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# Hardness, elastic modulus, and wear resistance of hafnium oxide-based films grown by atomic layer deposition

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# Hardness, elastic modulus, and wear resistance of hafnium oxide-based films grown by atomic layer deposition

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The investigation of mechanical properties of atomic layer deposition  $HfO_2$  films is important for implementing these layers in microdevices. The mechanical properties of films change as a function of composition and structure, which accordingly vary with deposition temperature and post-annealing. This work describes elastic modulus, hardness, and wear resistance of as-grown and annealed  $HfO_2$ . From nanoindentation measurements, the elastic modulus and hardness remained relatively stable in the range of 163–165 GPa and 8.3–9.7 GPa as a function of deposition temperature. The annealing of  $HfO_2$  caused significant increase in hardness up to 14.4 GPa due to film crystallization and densification. The structural change also caused increase in the elastic modulus up to 197 GPa. Wear resistance did not change as a function of deposition temperature, but improved upon annealing. © 2016 American Vacuum Society. [http://dx.doi.org/10.1116/1.4961113]

#### I. INTRODUCTION

Atomic layer deposition (ALD) technique is becoming promising for different applications because ALD thin films are pinhole-free, dense, conformal over complex 3D features, smooth, durable in various environments, and with good adhesion and high fracture strengths.<sup>1–3</sup> ALD films can be grown at temperatures ranging from 33 to 500 °C with extremely good thickness control.<sup>4</sup>

ALD hafnium oxide (HfO<sub>2</sub>) is attractive for many applications due to its high-k value, wide bandgap, optical transparency, and thermal and chemical stabilities.<sup>5–14</sup> Therefore, HfO<sub>2</sub> is attractive for a range of applications such as microelectromechanical systems (MEMS),<sup>6,9–11</sup> complementary metal oxide semiconductor,<sup>12</sup> and capacitive elements in memory devices.<sup>5,6,13,14</sup>

Mechanical properties of thin films are dependent on deposition temperature and these properties change during subsequent high temperature steps. It is therefore essential to evaluate the mechanical performance of a film in a systematic way. In free-standing MEMS structures, in particular, it is important to control mechanical properties of thin films to ensure stable and reliable performance of devices.

In this work, elastic modulus, hardness, and wear resistance (tribotesting) of ALD HfO<sub>2</sub> films were evaluated as a function of deposition temperature, and after post-deposition annealing by means of nanoindentation. Atomic force microscopy (AFM), x-ray reflectivity (XRR), grazing-incidence x-ray diffraction (GIXRD), and time-of-flight secondary ion mass spectrometry (ToF-SIMS) techniques were employed to correlate obtained mechanical properties to structure and composition of thin films.

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#### II. EXPERIMENT

 $HfO_2$  films were grown from tetrakis(ethylmethylamino)hafnium (TEMAHf) and ozone in a Savannah S-200 reactor (Ultratech-Cambridge Nanotech, Inc.). The pulse length was set to 3 s for TEMAHf, and 0.015 s for ozone. The ozone was generated with a constant concentration of 194 g/m<sup>3</sup>. Nitrogen served as a carrier and purge gas. The purge times were 6 and 8 s after TEMAHf precursor and ozone pulses, respectively. The deposition details are reported elsewhere.<sup>8,9</sup>

The deposition temperatures were 175, 200, and 225 °C for samples with thickness of 20 nm. To study the annealinginduced changes of the film mechanical properties, four samples of 100 nm nominal thickness were grown at 175 °C on Si (001) covered with 2-nm-thick chemical oxide (SiO<sub>2</sub>). Rapid thermal annealing was performed in nitrogen atmosphere for 1 min at 700, 800, and 900 °C.

XRR and GIXRD analyses were performed with a laboratory system equipped with a four circle goniometer and a position sensitive detector<sup>15</sup> with Cu K- $\alpha$  radiation (1.54 Å) to measure thin film roughness, thickness, and electronic density (XRR) and crystallinity (GIXRD).

