Enhanced electrical properties of Hf-aluminate thin films by crystal structure modulation

Ji-Hoon Ahn, Myoung-Jae Lee

Center for Artificial Low Dimensional Electronic Systems, Institute for Basic Science (IBS), 77 Cheingam-ro, Pohang 790-784, Republic of Korea

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The Hf-aluminate thin films were deposited by atomic layer deposition using super-cycle and modifed super-cycle concepts, and then enhanced electrical properties by crystal structure modulation were investigated. The high temperature tetragonal phase of HfO₂ was stabilized by Al₂O₃ doping and relevant electrical properties were improved through the monoclinic-to-tetragonal transformation. Moreover, the crystallographic direction was changed from the (111) to the (311) orientation by modification of super-cycle for uniform doping of Al₂O₃. The (311)-oriented-tetragonal phase Al₂O₃-doped HfO₂ films had an increased dielectric constant of 42 compared with that of 23 and 33 for monoclinic HfO₂ and (111)-oriented film, respectively.

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1. Introduction

In the semiconductor industry, the development of high-k dielectric materials is one of the most important issues for applications, as gate dielectrics in high-performance complementary metal-oxide-semiconductor transistors [1,2] and a capacitance dielectric for dynamic random access memory (DRAM) [3,4]. Especially for DRAM applications, HfO₂ or ZrO₂ based dielectrics have been used ever since DRAM half pitch of less than 100 nm⁵ and electrical performances of these materials continuously improved for device extension. Meanwhile, new high-k, such as TiO₂ [4,5], SrTiO₃ [6,7], based materials have come up and received considerable attention for next generation dielectric materials. However, these high-k materials should be formed on noble metals (such as Ru and Ir) electrode, because they have a relatively narrow band gap, and need to control of the interfacial crystallinity using bottom electrode. Unfortunately, however, mass production of noble metals has been met with challenges including the difficulty of their conformal deposition in 3-D structures with high aspect ratio, the high cost of the noble metal, and their compatibility with later processing steps. Therefore, improving electrical properties of Zr- or HF- based oxides, which are widely used in the mass production of semiconductor devices, is as important as developing new high-k materials. The known crystal structures of ZrO₂ or HfO₂ are monoclinic, cubic, or tetragonal depending on preparation temperature, and tetragonal phase have the highest dielectric constant compared with the other crystal structures of these oxides [8,9]. Especially, the estimated dielectric constant of tetragonal HfO₂ is about 70 by the first principle calculation [8]. However, the tetragonal phase of HfO₂ is only stable at high temperature (> 1400 K). Researchers have been focused on obtaining tetragonal structure with high dielectric constant through the use of stabilizer doping, e.g., Si doping of HfO₂, Er doping of HfO₂ [10,11]. The 100 nm thick tetragonal HfO₂ thin films became stabilized by Al₂O₃ doping (adopting a super-cycle concept), which affords higher charge storage factors and a dielectric constant as high as 47 demonstrated by Park et al. [12]. However, dielectrics thicker than 100 nm with relatively high annealing temperature of 700 °C are problematic in view of the continuing drive towards smaller integrated circuits; similar performances must now be achieved in films thinner than 10 nm with applicable annealing window.

In this paper, we investigate the enhanced electrical properties of Al₂O₃-doped HfO₂ films by crystal structure modulation through adopting the modified super-cycle concept of atomic layer deposition (ALD). The relationship between the crystal orientation and the dielectric constant is also investigated.

2. Experimental

Al₂O₃-doped HfO₂ thin films were deposited on a TiN (20 nm)/SiO₂/p-type Si using atomic layer deposition (ALD) adopting a super-cycle concept [13]. The used precursors were tetrakis(ethylmethylamino)hafnium (TEMA-Hf) and trimethylaluminum (TMA) for deposition of HfO₂ and Al₂O₃ respectively. The process temperature was kept at 280 °C, and ozone was used as an oxidant. For
uniform doping of a small amount of Al into HfO₂ films, the films were deposited by a normal super-cycle (SC) and a modified super-cycle (MSC) as shown in Fig. 1a and b, respectively. The MSC was composed of n sub-cycles of HO (HO) and one sub-cycle of HfAlOₓ (HAO). The HAO sub-cycle in MSC for Al2O3 doping was composed of six steps: (1) feeding of the TEMA-Hf, (2) purging, (3) feeding of the TMA, (4) purging, (5) feeding of ozone, (6) purging. The MSC method is favorable for uniformly incorporating small amounts of dopant, because the Al precursor only adsorbs on residual sites not already occupied by the Hf precursor on the bare surface. For crystallization, the as-deposited films underwent a rapid thermal annealing at 600 °C for 10 min under N₂ ambient.

The crystal structure of the Al₂O₃-doped HfO₂ thin films was determined by X-ray diffraction (XRD, X-pert APD, Philips) in 2θ scan mode using Cu Kα radiation (λ = 1.5405 Å). The film thickness and diffraction pattern were obtained by transmission electron microscopy (TEM). The dielectric constant was measured using a capacitance–voltage analyzer (Keithley 590) at a frequency of 10 kHz, with a top electrode of TiN deposited by ALD.

