Enhancement of dielectric constant in HfO_2 thin films by the addition of Al_2O_3

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HfO_2 films with an enhanced dielectric constant, prepared through phase transition engineering by the addition of Al_2O_3, were deposited by plasma-enhanced atomic layer deposition adopting a supercycle concept. After an annealing step at 700 °C, the tetragonal phase, which is a high-temperature phase of HfO_2, was stabilized completely at room temperature and the crystallographic direction was changed to the preferred (002) orientation. As a result, Hf aluminate film with a (002)-oriented tetragonal phase had a dielectric constant of 47, approximately twice as large as the reported value of HfO_2 film with a monoclinic phase. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2387126]

The development of high-k materials has recently been the focus of intensive efforts to replace SiO_2 or silicon oxide-/nitride-based systems for the application of capacitor dielectrics. Of various high-k materials under investigation, HfO_2 has displayed many of the promising properties for this purpose, which are primarily due to its high dielectric constant (k=20–25) and wide band gap (~5.68 eV).[1] However, since HfO_2 is easily crystallized at low temperatures (<500 °C), which results in the formation of a monoclinic polycrystalline phase during deposition or annealing processes, Hf-based alloys such as silicate (Hf–Si–O) or aluminate (Hf–Al–O) have been studied to avoid such crystallization.[2,3] It is particularly noteworthy that Hf aluminate has higher dielectric constant (k) as compared to Hf silicate at the same Hf composition because the k value of Al_2O_3 ($k\sim 9$) is higher than that of SiO_2 ($k\sim 3.9$). Therefore, Hf aluminate appears to be a much more suitable high-k material than Hf silicate.

In general, the dielectric properties of high-k materials can be affected by the degree of crystallinity, crystal structure, and crystallographic orientation, in addition to their stoichiometric composition. There have been several reports on the dependence of the dielectric constant upon the crystal structure or crystallographic orientation in high-k materials.[4–7] In the case of HfO_2, it possesses four crystalline phases (monoclinic, tetragonal, cubic, and orthorhombic).[8] Zhao and Vanderbilt reported density functional theory calculations on various crystal structures of HfO_2 and indicated that dielectric constants of 18, 70, and 29 for the monoclinic, tetragonal, and cubic HfO_2 phases, respectively, can be obtained.[9] Unfortunately, the tetragonal and cubic phases can be transformed thermodynamically at approximately 1720 and 2600 °C, respectively, whereas the monoclinic phase appears at room temperature (RT).[10] Therefore, in order to take advantage of these high-temperature phases with a higher dielectric constant, which are metastable at RT, control over the respective crystal structures must be developed. To date, however, few articles have been published that strive to understand how the dielectric constant is related to the crystal structure of HfO_2.[11] In this letter, we report an experimental approach based on phase transition engineering where the metastable phase of HfO_2 with high dielectric constant is stabilized completely by the addition of Al_2O_3. The relationship between the crystal structure and the dielectric constant in Hf aluminate films is also discussed.

Hf aluminate films were deposited on p-type Si (100) at a deposition temperature of 250 °C and a pressure of 3 Torr by plasma-enhanced atomic layer deposition adopting a supercycle concept for precise composition control.[12] Tetrakis(ethylmethylamino) hafnium [TEMAHf, $Hf(N(CH_3)(C_2H_5))_4$] and trimethyl aluminum [TMA, $Al(CH_3)_3$] were used as precursors, and O_2 plasma was used as an oxygen reactant. Prior to film deposition, the native oxide on Si substrates was removed by buffered-HF dipping and de-ionized water rinsing. TEMAHf and TMA, sustained at 90 and 30 °C respectively, were delivered to the reactor with Ar carrier gas at a flow rate of 100 SCCM (SCCM denotes cubic centimeter per minute at STP). The flow rates of purge Ar and O_2 were 150 and 50 SCCM, respectively. The plasma power was kept at 100 W. The details of the plasma conditions have been described in a previous publication.[13] The thicknesses per cycle obtained from the converged regime were 0.103 nm/cycle for HfO_2 films and 0.127 nm/cycle for Al_2O_3 films, respectively. The films were annealed by rapid thermal annealing at 700 °C for 1 min under N_2 ambient. Electrical properties were measured on metal-oxide-semiconductor structure with sputtered Pt electrodes after a forming gas anneal. The crystal structures of Hf aluminate films were investigated using an x-ray diffractometer (XRD, Rigaku) with Cu $K\alpha$ radiation at 1.5405 Å. The capacitance-voltage (C-V) measurement was determined using a C-V analyzer (Keithley 590) at a frequency of 1 MHz and the current-voltage (I-V) measurement was evaluated using a semiconductor parameter analyzer (HP 4145B).

