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Ferroelectricity in yttrium-doped hafnium oxide

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Structural and electrical evidence for a ferroelectric phase in yttrium doped hafnium oxide thin films is presented. A doping series ranging from 2.3 to 12.3 mol% YO_{1.5} in HfO₂ was deposited by a thermal atomic layer deposition process. Grazing incidence X-ray diffraction of the 10 nm thick films revealed an orthorhombic phase close to the stability region of the cubic phase. The potential ferroelectricity of this orthorhombic phase was confirmed by polarization hysteresis measurements on titanium nitride based metal-insulator-metal capacitors. For 5.2 mol% YO_{1.5} admixture the remanent polarization peaked at 24 $\mu\text{C}/\text{cm}^2$ with a coercive field of about 1.2 MV/cm. Considering the availability of conformal deposition processes and CMOS-compatibility, ferroelectric Y:HfO₂ implies high scaling potential for future, ferroelectric memories. © 2011 American Institute of Physics. [doi:10.1063/1.3667205]

INTRODUCTION

Ferroelectric memories are an extremely interesting approach to nonvolatile data storage, since they show a unique combination of very fast, low power writing with nonvolatile retention that is unmatched by charge based and other emerging concepts like magnetoresistive RAM's, phase change memories and resistive RAM's. Up till now mainly lead zirconate titanate (PZT) was used for the fabrication of ferroelectric memories.¹ However, PZT is quite complicated to integrate into a CMOS process and therefore the scaling has been much slower than the scaling of conventional charge based memories. This results in much higher production cost for ferroelectric memories compared to competing charge based technologies.

Integrating thin layers of doped HfO₂ on the other hand, has already become well-known to microelectronic engineering, since stabilization of the higher-k cubic (*Fm3m*) or tetragonal (*P4₂/nmc*) phase in the otherwise monoclinic (*P2₁/c*) HfO₂² is of considerable interest to dielectric scaling in the manufacturing of CMOS³ and DRAM⁴ devices. Recently, it has been demonstrated that doping of HfO₂ thin films with SiO₂⁵ or ZrO₂⁶ does not only stabilizes the tetragonal phase, but can also produce a spontaneous polarization at intermediate doping levels, that results in usable, ferroelectric hysteresis loops in these layers.

Phase stability in HfO₂, however, can also be influenced by YO_{1.5} admixture. As predicted by first principles calculations on trivalent dopants, stabilization of cubic HfO₂ can be achieved for moderate yttrium doping.⁷ Analogous to the

well-known yttrium stabilized zirconia (YSZ),⁸ successful stabilization of the cubic phase in epitaxial, as well as polycrystalline Y:HfO₂ thin films has been presented by several authors.^{9–17} Reported doping levels for complete stabilization of the cubic phase in HfO₂ range from 4 to 17 mol% YO_{1.5} admixture, thereby achieving k-values of about 18 to 32.

However, the exact nature of the crystalline phases that form close to the stability region of the cubic phase remains unclear. The bulk phase diagram allows for a monoclinic to cubic phase transition by passing through a coexistence region of both phases.¹⁸ At temperatures above 1350 K, an intermediate tetragonal phase has to be considered. However, when Y:HfO₂ is crystallized by rapid thermal processes (RTP) with fast cooling rates, such as those utilized in microelectronic applications, the diffusion of dopant atoms is limited and a number of metastable phases can be formed. Yashima *et al.*¹⁹ and Fujimori *et al.*²⁰ observed metastable tetragonal phases (*t'* and *t''*) in quenched Y:HfO₂ bulk samples between 10 and 13 mol% YO_{1.5}. Furthermore, they described the occurrence of two lower symmetry phases, γ_1 and γ_2 , that were only identifiable by Raman Spectroscopy for lower YO_{1.5} admixture. In addition, recent publications report the existence of a possibly orthorhombic/monoclinic phase mixture that forms prior to complete stabilization of the cubic phase in Y:HfO₂ thin films.^{21,22}

