_3$  type). These two structures are closely related<sup>10</sup> and the phase diagram of  $\text{HfO}_2$ – $\text{Y}_2\text{O}_3$  (Refs. 8, 11, and 12) shows that it is indeed possible to stabilize  $\text{HfO}_2$  in the fluorite

structure. The cubic solid solution is stable in a wide compositional range (from 8/15% up to 50/60% for temperatures of 1500 °C or higher). In the form of thin films, very few studies have been devoted to the system  $\text{HfO}_2$ – $\text{Y}_2\text{O}_3$  and only limited selected compositions were investigated.<sup>13–15</sup> In this letter, addition of yttrium in  $\text{HfO}_2$  thin films prepared on silicon by metal organic chemical vapor deposition was investigated in a wide compositional range. The microstructure and electrical properties are discussed.

$\text{HfO}_2$  thin films were grown on *p*-type (100) Si/ $\text{SiO}_2$  ( $\sim 0.8$  nm) using liquid injection metal organic chemical vapor deposition. Octane solutions with  $\text{Hf}(\text{O}^i\text{Bu})_2(\text{mmp})_2$  and  $\text{Y}(\text{tmhd})_3$  (both 0.05M) were used as liquid precursors. The precursor solutions were mixed in different ratios in order to vary the Y content in the films. The pressure in the reactor was fixed at 133 Pa and the total flow rate was 350 SCCM (SCCM denotes cubic centimeter per minute at STP) (250 SCCM of  $\text{O}_2$  and 100 SCCM of Ar). The deposition temperature was in the range of 470–600 °C. The growth rate was typically of the order of 0.02 nm/s. The cationic composition of the films was determined from Rutherford backscattering spectrometry (RBS). The Y atomic percentage in the film was varied from 0 to  $\sim 73.7$  at. % (plus one film prepared at 99.5 at. % Y). This percentage is defined as the number of Y atoms relative to the total number of Y and Hf atoms. Electrical properties were measured on MOS structure using gold top electrodes deposited by evaporation.

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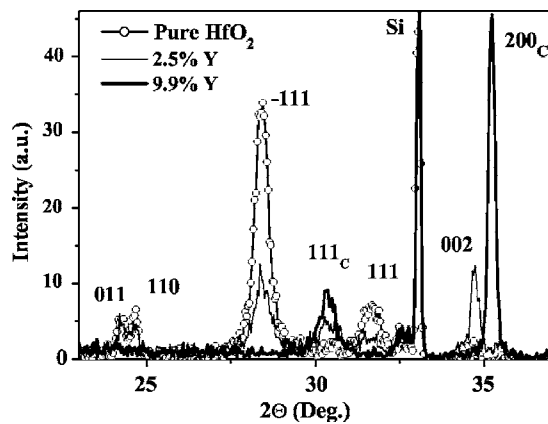


FIG. 1.  $\theta/2\theta$  scans of films with different Y contents (0, 2.5, and 9.9 at. %) grown at 600 °C on (100) Si (film thickness is of the order of 90 nm). The line with open circles is for pure  $\text{HfO}_2$ , the thin black line is for 2.5 at. % Y, and the thick black line is for 9.9 at. % Y.

In the investigated range of 470–600 °C, no effect of the substrate's temperature was found on the average composition of the films (as measured by RBS) and on the crystalline state. Figure 1 shows the x-ray diffraction  $\theta/2\theta$  scans for films (thickness  $t \sim 90$  nm) with two different Y contents as well as for a pure  $\text{HfO}_2$  film. The monoclinic structure of  $\text{HfO}_2$  is clearly observed. For a low Y content (2.5 at. %), another crystalline structure of  $\text{HfO}_2$  appears. For 9.9 at. % Y, only the cubic phase of  $\text{HfO}_2$  is crystallized<sup>16</sup> (diffraction peaks at  $2\theta=30.38^\circ$ ,  $35.22^\circ$ ,  $50.65^\circ$ ,  $60.15^\circ$ , and  $74.42^\circ$  are observed). The stabilization of the cubic phase was also evidenced by (ATR) attenuated total reflection Fourier transform infrared spectrometry. Analyses were performed on the same samples and on thinner ones ( $t < 20$  nm) to determine the Y content, at which the monoclinic phase completely disappears. The spectra are shown on Fig. 2. For  $\text{HfO}_2$  films, we observe a doublet at 690 and 760  $\text{cm}^{-1}$ , which has been already reported for films grown by metal organic chemical vapor deposition (MOCVD).<sup>17,18</sup> The peak at 760  $\text{cm}^{-1}$  is characteristic of the monoclinic structure. This peak disappears for 6.5 at. % and a single peak is observed at 690  $\text{cm}^{-1}$ . We have not found referenced infrared spectra for tetragonal or cubic  $\text{HfO}_2$ . From the x-ray diffraction spectra as well as from electron diffraction (ED) patterns, we attribute this peak at 690  $\text{cm}^{-1}$  to the cubic phase. For 2.0 at. % Y, the ED patterns indicate the presence of both monoclinic and cubic phases (the cubic phase was not detected by x-ray diffraction), while for 6.5 at. % of Y, only the cubic phase of  $\text{HfO}_2$  is observed. Thus, the cubic phase of  $\text{HfO}_2$ , with no mixing with the monoclinic one, is formed for addition of 6.5 at. % Y (the range in between 5.6% and 6.5% was not investigated). Moreover, it is obtained for films grown at a temperature as low as 470 °C. This content is lower than the one needed for bulk ceramics (8%–10%). Strain effect (due in part to the difference in thermal dilatation coefficients of the film and substrate) may play an important role in the stabilization. Among the Zr–Y–O studies of MOCVD films, the stabilization of the cubic phase and its mixing or not with the monoclinic phase depend on the Y content, substrate temperature, film's thickness, and nature of the substrate.<sup>19–22</sup> Kim *et al.*<sup>19</sup> obtained a cubic stabilization of zirconia for films containing 6 at. % yttrium and grown at 620 °C on Si, which is similar to our results. ATR spectra show the presence of a broad band around 944  $\text{cm}^{-1}$ , for Y

