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Electrical property improvements of high-*k* gate oxide by *in situ* nitrogen incorporation during atomic layer deposition

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Atomic layer deposition (ALD) process for oxynitrides of high-*k* gate dielectrics employing NH_4OH as a single source for reactants, water and NH_3, was studied. By this method, nitrogen was incorporated up to 1–3 at. % for ALD Al_2O_3 and Ta_2O_5 films from metal organic precursors. A comparative study with water based ALD showed that the electrical properties were improved. The leakage current of oxide films from NH_4OH based ALD had been reduced and, more importantly, the dielectric strength was found to be enhanced by more than two orders of magnitude from a time dependent dielectric breakdown measurement. © *2007 American Institute of Physics*.

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For nanoscale high performance and low power devices, small leakage current and good reliability of gate oxides are essential. Regarding these, the incorporation of nitrogen has been considered as a way to eliminate a number of concerns, since the incorporated nitrogen atoms reduce the generation of defects, prohibit boron penetration,[1] and passivate oxygen vacancy states.[2] Additionally, nitrogen incorporation can improve structural stability and can increase dielectric constant of gate oxide.[1] While direct thermal oxidation using nitrogen containing oxidants such as N_2O or NO gas has been widely used for the formation of Si oxynitride, thermal or plasma annealing using NH_3 or N_2O gas before or after gate oxide film deposition has been employed for high-*k* gate oxides.[3,4] Previous reports have shown that about 1%–2% of nitrogen composition in ZrO_2 and Ta_2O_5 is reported to improve device properties with high mobility and good reliability.[5,6] While high nitrogen concentration at a poly-Si gate-oxide interface is beneficial by preventing dopant diffusion, too much incorporation of nitrogen at the interface between the channel region and the gate oxide can induce a large flatband voltage shift caused by an interface positive charge and can degrade channel mobility. Thus, the ability to control the nitrogen profile with atomic layer accuracy can take a significant impact on the improvements of the gate oxide property for future nanoscale complementary metal-oxide semiconductor (CMOS) devices.[1]

Atomic layer deposition (ALD) is one of the most promising techniques for high-*k* gate oxides. Since the thickness and composition of the thin films can be controlled with atomic accuracy by ALD, the *in situ* nitrogen incorporation during ALD can be a promising technique that can lead to an atomically modulated nitrogen profile. Although *in situ* doping of nitrogen into high-*k* gate oxides has been reported for chemical vapor deposition (CVD) using nitrogen containing reactants such as N_2O (Ref. 7) and NO (Ref. 8) plasmas, *in situ* nitrogen incorporation during ALD has rarely been studied. Only a brief report on nitrogen addition to oxygen plasma for plasma enhanced ALD of ZrO_2 and Al_2O_3 is found, without a detailed study on electrical properties.[9]

In this report, we investigated the *in situ* nitrogen incorporation during ALD of high-*k* gate oxides. For nitrogen incorporation during ALD, we developed a simple ALD process using NH_4OH as a source for reactants, which produces a mixture of vapors of water and NH_3.[10] Considering their practical importance as capacitor dielectric materials in dynamic random access memory and as gate dielectrics for nanoscale CMOS devices, the film properties of the common water based ALD Ta_2O_5 and NH_4OH based ALD TaO_xN_y were comparatively studied focusing on the electrical properties of gate stack including interface trap density, leakage current, and dielectric breakdown. To demonstrate the universality of the process, another representative ALD high-*k* oxide, Al_2O_3, was also investigated using the same process. The results have shown that *in situ* nitridation is feasible during ALD by using NH_4OH as a single source for reactants and the electrical properties of high-*k* oxides are improved significantly without seperate nitridation.

A homemade ALD system was used using pentakis(dimethylamino)tantalum (PDMAT) and trimethyl aluminum (TMA) as Ta and Al precursors, respectively. The water and NH_4OH (ammonium hydroxide, 29% diluted in water) were contained in silicone oil to maintain a constant temperature, and the flow rate of vapor was controlled by a leak valve. Ar was used as a carrier and purging gas, and the flow was controlled by a mass flow controller upstream to the main chamber. The PDMAT (powder) was contained in a bubbler and its temperature was kept at 65 °C to generate high enough vapor pressure, while TMA was used in room temperature without carrier gas due to its high vapor pressure. A typical Ta_2O_5 or TaO_xN_y ALD sequence was composed of PDMAT with a reactant exposure time of 1.5 s and a purging time of 4 s between those. The growth temperature was 250 °C. Similar process parameters were employed for Al_2O_3 ALD. The stoichiometry and impurity content in the films were analyzed by x-ray photoemission spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS). The microstructures of the films were analyzed by x-ray diffraction (XRD) and transmission electron microscopy (TEM). For electrical measurements, Ta_2O_5 thin films were deposited on *p*-type (boron, $10^{18}/cm^3$) Si(001) substrates, which were cleaned by the RCA method following dipping in a buffered oxide etch solution for 1 min to remove native ox-

