Interface effect on dielectric constant of $\text{HfO}_2/\text{Al}_2\text{O}_3$ nanolaminate films deposited by plasma-enhanced atomic layer deposition

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The effect of the interface between Al_2O_3 and HfO_2 sublayers on the dielectric constant was investigated in $\text{HfO}_2/\text{Al}_2\text{O}_3$ nanolaminate films deposited using plasma-enhanced atomic layer deposition. After annealing at 700 °C, the dielectric constants of the nanolaminate films with a sublayer thickness of 40 Å or greater were the same as the calculated values for a series of capacitors consisting of amorphous Al_2O_3 and monoclinic or tetragonal HfO_2 . As the sublayer thickness was reduced to 10 Å, the dielectric constant increased up to 17.7 because a thin Hf–O–Al mixture layer, of which the number increases drastically in the nanolaminate films with thin sublayers, is formed at the interface. © 2007 American Institute of Physics.

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Hafnium oxide (HfO_2) has been intensively studied as a promising high- k dielectric for replacing SiO_2 or SiO_2 -based oxides because it has a high dielectric constant, a good thermodynamic stability with Si, and a large band gap.^{1,2} Despite several attractive advantages, however, HfO_2 suffers from crystallization at low temperature (<500 °C), which results in a high leakage current along the grain boundaries. To address this issue, its combination with other binary oxides with superior thermal stability, such as Al_2O_3 or SiO_2 , has been investigated.^{3,4} Note that the k value of Al_2O_3 ($k \sim 9$) is higher than that of SiO_2 ($k \sim 3.9$).

There are two kinds of film structure form when two or more binary oxides are combined: a nanomixture structure, in which the binary oxides mix homogeneously, and a nanolaminate structure, which consists of alternating sublayers of binary oxides. The dielectric and insulating properties of these film structures can be adjusted by varying the composition or sublayer thickness of binary oxides. Recently, the fabrication of nanolaminate films has drawn major attention because the control of sublayer thickness on a nanometer scale confers unique film properties that cannot be obtained in bulk films with larger thickness scales, including the electrical, mechanical, magnetic, and thermal properties.^{5–8} In particular, although the dielectric constant of a nanolaminate film, which is considered a series of capacitors, is lower than that of a nanomixture film in which local differences in composition can induce local variation in the electrical properties, an enhanced dielectric constant has been reported in some nanolaminate-structured high- k dielectrics.^{9,10} Of the various deposition techniques used to produce high- k nanolaminate films, atomic layer deposition (ALD) is one of the best because of its self-limited growth mechanism, which allows exact control of the thickness, even in ultrathin films and the conformal deposition of three-dimensional structures.^{11,12} In this letter, the effect of the interface between Al_2O_3 and HfO_2 sublayers on enhancing the dielectric constant of nanolaminate films deposited using plasma-enhanced ALD (PEALD) is reported. To control the number

of interfaces between the two sublayers, $\text{HfO}_2/\text{Al}_2\text{O}_3$ nanolaminate films in which the individual sublayers of HfO_2 and Al_2O_3 have the same thickness were prepared for different sublayer thicknesses within the same total film thickness.

$\text{HfO}_2/\text{Al}_2\text{O}_3$ nanolaminate films were deposited on p -type Si (100) at 250 °C and 3 Torr using PEALD. Tetrakis(ethylmethylamino) hafnium (TEMAHf) ($\text{Hf}[\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)]_4$) and trimethyl aluminum (TMA) [$\text{Al}(\text{CH}_3)_3$] were used as precursors, and O_2 plasma was used as the oxygen reactant. Before depositing the film, the native oxide on the Si substrates was removed by buffered-HF dipping and de-ionized water rinsing. TEMA and TMA, held 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 the 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 reported previously.¹³ The thickness/cycles of Al_2O_3 on HfO_2 or HfO_2 on Al_2O_3 surfaces were 1.27 and 1.03 Å/cycle, respectively. $\text{HfO}_2/\text{Al}_2\text{O}_3$ nanolaminate films were deposited by repeating a supercycle for precise thickness control.¹⁴ A supercycle of $\text{HfO}_2/\text{Al}_2\text{O}_3$ nanolaminate film consisted of two groups of subcycles used to deposit separate Al_2O_3 and HfO_2 films. A subcycle consisted of several unit cycles, with four sequential pulses in a unit cycle, comprising a precursor, purge, oxygen reactant, and final purge. The films were annealed by rapid thermal annealing at 700 °C for 1 min under ambient N_2 . After a forming gas annealing, the electrical properties were measured on a metal-oxide-semiconductor structure with Pt electrodes, which were deposited via sputtering through shadow mask with a diameter of 160 μm . The film thickness and nanolaminate structure were examined using transmission electron microscopy (TEM). The crystal structure and the chemical binding state were investigated using x-ray diffraction (XRD) with Cu $K\alpha$ radiation and x-ray photoelectron spectroscopy (XPS) applying Mg $K\alpha$ radiation, respectively. The capacitance-voltage (C - V) was measured with a C - V analyzer (Keithley 590) at a frequency of 1 MHz.