ToF-SIMS analysis was done with Ga<sup>+</sup> ions, with energy of 25 keV, for analysis and Cs<sup>+</sup> ions, with energy 0.5 keV, for sputtering, to collect depth profiles over an area of  $50 \,\mu\text{m} \times 50 \,\mu\text{m}$  centered on the sputtering crater  $200 \,\mu\text{m} \times 200 \,\mu\text{m}$  wide, in interlaced mode. Secondary ions were collected in negative polarity and signal intensity normalized to <sup>30</sup>Si signal in bulk Si, similarly to Ref. 16.

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Fig. 1. (Color online) XRR scans and corresponding fit lines for (a) 20-nm-thick  $HfO_2$  films as a function of deposition temperature and (b) 100-nm-thick  $HfO_2$  films before and after annealing used to determine thickness, electronic density, and roughness of  $HfO_2$ -based films.

Sample	Nominal thickness (nm)	Thickness by XRR (nm), (±0.1)	El. density by XRR $(e^{-}/\text{\AA}^3), (\pm 0.1)$	Roughness by XRR (nm), (±0.1)	AFM roughness (nm), (±10%)
HfO <sub>2</sub> (175 °C)	20	20.2	1.8	0.7	0.2
HfO <sub>2</sub> (200 °C)	20	19.4	2.0	0.7	0.4
$HfO_2 (225 \circ C)$	20	19.2	2.2	0.7	1.5
HfO <sub>2</sub> (175 °C)	100	97.3	1.9	1.0	0.3
HfO2 (700 °C)	100	74.7	2.3	1.1	1.1
HfO2 (800 °C)	100	74.1	2.2	1.3	1.1
$HfO_2~(900~^\circ C)$	100	75.8	2.3	1.6	1.1



Fig. 2. Surface roughness by AFM (3  $\times$  3  $\mu$ m<sup>2</sup> scan) of ALD HfO<sub>2</sub>: (a) 20-nm-thick, (b) 100-nm-thick, and (c) 100-nm-thick annealed at 800 °C showing the roughness of the film and round-shaped nanofeatures (not included into calculation of total surface roughness).

Surface roughness was measured by AFM, using a Bruker commercial system equipped with sharp silicon probes. The AFM analysis was performed in a noncontact mode. On each sample, at least five measurements at different locations were acquired (four  $1 \,\mu m^2$  and one of  $3 \times 3 \,\mu m^2$  scan sizes) to obtain statistical data.

Nanoindentation was conducted with a Hysitron TriboIndenter TI-900 nanomechanical test system. Detailed information on the instrument setup can be found in the previous reports.<sup>2,17</sup> The hardness and elastic modulus values were extracted from the average of nine indents performed at fixed depth (displacement-control mode). HfO<sub>2</sub> elastic modulus and hardness were obtained by analyzing the unloading curves following the Oliver–Pharr method<sup>18</sup> using the equations

$$\frac{1}{E^*} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_f^2}{E_f},\tag{1}$$

$$H = \frac{P_{\max}}{A},\tag{2}$$

where  $\nu_i$  and  $\nu_f$  are Poisson's ratio for the tip and the film, respectively. For the diamond tip,  $\nu_i$  is assumed as 0.07, and for HfO<sub>2</sub>,  $\nu_f$  is taken as 0.30.<sup>2,19,20</sup>  $P_{\text{max}}$  is the maximum force required to produce the defined indent depth and A is the contact area at the corresponding depth at  $P_{\text{max}}$ . The force for wear resistance measurements was set as 10  $\mu$ N for 20-nm-thick films and  $25 \,\mu$ N for 100 nm-thick films. Two wear passes were performed on each film at a selected area of  $2 \,\mu$ m<sup>2</sup>. The volume loss was calculated from analyzing the wear depth across the worn surface.

### **III. RESULTS AND DISCUSSION**

Thickness, electronic density, and roughness of HfO<sub>2</sub> films as extracted from the fitting of XRR data (Fig. 1) are reported in Table I. The growth rate is calculated from the measured thickness. The growth rate for HfO<sub>2</sub> increased from 0.147 to 0.152 nm/cycle with increasing of deposition temperature. The electronic density also slightly increased as a function of deposition temperature from 1.8 to  $2.2 \text{ e}^-/\text{Å}^3$ . Furthermore, density significantly increased (by 24%) after annealing at high temperatures. From another point of view, thickness decreased by 22% after annealing.