In this paper we investigate the electronic properties of metastable crystalline phases in Y:HfO₂ thin films, and report the observation of ferroelectricity. We demonstrate that a spontaneous polarization in HfO₂ can be provoked by YO_{1.5} admixture, while at the same time easing some of the processing constraints present in the previously published systems. On the basis of a structural investigation we claim that this crystal property originates from a non-centrosymmetric orthorhombic phase located close to the stability region of

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the cubic phase. Y:HfO_2 thin films have a large bandgap,¹¹ are temperature stable,²¹ CMOS compatible,^{23,24} and due to the availability of mature atomic layer deposition (ALD) processes,¹³ they are capable of conformal 3D integration. Therefore Y:HfO_2 is considered a promising material for future, highly scaled ferroelectric memories.

EXPERIMENTAL

Y:HfO_2 thin films were deposited by thermal ALD on 300 mm Si substrates that, prior to dielectric deposition, received a 18 nm chemical vapor deposited (CVD) TiN ($\text{TiCl}_4/\text{NH}_3$) bottom electrode in a batch furnace. The ALD process was based on the commercially available metal organic precursors tetrakis(ethylmethylamino)hafnium (TEMAH) and tris(methylcyclopentadienyl)yttrium ($\text{Y}(\text{MeCp})_3$). Ozone was used as the oxidant and argon as the purge and carrier gas. The $\text{YO}_{1.5}$ content in HfO_2 was defined by varying the cycle ratio of the precursors and monitored by inline X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering (RBS). A constant thickness of 10 nm for all films was achieved by adjusting the number of Hf:Y super cycles, and was confirmed by inline spectral ellipsometry and HR-TEM. Crystallization of the as deposited amorphous Y:HfO_2 thin films was induced by a $600^\circ\text{C}/20\text{ s}/\text{N}_2$ RTP step, referred to in text as post deposition anneal (PDA). Samples annealed after room temperature deposition of a 4 nm physical vapor deposited (PVD) TiN top electrode are referred to in the text as samples treated with post metallization anneal (PMA). Samples with yttrium concentrations ranging from 2.3 to 12.3 mol% $\text{YO}_{1.5}$ in HfO_2 were manufactured using both schemes (Fig. 1(a)). This allowed access to the range of metastable phases formed from almost pure hafnium oxide to fully cubic Y:HfO_2 . Grazing incidence X-ray diffraction (GI-XRD) on crystalline and high temperature X-ray diffraction (HT-XRD) on as deposited Y:HfO_2 thin films was measured on a Bruker D8 Discover diffractometer using Cu K-alpha radiation from a Cu tube operated at 40 kV/40 mA. The incident angle was set to 0.5° . For HT-XRD analysis, samples were heated from room temperature to 650°C under constant nitrogen purging in a furnace covered with a hemispherical beryllium dome. During temperature ramp up, *in situ* GI-XRD measurements were performed.

For electrical measurements, Pt dots were evaporated on the TiN top electrode, forming structured metal-insulator-metal (MIM) capacitors in a subsequent etching step. For samples that received PDA treatment, Pt dots were directly evaporated on top of the Y:HfO_2 thin film. Polarization hysteresis was characterized using an aixACCT TF Analyzer 2000 system and a custom built setup at a frequency of 1 kHz. The small signal capacitance-voltage characteristics of the MIM capacitors were determined with an Agilent 4284 LCR Meter. Typical measurement conditions were a frequency of 10 kHz and a 50 mV ac probing signal on device areas of $1.15 \times 10^{-4}\text{ cm}^2$.

RESULTS AND DISCUSSION

The controlled incorporation of $\text{YO}_{1.5}$ into HfO_2 can be realized by the variation of the TEMAH to $\text{Y}(\text{MeCp})_3$ ^{12,13,17}

FIG. 1. (Color online) (a) Fabrication flow of MIM capacitors based on atomic layer deposited Y:HfO_2 dielectrics with post deposition anneal (PDA) or post metallization anneal (PMA) in N_2 atmosphere. (b) TEM micrograph and HRTEM enlargement of the fully crystalline TiN/ Y:HfO_2 /TiN MIM stack on silicon treated with PMA.