Figure 1(a) shows the dependence of the dielectric constant on the sublayer thickness in the $\text{HfO}_2/\text{Al}_2\text{O}_3$ nanolami-

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FIG. 1. (Color online) (a) Dependence of the dielectric constant on the sublayer thickness in $\text{HfO}_2/\text{Al}_2\text{O}_3$ nanolaminate films before and after the annealing process and (b) cross-sectional TEM image of HfO_2 (10 Å)/ Al_2O_3 (10 Å) nanolaminate film where the dark and bright layers are HfO_2 and Al_2O_3 , respectively, after the annealing process.

nate films before and after annealing. The dielectric constant was extracted from the accumulation capacitance in C - V curve for all nanolaminate films. The sublayer thicknesses of Al_2O_3 and HfO_2 were the same in each film, and the sublayer thicknesses were varied from 500 to 10 Å in different nanolaminate films. The total thickness of each nanolaminate film was fixed at about 1000 Å. A nanomixture film with a dielectric constant of 17.7 that was formed by repeating a single unit cycle of each Al_2O_3 and HfO_2 was included as a reference. After annealing at 700 °C, as the sublayer thickness decreased from 500 to 70 Å, the dielectric constant remained constant at a value of 13.5, which is close to the value of 13.3 calculated by considering a nanolaminate film as a series of capacitors comprising amorphous Al_2O_3 and monoclinic HfO_2 sublayers. A series model was assumed here because the nanolaminate structure was maintained up to the film with 10-Å-thick sublayers after the annealing process, as shown in Fig. 1(b). In the series model, the dielectric constants of amorphous Al_2O_3 and monoclinic HfO_2 were determined experimentally to be 9.7 and 21.3, respectively. As the sublayer thickness decreased from 60 to 40 Å, the dielectric constant increased to about 14.6, which is larger than the value calculated in the series model. XRD analysis detected a tetragonal phases in the nanolaminate films with sublayer thicknesses from 40 to 60 Å, as shown in Fig. 2. In the nanolaminate film with 60-Å-thick sublayers, small peaks corresponding to the monoclinic phase were observed together with the tetragonal phase. HfO_2 with a tetragonal or

FIG. 2. (Color online) XRD patterns of $\text{HfO}_2/\text{Al}_2\text{O}_3$ nanolaminate films with respect to the sublayer thickness after the annealing process. The total thickness of each nanolaminate film is about 1000 Å.

FIG. 3. Dependence of the number of interface on the sublayer thickness in $\text{HfO}_2/\text{Al}_2\text{O}_3$ nanolaminate films.

cubic phase has a higher dielectric constant than HfO_2 with a monoclinic phase.^{15,16} Therefore, when the dielectric constant of the tetragonal HfO_2 phase is used in the series model instead of that of the monoclinic HfO_2 phase ($k_{\text{t-HfO}_2}=28.5$),¹⁵ the calculated value of nanolaminate films consisting of amorphous Al_2O_3 and tetragonal HfO_2 is 14.5, which is very close to the measured value of 14.6. Therefore, the increase in the dielectric constant in the nanolaminate films with sublayer thicknesses from 40 to 60 Å may have been attributable to the appearance of a tetragonal phase in the HfO_2 sublayer with a higher dielectric constant than that of HfO_2 with a monoclinic phase. As the sublayer thickness decreased from 30 to 10 Å, the dielectric constant increased rapidly and approached that of the nanomixture reference film. In this case, the appearance of the phase with a higher dielectric constant could not explain the rapid increase in the dielectric constant in the nanolaminate films because no diffraction peaks were observed, as shown in Fig. 2. Rather, a more viable explanation for the increase in the dielectric constant is the effect of the interface between two different sublayers. As shown in Fig. 3, the number of interfaces between the two sublayers increased drastically as the sublayer thickness decreased. For example, the nanolaminate film with 10-Å-thick sublayers contained 99 interfaces whereas the film with 40-Å-thick sublayers had 25 interfaces.