From XRR measurement, the roughness of as-grown  $HfO_2$  was in range of 0.7–1.0 nm. The annealing provoked a slight increase in roughness up to 1.6 nm. The observed trend of increased XRR roughness with annealing is likely due to grain coarsening. A typical analysis of surface morphology performed by AFM is shown in Fig. 2. The extracted root mean square roughness values are reported in the Table I. The AFM roughness increased as a function of temperature due to the emergence of crystalline nanofeatures, as discussed in our previous report.<sup>9</sup>



Fig. 3. (Color online) XRD analysis of annealed HfO<sub>2</sub>: Left: superposition of patterns and comparison with powder files. Right: data (dots) and simulation (line) for 700  $^{\circ}$ C (a), 800  $^{\circ}$ C (b), and 900  $^{\circ}$ C (c) annealed samples.

The roughness values for HfO<sub>2</sub> obtained by AFM (independently of scan size) were slightly different in comparison with XRR roughness. The differences in XRR and AFM roughness are most likely due to different size areas considered: XRR (mm<sup>2</sup>) or AFM ( $\mu$ m<sup>2</sup>).

According to XRD analysis, for all the explored thickness and deposition temperatures, the as-grown HfO<sub>2</sub> films were amorphous. More details about the morphology and crystallinity of 20 nm-thick-HfO<sub>2</sub> grown at 175, 200, and 225 °C can be found in Ref. 9. After annealing, HfO<sub>2</sub> became polycrystalline. This phase change can be related to the observed increase in electronic density, as measured by XRR, and to the increased surface roughness (Table I). After annealing at 700, 800, and 900 °C, the layers became polycrystalline in a mixture of monoclinic and cubic (or orthorhombic, or tetragonal) HfO<sub>2</sub> polymorphs; it was not possible, however, within the resolution of the laboratory diffractometer, to discern among such polymorphs. The XRD analysis is shown in Fig. 3. The XRD patterns were analyzed by Rietveld refinement by considering a mixture of monoclinic and cubic structures of HfO<sub>2</sub>.<sup>21</sup> As compared with powder diffraction reference,<sup>21</sup> the monoclinic phase developing in our HfO<sub>2</sub>



Fig. 4. (Color online) ToF-SIMS depth profiles for as-grown (a), annealed at 700  $^{\circ}$ C (b), 800  $^{\circ}$ C (c), and 900  $^{\circ}$ C (d) HfO<sub>2</sub> films. Each panel shows the elements of film composition and the levels of impurities, as C for carbon, CN for nitrogen, and OH for hydrogen.

films annealed at 700 °C shows a higher intensity of the peak at  $2\Theta \sim 31.6^{\circ}$  which is associated with the (111) planes with respect to the intensity of the (-111) planes at  $2\Theta$  $\sim 28.4^{\circ}$ . Such discrepancy may claim for a preferential orientation out of plane in the [111] direction, as sustained by the observation that when annealed at 800 °C, the (111) peak increases, whereas the (-111) one remains almost constant. At the same time, a reduction in intensity of the peaks associated with the cubic phase is observed. Such variation corresponds to the increase in the monoclinic component, together with an increase in the preferentially oriented crystallites, and the relative reduction of the cubic phase. After annealing at 900 °C, the (111)/(-111) intensity ratio remains similar to the ratio measured after annealing at 800 °C, but there is a drastic reduction of the cubic component. Due to the lack of information that can be retrieved from a single spectrum about the full distribution of preferential orientations, the data were fitted by Rietveld refinement by imposing an arbitrary texture, i.e., by setting the peak intensities as free parameters, and by refining the volume percentage phase distribution. The best simulation is shown on the right panel in Fig. 3. The monoclinic percentage is found to increase from 64% to 68% and then to 83% with increasing annealing temperature from 700 to 800°C and then to 900 °C.