precursor pulsing ratio during the ALD process. RBS measurements on as deposited films reveal a linear correlation between precursor cycling ratio and $\text{YO}_{1.5}$ incorporation (Fig. 2). Figure 1(b) shows a HR-TEM micrograph of the complete MIM stack after thermal treatment. The polycrystalline structure of the Y:HfO_2 , as well as the TiN metal electrode, is clearly visible. Additional HT-XRD experiments confirmed no significant influence of $\text{YO}_{1.5}$ content on the crystallization temperature (Fig. 3), which is in good

FIG. 2. (Color online) RBS measurements on 10 nm thick films reveal a linear incorporation of $\text{YO}_{1.5}$ into HfO_2 with ALD cycle ratio of TEMAH and $\text{Y}(\text{MeCp})_3$ precursor. Structural drawings of the metal organic precursors are given.

agreement with literature data.⁹ The crystallization temperature was approximately 400 °C for all of the YO_{1.5} concentrations investigated. Based on these data, complete crystallization of the as deposited amorphous dielectric was induced by a RTP step at 600 °C in samples that were prepared for electrical characterization. This is a significant improvement to the Hf_{1-x}Zr_xO₂ system that, depending on the ZrO₂ content, suffers from premature crystallization during deposition, resulting in considerable interface roughening.²⁵ Due to the higher crystallization temperature of Y:HfO₂, crystallization can either be induced before (PDA) or after (PMA) top electrode deposition (Fig. 1(a)).

Polarization-voltage hysteresis measurements of a 10 nm HfO₂ sample with 5.2 mol% YO_{1.5} admixture are shown in Fig. 4(a). A remanent polarization P_r of 24 $\mu\text{C}\cdot\text{cm}^{-2}$ and a coercive field of 1.2 MV $\cdot\text{cm}^{-1}$ were observed. Unsaturated polarization hysteresis loops occur when excitation voltages below 4 V are used. This so called sub loop behavior is typical for ferroelectric materials and, as in this case, is usually accompanied by a drop in remanent polarization and coercive field with decreasing excitation signal.²⁶

Further proof for the ferroelectric nature of Y:HfO₂ thin films is given by their non-linear small signal capacitance-voltage response. Two capacitance maxima in the vicinity of the coercive field values are observed when a full hysteresis loop is swept (Fig. 4(b)). These maxima are a well-known property of ferroelectric capacitors and are attributed to an increased domain wall movement at the coercive fields.²⁷

As can be seen from the polarization hysteresis measurements in Fig. 5 and the summarized polarization values in Fig. 6(a), a gradual transition from a linear dielectric to a ferroelectric response can be observed with decreasing YO_{1.5} content in HfO₂. When the YO_{1.5} content is lowered further, the polarization starts to decline and the coercive field increases. A similar trend is observed for the dielectric constant (Fig. 6(b)). Due to the stabilization of the higher-k cubic phase instead of the lower-k monoclinic phase with increasing YO_{1.5} content in HfO₂, the dielectric constant increases with higher YO_{1.5} content. Once the cubic phase is fully stabilized, further addition of the lower-k YO_{1.5} decreases the effective permittivity of HfO₂ again.

However, when directly comparing PMA against PDA samples, PDA samples exhibit lower P_r values and the P_r

FIG. 4. (Color online) A characteristic transformation from sub-loop behavior to saturation with increasing P-V sweep voltage (a), as well as ferroelectric capacitance peaks in dual sweep C-V (b) are observed for TiN/10 nm 5.2 mol% Y:HfO₂/TiN MIM capacitors.