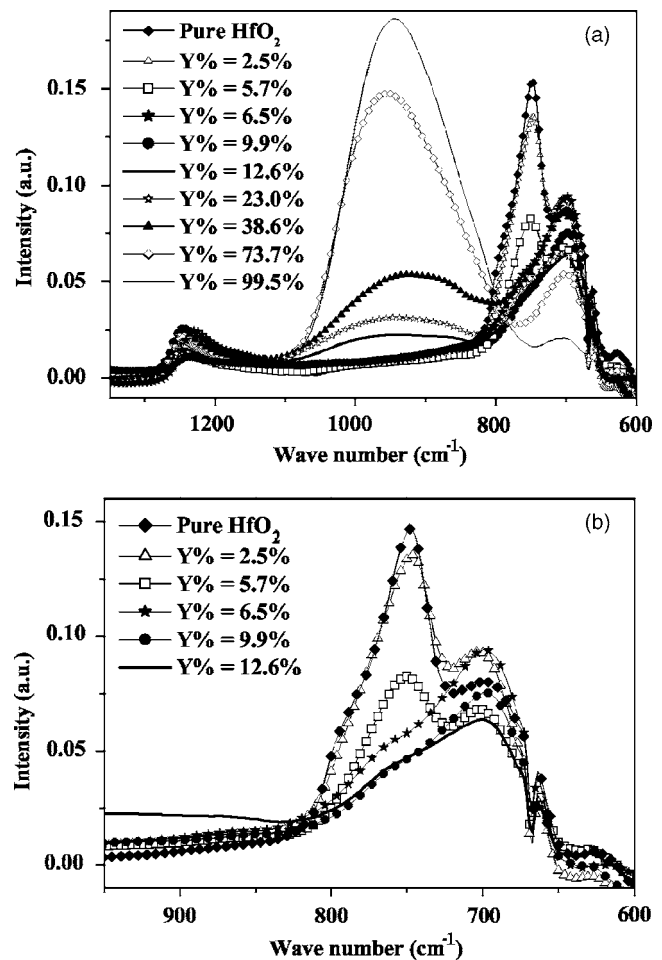


FIG. 2. (a) Attenuated total reflection-FTIR spectra of films with different Y contents; (b) zoom showing the signature of  $\text{HfO}_2$  for Y contents in the range of 0–12.6 at. %. All films shown here were grown at 600 °C, except the 6.5 at. % film, which was grown at 470 °C, and the 73.7 and 99.5 at. % films, which were grown at 570 °C.

content larger than 10 at. %, which is attributed to an amorphous silicate. As shown in Fig. 2, this peak becomes predominant for large Y contents (73.7 at. %) and for a 99.5 at. % Y film. The amorphous nature of the silicate is deduced from the absence of diffraction peaks on the  $\theta/2\theta$  spectra. X-ray photoelectron spectroscopy (XPS) measurements were performed on a 6.4 nm film with Y content of 8.8 at. %. In the Si 2p region, the  $\text{Si}^0$  contribution from the monocrystalline silicon substrate is observed, with the Si 2p<sub>3/2</sub> peak centered at 99.3 eV. In addition, a broad peak centered at 103.0 eV is measured and corresponds to a Si–O bonding environment. The Si–O peak is shifted towards lower binding energy than the one in  $\text{SiO}_2$  (103.3 eV). In the Hf 4f and Y 3d regions, the contribution from the cubic phase does not allow to precisely determine the nature of the silicate. In previous studies of yttrium oxide grown by a similar method and using the same precursor, we showed that yttrium silicate forms in contact with Si.<sup>23</sup> For a film with 26 at. % Y, the Si–O peak is shifted down to 102.7 eV. These binding energies of 102.7–103.0 eV agree with the values reported for yttrium silicates (the position of the Si–O peak depends on the silicate composition).<sup>24</sup> Figure 3 shows transmission electron microscopy (TEM) images for two films. The interfacial layer thickness increases with increasing Y content (0.7 and 1.0 nm for, respectively, 2.0 and