Table I summarizes the supercycle design for the preparation of Hf aluminate films. The four samples are labeled as A–D, respectively. A supercycle of Hf aluminate film is composed of two groups of subcycles allocated to deposit Al_2O_3 and HfO_2 films. A subcycle comprises several numbers of unit cycles, and four sequential pulses in a unit cycle, which

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TABLE I. Summary of supercycle design for the preparation of Hf aluminate films.

Samples (a,b)	Number of unit cycles allocated to each subcycle: Al_2O_3 (TMA–O_2 plasma) a	HfO_2 (TEMAHf–O_2 plasma) b	Number of supercycles
A (1,9)	1	9	100
B (1,15)	1	15	63
C (1,20)	1	20	48
D (1,30)	1	30	32

consist of a precursor, purge, oxygen reactant, and final purge, are supplied. The supercycles are repeated until a film of the desired thickness is obtained. Using this method, the composition can be digitally controlled by changing the number of unit cycles dedicated to each subcycle. The letters a and b denote the number of unit cycles in an Al_2O_3 and a HfO_2 subcycle, respectively. In order to control the relative ratio of Al and Hf, the number of unit cycles in a HfO_2 subcycle is varied from 9 to 30, while the number of unit cycles in an Al_2O_3 subcycle is fixed at 1. The film thickness is fixed at about 100 nm to show clearly the film crystallinity by XRD analysis.

Figure 1(a) shows the XRD patterns of Hf aluminate films with respect to the number of unit cycles in a HfO_2 subcycle after the annealing process recorded by θ-2θ scanning. In order to compare the difference in phase, the XRD pattern of a pure HfO_2 film with a monoclinic phase is included. After annealing at 700 °C, Hf aluminate films (samples A, B, and C) were crystallized to the tetragonal phase characterized by (111), (002), and (220) diffraction peaks, which is a high-temperature phase of HfO_2. As the number of unit cycles in a HfO_2 subcycle increased, a multiphase with the monoclinic and the tetragonal phases was observed (sample D). Besides the observed phase transition, a change in preferred orientation within the same tetragonal phase also occurred. When the number of unit cycles in a HfO_2 subcycle increased from 9 to 30, preferentially (002)-oriented films were obtained while the (111) orientation decreased significantly. In addition, as shown in Fig. 1(b), a superimposed view of XRD patterns reveals the peak position shift towards larger 2θ values with a decrease of the number of unit cycles in a HfO_2 subcycle. According to

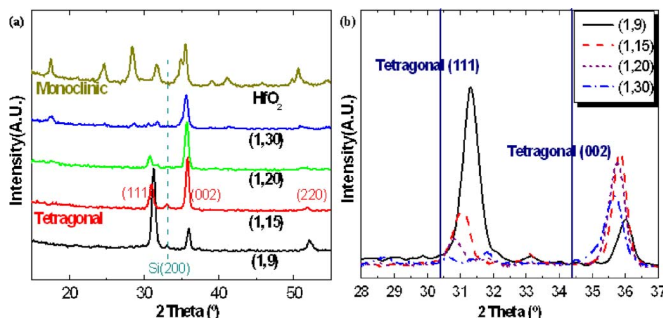

FIG. 1. (Color online) (a) XRD patterns of Hf aluminate films with respect to the number of unit cycles in a HfO_2 subcycle after the annealing process at 700 °C recorded by θ-2θ scanning. (b) A superimposed view of XRD patterns of Hf aluminate films showing the peak position shift towards larger 2θ values.