According to ToF-SIMS, the impurities in as-grown films, nitrogen, hydrogen content (OH-groups), and carbon, were reduced as a function of deposition temperature, in accordance with our previous report.<sup>9</sup> Annealing resulted in more stoichiometric films in comparison with as-grown films due to a relative reduction in the hydrogen content (OH-groups) (Fig. 4). The hydrogen most probably diffused out of the film upon annealing. Nitrogen and carbon impurities, however, remained relatively stable in the bulk region of the film. The surface and subsurface region is seen to be affected by a reduction of such impurities possibly related with the film crystallization upon annealing. Chemical SiO<sub>2</sub> served as a diffusion barrier between ALD film and silicon. No



FIG. 5. (Color online) Load ( $\mu$ N) and depth (nm) indentation curves of HfO<sub>2</sub> films grown at 175, 200, 225 °C.

intermixing of  $HfO_2$  and  $SiO_2$  was observed in any of the samples. The interface of sample annealed at 900 °C shows signs of only minor diffusion of silicon into hafnium oxide [Fig. 4(d)].

In the nanoindentation measurements, for the 20-nm-thick films, the depth was set at 7 nm, and for the 100-nm-thickfilms, the depth was set at 10 nm. Here, the indent depth for the 20-nm-thick films was about 35% of the total film thickness, suggesting substrate effect to the measured property value could be significant, as the indent depth should be less than 10%-15% of total film thickness to minimize the substrate effect in nanoindentation of thin films.<sup>22</sup> Film surface roughness, indenter bluntness, and high noise-to-data ratio at shallow depths always limit the minimum depth at which a nanoindentation test that yields film-only results can be performed. Here, indentation at 7 nm for the thinner films appeared to be an optimal depth to grant repeatable measurements with reasonably small standard deviation. The loaddepth curves of films grown at 175, 200, and 225 °C are shown in Fig. 5.

Table II summarizes the hardness, elastic modulus, and volume loss under applied wear load. Hardness slightly reduced as a function of deposition temperature (from 9.7 to 8.3 GPa); however, the difference is insignificant and it stays within the experimental error. After annealing at 700 °C, the hardness is increased nearly twofold from 7.6 to 14.4 GPa. This increase is most likely related to the crystal evolution. Interestingly, annealing at higher temperature led to decreased hardness. The further increase in annealing temperature provoked the evolution of crystal structure, which at the same time reduced the hardness of the films. Annealing at 800 °C gave an increase of preferential [111] out of plane orientation and decrease of cubic polymorph. As a consequence, the hardness slightly dropped. A further increase in annealing temperature to 900 °C generated further reduction of the cubic phase decreasing HfO<sub>2</sub> hardness. Furthermore, annealing provoked out-diffusion of hydrogen and film densification; thus, films became mechanically harder compared with the reference sample.

The elastic modulus stayed nearly constant as a function of deposition temperature (163–165 GPa) due to amorphous nature of as-deposited films and insignificant changes in film density with deposition temperature. Similarly to hardness,

TABLE II. Mechanical properties of ALD HfO2 films.

Sample	Hardness (GPa)	Elastic modulus (GPa)	Volume loss $(10^{-3} \mu m^3)$ , $(\pm 10\%)$	Applied load for tribotesting (µN)
HfO <sub>2</sub> (175 °C)	$9.7\pm0.5$	$165 \pm 13$	27	10
HfO2 (200 °C)	$8.9\pm0.3$	$165\pm15$	21	10
$\mathrm{HfO}_{2}\left(225^{\circ}\mathrm{C}\right)$	$8.3\pm0.8$	$163\pm19$	22	10
HfO <sub>2</sub> (175 °C)	$7.6 \pm 0.2$	$143 \pm 7$	184	25
HfO <sub>2</sub> (700 °C)	$14.4\pm1.2$	$177 \pm 5$	87	25
HfO2 (800 °C)	$13.7\pm1.0$	$197\pm56$	114	25
HfO <sub>2</sub> (900 °C)	$12.9\pm1.5$	$183\pm33$	142	25

the annealing provoked considerable changes in elasticity: dense polycrystalline films become stiffer after annealing. Elastic modulus increased from  $143 \pm 7$  to 177-197 GPa. The peaked value of 197 GPa with larger scatter of the elastic modulus at 800 °C annealing temperature may be related to reduction of the cubic component. The cubic structure of bulk HfO<sub>2</sub> is known to have higher elastic and shear moduli in comparison with the monoclinic structure.<sup>23</sup>