evolution slightly shifts to higher YO_{1.5} content. A similar shift is observed when comparing the dielectric constant at corresponding YO_{1.5} content. The mechanical confinement offered by the top electrode during the crystallization of the PMA samples can serve as an explanation. As can be seen from the weighing of the integral intensity of monoclinic against higher symmetry reflections in Fig. 6(c) and the direct comparison of GI-XRD diffractograms in Fig. 7, the monoclinic phase in HfO₂ can effectively be suppressed utilizing PMA processing. This suppression mechanism of monoclinic HfO₂ in thin films by a mechanically confined crystallization (e.g. reported for TiN/HfO₂ gate stacks²⁸) was identified to be the origin of the orthorhombic, ferroelectric, phase in SiO₂-doped HfO₂.⁵ The increased P_r observed in PMA samples at low YO_{1.5} content suggests a larger ferroelectric phase fraction due to the suppressed monoclinic phase. However, even though PDA samples exhibit lower P_r , they still show the presence of ferroelectricity, suggesting that the presence of a top electrode (“cap”) is preferred, but not mandatory, for the formation of the ferroelectric phase in Y:HfO₂ thin films. This advantageous discrepancy to ferroelectricity in Si:HfO₂,⁵ for which PMA treatment was found to be necessary, may be explained by the difference in crystallization temperatures of both systems. The crystallization

FIG. 3. (Color online) HT-XRD analysis of 10 nm HfO₂ thin films with YO_{1.5} admixture ranging from 2.3 to 6.9 mol%. With increasing YO_{1.5} content the monoclinic phase in HfO₂ is suppressed, whereas crystallization temperature remains at approximately 400 °C.

FIG. 5. (Color online) P-V hysteresis loops acquired on 10 nm Y:HfO₂ MIM capacitors treated with PMA (a) and PDA (b) processing clearly exhibit ferroelectric nature. For PDA treated samples a linear dielectric response is observed at low YO_{1.5} content. For high YO_{1.5} admixture to HfO₂ a linear dielectric response is observed for both processing schemes.

of Si:HfO₂ requires temperatures in excess of 700 °C and may therefore lead to a more rapid formation of stable crystalline phases instead of quenchable, metastable intermediates.

FIG. 6. (Color online) Remanent polarization (a) and dielectric permittivity (b) maxima for PMA and PDA treated Y:HfO₂ MIM capacitors are contrasted to the monoclinic phase fraction (c) evaluated from weighing the integral intensity of monoclinic against higher symmetry reflections.

FIG. 7. (Color online) GI-XRD diffractograms of Y:HfO₂ samples reveal the coexistence of monoclinic and orthorhombic phase for low YO_{1.5} doping and complete stabilization of the cubic phase for higher doping content. When directly comparing PMA against PDA treated samples a higher monoclinic phase fraction for PDA samples is observed. Reference patterns are computed from ab initio calculations presented by Lowther *et al.*³¹ on HfO₂ phase stability (cubic Fm3m, orthorhombic Pbc2₁, monoclinic P2₁/c). D-spacing was adjusted. For better visibility, reference patterns were scaled to the 2nd highest square root intensity (highest intensity for all patterns: 111 reflections). Stars indicate Pt reflections.

Stabilization of the cubic phase in the predominantly monoclinic HfO₂ by YO_{1.5} admixture is widely accepted in literature and has been reported several times.^{9–17} However, considering the occurrence of ferroelectricity in Y:HfO₂ thin films, a simple monoclinic/cubic phase mixture or intermediate tetragonal phases seem contradictory, since neither the cubic/tetragonal nor the monoclinic phases in HfO₂ possess ferroelectric space groups.²⁹ A close examination of the GI-XRD diffractograms presented in Fig. 7 revealed the presence of an orthorhombic phase, whose phase fraction increases against the monoclinic phase until a full stabilization of the cubic phase is reached for high YO_{1.5} content. These findings are in good agreement with data on Y:HfO₂ thin films shown by Rauwel *et al.*²¹ and Dubourdieu *et al.*,²² who observed a possibly orthorhombic phase coexisting with the monoclinic phase until a stable cubic phase is reached. This orthorhombic phase, however, was identified as centrosymmetric Pbc_a and was seemingly not tested for ferroelectric properties.