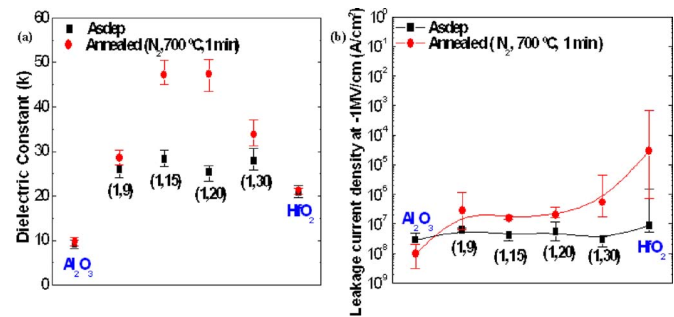

FIG. 2. (Color online) (a) Dielectric constants and (b) leakage current densities at -1 MV/cm of Hf aluminate films with respect to the number of unit cycles in a HfO_2 subcycle before and after the annealing process.

Bragg's law, the reduction of the lattice parameter produces the increase of 2θ values. Thus, the substitution of Al atoms with a smaller atomic radius for larger Hf atoms in the HfO_2 lattice causes the lattice parameter of Hf aluminate films to decrease in agreement with Vegard's law.[14]

Figures 2(a) and 2(b) present the electrical properties of Hf aluminate films before and after the annealing process. As illustrated in Fig. 2(a), the dielectric constants of pure HfO_2 and Al_2O_3 films were 21.3 and 9.7, respectively. In the case of Hf aluminate films where the addition of Al_2O_3 has lowered the dielectric constant in most previous studies, a higher dielectric constant was observed as compared to that of pure HfO_2 film after annealing at 700 °C. In order to explain the enhanced dielectric constant of Hf aluminate films, the effect of the crystal structure on the dielectric constant can be considered. The Clausius-Mossotti equation identifies the relationship between the dielectric constant (k), the molecular polarizability (α), and the molar volume (V_m) of a material $[k=(V_m+2\alpha/3)/(V_m-\alpha/3)]$.[15] Assuming that the molecular polarizability is independent of HfO_2 crystal structures because the polarizability contribution to the dielectric constant is equal to the square of the refractive index, which was found to be 2.1 for all HfO_2 phases, a large increase in the dielectric constant can be achieved by decreasing the molar volume.[6,11] From the XRD analysis in Fig. 1(a), the molar volume of Hf aluminate films with a tetragonal phase decreased as compared with that of pure HfO_2 film with a monoclinic phase, and thus, a dielectric constant of 28.5 was obtained (sample A). Furthermore, when the preferred orientation within the same tetragonal phase was changed from (111) to (002), it was determined that the dielectric constant increased up to 47, which is approximately twice as large as the value of HfO_2 film with a monoclinic phase (samples B and C). This may be due to the soft phonons that contribute a large amount to the dielectric constant of a (002)-oriented tetragonal phase. However, the appearance of a mixture consisting of monoclinic and tetragonal phases decreased the dielectric constant again (sample D). These results mean that both the phase transition and the change in preferred orientation by the addition of Al_2O_3 are plausible reasons for the enhanced dielectric constant of Hf aluminate films with a (002)-oriented tetragonal phase. A similar result has been reported previously for an Al_2O_3-added Ta_2O_5 film.[16] The leakage current densities of Hf aluminate films are also provided in Fig. 2(b). The leakage current densities of as-deposited Hf aluminate films with an amorphous phase were lower than those of crystalline films. It was also noted that the leakage current densities of Hf aluminate films were im-

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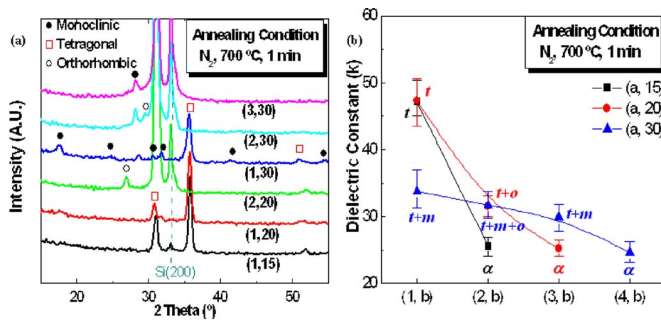

FIG. 3. (Color online) (a) XRD patterns and (b) the dielectric constants of Hf aluminate films with respect to various supercycle designs after the annealing process at 700 °C. The notation refers to each phase (α: amorphous, t: tetragonal, m: monoclinic, and o: orthorhombic).

proved as compared to that of pure HfO_2 film, which increased drastically after the annealing process. This may be associated with the modulation of band gap energy via the addition of Al_2O_3 with high band gap energy.