The obtained values of hardness and elastic modulus of as-grown HfO<sub>2</sub> are in agreement with our previous studies where elastic modulus of  $148 \pm 25$  GPa and hardness of  $7 \pm 1$  GPa was measured with nanoindentation.<sup>19</sup> The values are also in agreement with reported values of  $220 \pm 40$  GPa for elastic modulus and  $9.5 \pm 1$  GPa for hardness.<sup>24</sup>

Wear resistance was comparable for all films grown at 175, 200, and 225 °C. The volume loss was  $21-27\cdot10^{-3} \,\mu\text{m}^3$  under applied load of  $10 \,\mu\text{N}$  (Table II). Annealing of the films improved wear properties: the volume loss was reduced from 184 to  $87\cdot10^{-3} \,\mu\text{m}^3$  under applied load of  $25 \,\mu\text{N}$ . However, a further increase in the annealing temperature decreased wear resistance. Similarly to hardness, the decrease may be related to crystalline anisotropy. As a consequence, the shear stress can decrease along the crystal planes influencing the wear resistance and hardness properties, as observed for other compounds such as MgO, TiO<sub>2</sub>, or SnO<sub>2</sub>.<sup>25,26</sup> This is to say that it may become more difficult to remove material as the orientation preference becomes more pronounced in polycrystalline materials.

In addition, it has been reported that annealing of  $HfO_2$  changes the amount of residual stress associated with the conversion of the structure to polycrystalline phase and outdiffusion of impurities.<sup>27</sup> Therefore, it is also possible that the decreased wear resistance is partially due to the changes in the residual stress. Furthermore, according to some reports,  $HfO_2$  grown on silicon formed silicides and silicates at the interface during annealing.<sup>28</sup> However, in our case, the chemical oxide on the silicon substrate served as a diffusion barrier against the formation of silicides and silicates. Therefore, it is most probably that the observed changes in wear resistance were due to crystallization and densification of  $HfO_2$  films.

#### **IV. SUMMARY AND CONCLUSIONS**

To assess the mechanical properties of thin films is key for their integration in applications, especially in MEMS. The novelty of this work is to systematically evaluate the mechanical properties of ALD HfO<sub>2</sub> films deposited from TEMAHf and O<sub>3</sub> as a function of deposition and annealing temperature. The results were correlated with microstructure and composition. From nanoindentation measurements, hardness, elastic properties, and wear resistance remain relatively constant as a function of deposition temperature due to amorphous structure of HfO<sub>2</sub> films. Annealing led to HfO<sub>2</sub> microstructure evolution, densification and, as a result, increase in hardness, elastic modulus, and wear resistance. However, following increase in annealing temperature from 700 to 900 °C led to reduction of hardness and wear resistance. The effect can be associated with the dependence of hardness on preferential crystal planes, as observed with XRD, and on the grain coarsening of the crystal structure.

The knowledge of the mechanical properties of ALD  $HfO_2$  as a function of composition and structure is important for future applications of these films in microdevices like MEMS. The change in mechanical properties after high temperature annealing or thermal cycling can influence MEMS performance and life-time. Therefore, it is significant to possess data on elastic properties, wear resistance, and hardness of thin films. In the future, it may be relevant to evaluate the changes in stress as a function of deposition temperature and after post-annealing.