On the basis of the electrical data presented, it seems likely that this orthorhombic phase can be assigned to the non-centrosymmetric, and therefore potentially ferroelectric, space group Pbc2₁. This phase has already been observed in the closely related PSZ³⁰ and was predicted for HfO₂³¹ by an

ab initio approach. It can be separated from the monoclinic and cubic phase by the characteristic features labeled in Fig. 7. This analogy to ferroelectric Si:HfO₂ supports the hypothesis that the structural origin of spontaneous polarization in doped HfO₂ is linked to the stabilization of this particular phase and does not originate from the dopant itself.⁵

The anti-ferroelectric like behavior observed for the fully stabilized Si:HfO₂, however, was not observed in the Y:HfO₂ system within our experimental conditions. Tomida *et al.*¹⁶ clearly distinguished the tetragonal Si:HfO₂ from the cubic Y:HfO₂ system. This further supports the hypothesis that the field driven phase transition observed in Si:HfO₂⁵ is related to the tetragonal phase stabilized for high SiO₂ doping and is not present in the cubic configuration favored by YO_{1.5} incorporation.

In the context of ferroelectricity being present in Y:HfO₂, it is interesting to note that unusual threshold voltage shifts have been observed for Y:HfO₂ based transistors under constant voltage stress.²³ The phenomenon described in the present work could serve as an explanation, since even residual ferroelectricity being present in the gate stack would counteract the usual polarity correlation of threshold voltage shift and stress voltage by slow polarization reversal.

CONCLUSION

In conclusion, we have demonstrated the stabilization of a ferroelectric phase in 10 nm thick, atomic layer deposited Y:HfO₂ thin films for doping levels below 8 mol% YO_{1.5}. The origin of ferroelectricity was attributed to an orthorhombic phase of space group Pbc2₁, which was found to coexist with the monoclinic phase until complete stabilization of the cubic phase is reached. Given the vast industry experience integrating HfO₂-based thin films, ferroelectricity in Y:HfO₂ has the potential to enable high density ferroelectric memories. Besides its thermal stability on contact with Si, Y:HfO₂ offers excellent scaling potential due to its large bandgap and highly conformal deposition processes (3D integration capability), rendering it superior to commonly integrated ferroelectrics in microelectronic devices.