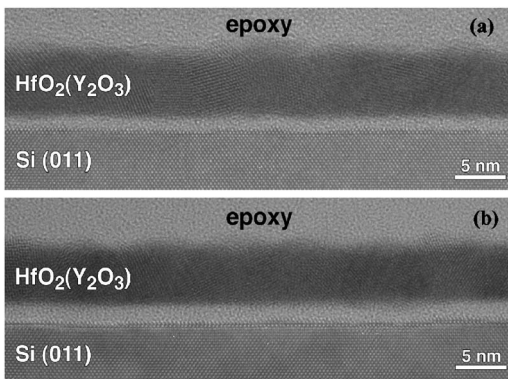


FIG. 3. Transmission electron microscopy images of films grown at 500 °C, containing (a) 2.0 at. % and (b) 8.8 at. % of yttrium. The thicknesses of the films are 6.7 and 5.3 nm, respectively, with interfacial layers of 0.7 and 1.0 nm, respectively.

8.8 at. %). This tendency was also confirmed for larger Y doping. Electrical measurements were performed on MOS structures. The equivalent oxide thickness (EOT) of the films was determined from the capacitance in the accumulation mode from  $C(V)$  curves. EOT values are plotted on Fig. 4 as a function of film thickness for Y contents of 2.0 at. % ( $\pm 0.2$ ) and 9.0 at. % ( $\pm 0.2$ ). A linear relationship between the EOT and the film thickness is observed, which allows the determination of the equivalent interfacial layer thickness from the intercept with the origin and of the dielectric permittivity from the slope. We calculate equivalent interfacial layer thicknesses of  $\sim 1.1$  and 1.9 nm for 2.0 and 9.0 at. % Y, respectively. These values are larger than the physical thickness observed by TEM. The effective dielectric permittivities are, respectively, 11 and 22 for 2.0 and 9.0 at. % Y. The highest permittivities ( $\sim 22$ ) were obtained in the range of 6.5–10 at. % Y. However, values up to 29 are expected for the cubic  $\text{HfO}_2$  phase.<sup>6</sup> The lower effective permittivity and the larger electrical interfacial layer thickness could be attributed to the presence of silicate both at the interface and in the film.  $I$ - $V$  measurements indicate that low leakage current densities are obtained for as-grown films for thickness larger than 2 nm ( $5 \times 10^{-7}$  A  $\text{cm}^{-2}$  at  $-1$  V for a thickness of 6.4 nm). Rapid thermal annealing under  $\text{NH}_3$  at 900 °C for

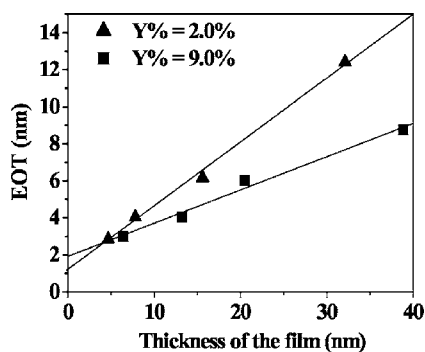


FIG. 4. Equivalent oxide thickness (EOT) determined from the  $C(V)$  curves in the accumulation capacitance mode as a function of film thickness for two sets of films grown at 500 °C (Y contents of  $2.0 \pm 0.2$  and  $9.0 \pm 0.2$  at. %).

60 s was performed on selected films. ATR spectra show that the cubic phase is stable upon such a high temperature treatment. The annealing is beneficial for reducing the interfacial state density and the charges in the oxide. Typical values of  $D_{it}$  and  $Q_{ox}$  are of  $5.0 \times 10^{10}$   $\text{eV}^{-1} \text{cm}^{-2}$  and  $7.0 \times 10^{10}$   $\text{cm}^{-2}$  for 8.8 at. % Y cubic films with a thickness of 6.4 nm (before annealing, the corresponding values were of  $2.0 \times 10^{12}$   $\text{eV}^{-1} \text{cm}^{-2}$  and  $6.7 \times 10^{12}$   $\text{cm}^{-2}$ , respectively).

In summary, the yttrium addition in  $\text{HfO}_2$  thin films deposited on (100) Si/SiO<sub>2</sub> substrates by injection MOCVD was investigated. A pure cubic phase of  $\text{HfO}_2$  is stabilized for Y content of  $\sim 6.5$  at. %. The cubic phase is stable upon high temperature rapid thermal annealing at 900 °C under  $\text{NH}_3$ .

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