3. Results and discussion

First, we investigated the variation of crystallinity Al₂O₃-doped HfO₂ films deposited using SC with respect to the cycle ratio (HO:AO) by XRD analysis as shown in Fig. 2a. Whereas the crystal structure of pure HfO₂ film was monoclinic (the single Al₂O₃ thin film always shows amorphous phase), the tetragonal peak intensity of Al₂O₃-doped HfO₂ thin films increased with decreasing HO cycles in one SC, which means that the tetragonality of films increased with increasing Al contents in our experimental range. In addition, the peak position of tetragonal Al₂O₃-doped HfO₂ thin films was shifted toward higher angle compared with HfO₂ reference, which might due to the reduction of lattice parameter caused by the incorporation of Al atoms with a smaller atomic radius [12]. In order to observe more detail the crystallinity of the Al₂O₃-doped HfO₂ thin film deposited with HO:AO = 10:1, which shows the biggest intensity of tetragonal in XRD, we obtained the TEM diffraction pattern, as shown in Fig. 2b, and confirmed that the Al₂O₃-doped HfO₂ thin film had tetragonal phase with (111) preferred orientation.

Next, we investigated the variation of electrical properties of the Al₂O₃-doped HfO₂ thin films with HO:AO as shown in Fig. 3. Compared to the monoclinic-pure HfO₂ film, the dielectric constant of Al₂O₃-doped HfO₂ thin films increased with increasing Al contents in the films, up to 36 for HO:AO = 10:1 film. The increment of dielectric constant with decreasing HO cycle was consistent with the results of change from monoclinic to tetragonal. In the case of HO:AO = 10:1, which had the largest value of measured dielectric constant, the intrinsic dielectric constant extracted by the slope of the linear fitting of equivalent oxide thickness (EOT) values as a function of thickness was about 45, and film had the EOT value of interfacial layer of 2.58 Å, obtained from the y-axis intercept. As shown Fig. 3b, the leakage current properties were also improved by Al₂O₃ doping in HfO₂ film and that of HO:AO = 10:1, measured at 1 V, was reduced by about 6 orders of magnitude compared with pure HfO₂.

In order to improve the electrical properties, we adopted the MSC concept, as mentioned above in Section 2, for more uniform doping of a small amount of Al into HfO₂ films, and the structural and electrical properties were investigated. First, we have investigated the condition for forming films of similar Al composition with HO:AO = 10:1 film by varying cycle ratio of MSC and confirmed that films deposited at a cycle ratio (HO:HAO) of 7:1 and 8:1 had similar Al contents of about 4% (measured by X-ray photoelectron spectroscopy, data not shown). By using XRD analysis, as shown in Fig. 4a, a significant difference of the crystal structure between of Al₂O₃-doped HfO₂ thin films deposited using the MSC and the SC was not observed. However, the TEM diffraction pattern of HO:HAO = 8:1 sample showed a strong tetragonal (311) diffraction pattern. In other words, although the reason of preferred orientation changes in doping sequence is
unclear and further investigation is needed, Al$_2$O$_3$-doped HfO$_2$ thin film deposited using the MSC had tetragonal phase with (311) preferred orientation, while film deposited SC had (111) preferred orientation.

Finally, the electrical properties of Al$_2$O$_3$-doped HfO$_2$ thin films are summarized in Fig. 4. As compare with the pure HfO$_2$ film, both the dielectric constant and the leakage current notably improved by Al$_2$O$_3$ doping. Moreover, by adopting MSC concept in ALD, the measured dielectric constant further increased to about 42, compared with the value of about 33 of film deposited using SC at the similar leakage current level. The dielectric constant slightly increased with decreasing the amount of Al doping, and the optimum cycle ratio of HO:HAO was 8:1. Although the Al content and crystal phase of two cases of SC and MSC are similar, the reason for having different values of dielectric constant might be from their different crystal orientations. As the previous result of first principle calculation about tetragonal HfO$_2$ [8], the x, y components of the lattice dielectric tensor become more than nine times as large as for z component and therefore, tetragonal HfO$_2$ thin films could have different dielectric constants depending on the crystal orientation. In the case of Al$_2$O$_3$-doped HfO$_2$ thin film deposited using MSC, the preferred orientation was in the (311) direction, which has a larger x, y component compared with (111) for film deposited using SC, therefore the MSC film has larger dielectric constant than the SC case. As a result, the electrical properties of Al$_2$O$_3$-doped HfO$_2$ thin film enhanced by crystal structure modulation which had EOT value of 6.8 Å with leakage current density of 2.0E$^{-7}$ A/cm$^2$ measured at $+1$ V. Fig. 5

4. Summary

The Al$_2$O$_3$-doped HfO$_2$ thin films were prepared through deposition by ALD using the SC and MSC concept and the enhanced the electrical properties were investigated. Increasing the amount of Al$_2$O$_3$ doping caused the crystal structure to change from monoclinic to tetragonal phase. The dielectric constant increased with the monoclinic-to-tetragonal transformation, and leakage current properties also improved. Moreover, the preferred orientation of crystal structure could be modulated by adopting MSC and the dielectric constant of Al$_2$O$_3$-doped HfO$_2$ thin films deposited using MSC additionally increased to 42 compared with
that of 23 and 33 for monoclinic HfO2 film and tetragonal Al2O3-doped HfO2 film deposited using SC.

Reference