To clarify the effect of the interfaces between two sublayers on the dielectric constant in nanolaminate films, the chemical binding states of the interface are investigated using angle-resolved XPS at takeoff angles of 30° and 90° after annealing. The film consisted of 30-Å-thick HfO_2 and 50-Å-thick Al_2O_3 on Si substrate, as shown in Fig. 4(a). The

FIG. 4. (Color online) (a) Cross-sectional TEM image of (a) HfO_2 (30 Å)/ Al_2O_3 (50 Å)/p Si and (b) XPS peak for Hf 4f taken at a takeoff angle of 90° after the annealing process.

takeoff angle is the angle between the surface of the film and the detector, and two different angles were used to change the probing depth. The chemical binding state at the interface between the Al_2O_3 and HfO_2 sublayers is obtained at a takeoff angle of 90° , whereas only the information on the upper HfO_2 layer is obtained at a takeoff angle of 30° , which is more sensitive to the surface. As a result, only the O–Hf peak consisting of a unique $4f_{7/2}, 4f_{5/2}$ component at a 16.9 eV binding energy with a spin-orbit splitting value of 1.7 eV was obtained at a takeoff angle of 30° . However, in Fig. 4(b) an optimized fit required an additional component with a 0.7 eV shift to a higher binding energy near the interface between Al_2O_3 and HfO_2 , indicating the aluminate-type Hf–O–Al groups. The shift to a higher binding energy for Hf–O–Al was due to the reduced electron-donating nature of Al relative to Hf (i.e., it is more electronegative), followed by an increase in the measured binding energy through the reduction in the screening of the metal core levels. Therefore, it can be postulated that a thin Hf–O–Al mixture layer is formed at the interface between the two sublayers during the annealing process, although the incoherent interfaces between the Al_2O_3 and HfO_2 sublayers are maintained, as shown in Fig. 1(b). When the sublayers are relatively thick in nanolaminate films, the number of interfaces where the mixture layer is formed is small, and the effect of the thin mixture layer on the dielectric constant is trivial and ignorable. However, when the sublayer thickness is below $30 \text{ \AA}$, the number of thin mixture layers increases drastically, and the thickness of the thin mixture layer is no longer negligible compared to the thickness of the two sublayers. This was evident because the film with $10\text{-\AA}$ -thick sublayers has almost the same dielectric constant as the nanomixture reference film after annealing. Aita *et al.* reported that a mixed interface is formed in a nanolaminate film and can affect the properties of the nanolaminate film.¹⁷ Therefore, it can be concluded that the dielectric constant of nanolaminate films with thin sublayers is enhanced above the value calculated using the series model because of the formation of a mixture layer (Hf–O–Al) at the interface between the two sublayers and the dramatic increase of the number of mixture layers.

In summary, $\text{HfO}_2/\text{Al}_2\text{O}_3$ nanolaminate films with a dielectric constant higher than that calculated from the series

model were presented. After annealing, a dielectric constant of 13.5 was observed in the nanolaminate films with a sublayer thickness of $70 \text{ \AA}$ or greater, which is close to the 13.3 calculated by considering the nanolaminate film as a series of capacitors consisting of amorphous Al_2O_3 and monoclinic HfO_2 . When the sublayer thickness was reduced to $40 \text{ \AA}$, the dielectric constant increased slightly due to the appearance of a tetragonal HfO_2 phase, which has a higher dielectric constant. In addition, as the sublayer thickness decreased from 30 to $10 \text{ \AA}$, the dielectric constant increased rapidly to 17.7, since the effect of the thin Hf–O–Al mixture layer that formed at the interfaces between the Al_2O_3 and HfO_2 sublayers during the annealing process was not negligible compared to the two sublayers, and the number of mixture layers increased markedly in nanolaminate films with thin sublayers.

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