Figures 3(a) and 3(b) present the comprehensive relationship between the crystal structure and the dielectric constant in Hf aluminate films. In Fig. 3(a), the phases of Hf aluminate films were identified by XRD analysis. When the Al_2O_3 unit cycles were over 2, 3, and 4, respectively, with the HfO_2 unit cycles fixed in samples B, C, and D, Hf aluminate films had an amorphous phase even after the annealing process (not shown). At certain Hf aluminate films with more than one Al_2O_3 unit cycle, a multiphase consisting of a mixture of tetragonal, monoclinic, or orthorhombic phases was observed. As can be seen in Fig. 3(b), Hf aluminate films with an amorphous phase had a lower dielectric constant than those with a crystalline phase. Also, Hf aluminate films with the multiphase nature revealed a lower dielectric constant than that of those with the single tetragonal phase because the monoclinic phase has the lowest dielectric constant among the HfO_2 crystal system. In the case of orthorhombic phase, the dielectric constant is presumed to be low even though there are few literatures which report the dielectric constant of HfO_2 with an orthorhombic phase. It is of interest to note that a single tetragonal phase with an enhanced dielectric constant can be obtained by the supercycle design within a limited Al composition window where HfO_2 and Al_2O_3 form the solid solution. The incorporation of cations with lower valence into HfO_2 is one of the methods used to artificially achieve the stabilization of the metastable phase at RT.[10] When the tetravalent cations of Hf^{4+} are replaced with the trivalent cations of Al^{3+}, oxygen vacancies are formed for charge compensation. The creation of oxygen vacancies leads to a change in cation-oxygen coordination since the ionic positions are displaced away from the stoichiometric form, followed by a phase transition from the amorphous to metastable tetragonal or cubic phases and not to the equilibrium monoclinic phase. According to the $HfO_2-Al_2O_3$ equilibrium phase diagram, the solubility of Al_2O_3 in HfO_2 with a monoclinic phase is negligible at low temperatures due to the large difference in their ionic sizes.[17] However, the extended solubility of Al_2O_3 in HfO_2 results from the formation of a metastable tetragonal phase, which easily accommodates the disorder and nonstoichiometry as compared to the equilibrium phase.[18] The above observation provides clues to engineer the dielectric constant of high-k materials for the application of novel electronic devices. First, the stabilization of a high-temperature phase can be considered. Since high-k materials, such as HfO_2, ZrO_2, TiO_2, or Ta_2O_5, have a high-temperature phase with a high dielectric constant, this can be achieved through phase transition engineering by the addition of dopants. Moreover, if the cation with the high polarizability (i.e., Ba^{2+}, Sr^{2+}, Y^{3+}, La^{3+}, Ti^{4+}, or Ta^{5+}) is used as the dopant, enhancement of the dielectric constant can be achieved by the increase of the polarization in parent oxides, as well as by the phase transition.[19]

In summary, HfO_2 films with a higher dielectric constant than one reported previously were presented through phase transition engineering by the addition of Al_2O_3. The higher dielectric constant was due to the stabilization of a metastable tetragonal phase and the change in preferred orientation. Consequently, Hf aluminate films with a (002)-oriented tetragonal phase exhibited a dielectric constant of 47. Also, the increase in leakage current density was not quite as large, in spite of crystallization after the annealing process. When Hf aluminate films had a multiphase, however, the dielectric constant decreased again. This observation suggests that Hf aluminate films with a single tetragonal phase demonstrate better electrical properties as compared to pure HfO_2 film.

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