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- ¹K. Kim and S. Lee, *J. Appl. Phys.* **100**, 51604 (2006).
- ²X. Zhao and D. Vanderbilt, *Phys. Rev. B* **65**, 233106 (2002).
- ³K. Kita, K. Kyuno, and A. Toriumi, *Appl. Phys. Lett.* **86**, 102906 (2005).
- ⁴T. S. Börscke, S. Govindarajan, P. D. Kirsch, P. Y. Hung, C. Krug, B. H. Lee, J. Heitmann, U. Schröder, G. Pant, B. E. Gnade, and W. H. Krautschneider, *Appl. Phys. Lett.* **91**, 72902 (2007).
- ⁵T. S. Börscke, J. Müller, D. Bräuhäus, U. Schröder, and U. Böttger, *Appl. Phys. Lett.* **99**, 102903 (2011).
- ⁶J. Müller, T. S. Börscke, D. Bräuhäus, U. Schröder, U. Böttger, J. Sundqvist, P. Kücher, T. Mikolajick, and L. Frey, *Appl. Phys. Lett.* **99**, 112901 (2011).
- ⁷C.-K. Lee, E. Cho, H.-S. Lee, C. S. Hwang, and S. Han, *Phys. Rev. B* **78**, 12102 (2008); G. H. Chen, Z. F. Hou, X. G. Gong, and Quan Li, *J. Appl. Phys.* **104**, 74101 (2008).
- ⁸R. C. Garvie, R. H. J. Hannink, and R. T. Pascoe, *Nature* **258**, 703 (1975).
- ⁹S. V. Ushakov, C. E. Brown, and A. Navrotsky, *J. Mater. Res.* **19**, 693 (2004).
- ¹⁰J. Y. Dai, P. F. Lee, K. H. Wong, H. L. W. Chan, and C. L. Choy, *J. Appl. Phys.* **94**, 912 (2003).
- ¹¹M. Komatsu, R. Yasuhara, H. Takahashi, S. Toyoda, H. Kumigashira, M. Oshima, D. Kukuruznyak, and T. Chikyow, *Appl. Phys. Lett.* **89**, 172107 (2006).
- ¹²J. Niinisto, K. Kukli, T. Sajavaara, M. Ritala, M. Leskela, L. Oberbeck, J. Sundqvist, and U. Schröder, *Electrochem. Solid-State Lett.* **12**, G1–G4 (2009).
- ¹³Q. Tao, G. Jursich, P. Majumder, M. Singh, W. Walkosz, P. Gu, R. Klie, and C. Takoudis, *Electrochem. Solid-State Lett.* **12**, G50–G53 (2009).
- ¹⁴L. Shi, Y. Zhou, J. Yin, and Z. Liu, *J. Appl. Phys.* **107**, 14104 (2010).
- ¹⁵Z. K. Yang, W. C. Lee, Y. J. Lee, P. Chang, M. L. Huang, M. Hong, K. L. Yu, M.-T. Tang, B.-H. Lin, C.-H. Hsu, and J. Kwo, *Appl. Phys. Lett.* **91**, 202909 (2007).
- ¹⁶K. Tomida, K. Kita, and A. Toriumi, *Appl. Phys. Lett.* **89**, 142902 (2006).
- ¹⁷T. Rössler, J. Gluch, M. Albert, and J. W. Bartha, *Thin Solid Films* **518**, 4680 (2010).
- ¹⁸D. W. Stacy and D. R. Wilder, *J. Am. Ceram. Soc.* **58**, 285 (1975); M. F. Trubelja and V. S. Stubican, *J. Am. Ceram. Soc.* **71**, 662 (1988).
- ¹⁹M. Yashima, H. Takahashi, K. Ohtake, T. Hirose, M. Kakihana, H. Arashi, Y. Ikuma, Y. Suzuki, and M. Yoshimura, *J. Phys. Chem. Solids* **57**, 289 (1996).
- ²⁰H. Fujimori, M. Yashima, S. Sasaki, M. Kakihana, T. Mori, M. Tanaka, and M. Yoshimura, *Chem. Phys. Lett.* **346**, 217 (2001).
- ²¹E. Rauwel, C. Dubourdieu, B. Hollander, N. Rochat, F. Ducroquet, M. D. Rossell, G. Van Tendeloo, and B. Pelissier, *Appl. Phys. Lett.* **89**, 12902 (2006).
- ²²C. Dubourdieu, E. Rauwel, H. Roussel, F. Ducroquet, B. Hollander, M. Rossell, G. Van Tendeloo, S. Lhostis, and S. Rushworth, *J. Vac. Sci. Technol. A* **27**, 503 (2009).
- ²³S. Motoyuki, K. Satoshi, and M. Takeo, *Jap. J. Appl. Phys.* **49**, 04DC24 (2010).
- ²⁴K. J. Hubbard and D. G. Schlom, *J. Mater. Res.* **11**, 2757 (1996).
- ²⁵J. Müller, T. S. Börscke, U. Schröder, M. Reinicke, L. Oberbeck, D. Zhou, W. Weinreich, P. Kücher, M. Lemberger, and L. Frey, *Microelectronic Engineering* **86**, 1818 (2009).
- ²⁶S. L. Miller, R. D. Nasby, J. R. Schwank, M. S. Rodgers, and P. V. Dressendorfer, *J. Appl. Phys.* **68**, 6463 (1990).
- ²⁷D. Bolten, O. Lohse, M. Grossmann, and R. Waser, *Ferroelectrics* **221**, 251 (1999).
- ²⁸D. H. Triyoso, P. J. Tobin, B. E. White, J. R. R. Gregory, and X. D. Wang, *Appl. Phys. Lett.* **89**, 132903 (2006).
- ²⁹D. B. Litvin, *Acta Crystallogr. A* **42**, 44 (1986).
- ³⁰E. H. Kisi, C. J. Howard, and R. J. Hill, *J. Am. Ceram. Soc.* **72**, 1757 (1989).
- ³¹J. E. Lowther, J. K. Dewhurst, J. M. Leger, and J. Haines, *Phys. Rev. B* **60**, 14485 (1999).