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- <sup>1</sup>E. K. Baumert, P. O. Theillet, and O. N. Pierron, Scr. Mater. **65**, 596 (2011).
- <sup>2</sup>O. M. Ylivaara et al., Thin Solid Films 552, 124 (2014).
- <sup>3</sup>M. Berdova et al., Acta Mater. 66, 370 (2014).
- <sup>4</sup>M. D. Groner, F. H. Fabreguette, J. W. Elam, and S. M. George, Chem. Mater. 16, 639 (2004).
- <sup>5</sup>S. Brivio, G. Tallarida, E. Cianci, and S. Spiga, Nanotechnology **25**, 385705 (2014).
- <sup>6</sup>B. Lee, T. Moon, T. Kim, D. Choi, and B. Park, Appl. Phys. Lett. **87**, 012901 (2005).
- <sup>7</sup>A. J. Haemmerli, J. C. Doll, J. Provine, R. T. Howe, D. Goldhaber-Gordon, and B. L. Pruitt, *Solid-State Sensor, Actuator and Microsystems Conference* (2013), pp. 1931–1934.
- <sup>8</sup>E. Cianci, A. Molle, A. Lamperti, C. Wiemer, S. Spiga, and M. Fanciulli, ACS Appl. Mater. Interface 6, 3455 (2014).
- <sup>9</sup>M. Berdova et al., Appl. Surf. Sci. 368, 470 (2016).
- <sup>10</sup>L. W. Hung, Z. A. Jacobson, Z. Ren, A. Javey, and C. T. C. Nguyen, 2008 Solid-State Sensor, Actuator, and Microsystems Workshop, Hilton Head, SC (2008), Vol. 8, pp. 208–211.
- <sup>11</sup>M. Akgul, B. Kim, L. W. Hung, Y. Lin, W. C. Li, W. L. Huang, I. Gurin, A. Borna, and C. T. Nguyen, *Solid-State Sensor, Actuator and Microsystems Conference* (2009), pp. 798–801.
- <sup>12</sup>G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. 89, 5243 (2001).
- <sup>13</sup>J. Niinistö, K. Kukli, M. Heikkilä, M. Ritala, and M. Leskelä, Adv. Eng. Mater. 11, 223 (2009).
- <sup>14</sup>S. Spiga, F. Driussi, A. Lamperti, G. Congedo, and O. Salicio, Appl. Phys. Express 5, 021102 (2012).
- <sup>15</sup>C. Wiemer, S. Ferrari, M. Fanciulli, G. Pavia, and L. Lutterotti, Thin Solid Films 450, 134 (2004).
- <sup>16</sup>A. Lamperti, E. Cianci, O. Salicio, L. Lamagna, S. Spiga, and M. Fanciulli, Surf. Interface Anal. 45, 390 (2013).
- <sup>17</sup>X. Liu, E. Haimi, S. P. Hannula, O. M. Ylivaara, and R. L. Puurunen, J. Vac. Sci. Technol., A **32**, 01A116 (2014).
- <sup>18</sup>W. C. Oliver and G. M. Pharr, J. Mater. Res. 7, 1564 (1992).
- <sup>19</sup>M. Berdova, N. Y. Garces, X. Liu, A. Nath, M. Rao, D. K. Gaskill, C. R. Eddy, and S. Franssila, *Atomic Layer Deposition Conference, ALD AVS* (2013).
- <sup>20</sup>B. Ilic, S. Krylov, and H. G. Craighead, J. Appl. Phys. **108**, 044317 (2010).

- $^{21}$  FIZ Karlsruhe, ICSD International Crystal Structure database, patterns 53033 for cubic and 27313 for monoclinic HfO<sub>2</sub> (2015).
- <sup>22</sup>R. Saha and W. D. Nix, Acta Mater. **50**, 23 (2002).
- <sup>23</sup>C. A. Ponce, R. A. Casali, and M. A. Caravaca, J. Phys.: Condens. Matter 20, 045213 (2008).
- <sup>24</sup>K. Tapily, J. E. Jakes, D. S. Stone, P. Shrestha, G. Gu, H. Baumgart, and A. A. Elmustafa, J. Electrochem. Soc. 155, H545 (2008).
- <sup>25</sup>C. A. Brookes, J. B. O'neill, and B. A. W. Redfern, Proc. R. Soc. London, A **322**, 73 (1971).
- <sup>26</sup>H. Li and R. C. Bradt, J. Mater. Sci. **28**, 917 (1993).
- <sup>27</sup>S. Yan-Ming, S. Shu-Ying, D. Zhen-Xia, H. Hong-Bo, S. Jian-Da, and F. Zheng-Xiu, Chin. Phys. Lett. 24, 2963 (2007).
- <sup>28</sup>R. Katamreddy, R. Inman, G. Jursich, A. Soulet, and C. Takoudis, Appl. Phys. Lett. **89**, 262906 (2006).