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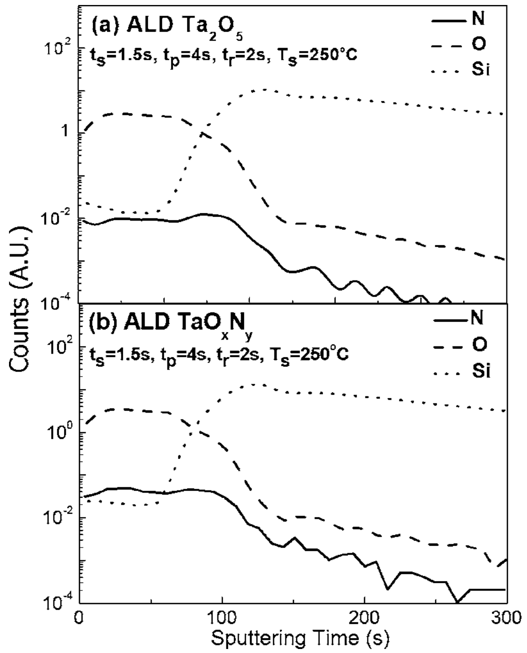

FIG. 1. SIMS profiles of as-deposited (a) ALD Ta_2O_5 and (b) ALD TaO_xN_y films using water and NH_4OH as a single source for reactants, respectively.

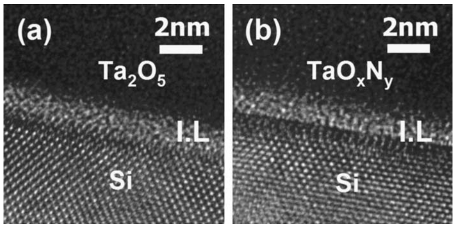

FIG. 2. TEM image of as-deposited (a) ALD Ta_2O_5 and (b) ALD TaO_xN_y films using water and NH_4OH as a single source for reactants, respectively.

ide. After deposition, a metal-oxide-semiconductor (MOS) capacitor structure was fabricated by patterning a 50 nm thick evaporated Al film through photolithography and dry etching using BCl_3. Capacitance-voltage and current-voltage characteristics were determined using a Keithley 4200 semiconductor analyzer with a HP4284 LCR meter.

Growth characteristics of thermal Ta_2O_5 using PDMAT were discussed in detail in our previous report.[11] The growth characteristics of TaO_xN_y using PDMAT and NH_4OH were similar to those of thermal ALD using water. The growth rate was 0.8 Å/cycle at saturation conditions of exposure times longer than 1.5 s, which is almost the same as that of Ta_2O_5 ALD using water. Also, the microstructure of the as-deposited film was determined to be amorphous by XRD, which is same as ALD Ta_2O_5 using water. The film composition was initially analyzed by XPS. A small nitrogen peak was observed for ALD TaO_xN_y, and the concentration was determined to be about 1.2% while no nitrogen peak was observed for ALD Ta_2O_5. But since the exact comparison of nitrogen concentration in each sample was difficult by XPS due to the similar locations of N 1*s* and Ta 4*p*, a SIMS measurement was performed for better sensitivity of the nitrogen content. SIMS depth profiles of the as-deposited water and ALD TaO_xN_y film are shown in Figs. 1(a) and 1(b), respectively. Figure 1(a) shows a small nitrogen composition even for ALD Ta_2O_5 in spite of the use of water as a reactant, which is probably caused by nitrogen incorporation from an alkylamide precursor used in this study. However, for ALD TaO_xN_y, at least five times more nitrogen incorporation was observed. Meanwhile, the contents of other possible contaminants, such as hydrogen and oxygen, were similar. After postdeposition annealing (PDA) at 700 °C for 1 min in O_2 ambient, the nitrogen contents in the bulk of both films were slightly decreased to about 60%–70% level, with relatively small change at the Si-dielectric interface (data not shown). Higher nitrogen content at the TaO_xN_y-Si interface is a common observation for nitrided high *k* made by other methods.[12] One possible explanation of this phenomenon is SiN_x formation at the interface.[13] Although these results show the nitrogen incorporation from NH_4OH, the experimental results of nitrogen incorporation might be ambiguous since TDMAT contains N in its ligands. To clarify this point, we have carried out the Al_2O_3 ALD process from TMA, which does not have nitrogen atoms in it, and NH_4OH at $T_s = 150$ °C. By XPS, the nitrogen incorporation up to 3.5% was observed, indicating that the nitrogen incorporation by using NH_4OH is applicable to other high-*k* ALD. Previously, it has been reported that NH_4OH produces vapors composed of water and NH_3 molecules, whose ratio is dependent on NH_3 concentration and temperature.[10] Thus, we can infer that the nitrogen incorporation in the current study is from the NH_3 vapor produced by the NH_4OH solution. For quantification of ammonia verus water flow from the NH_4OH solution, separate experiments were carried out based on NH_3 concentration measurements with exposure time, and the generation rate of NH_3 vapors was determined to be about 1.8 times larger than that of water vapors for our experimental conditions.

Cross sectional high resolution TEM images of as-deposited ALD Ta_2O_5 and ALD TaO_xN_y thin films are shown in Figs. 2(a) and 2(b), respectively. The TEM images show a clean and smooth interface with an amorphous structure for both cases. Although both of the films show the interface layer formation, the thickness of the interlayer for the ALD TaO_xN_y film (1.3 nm) is thinner than that of ALD Ta_2O_5 (1.5 nm). These results indicate that the nitrogen incorporation can reduce the formation of an interfacial layer. In a previous report on CVD HfO_2 gate oxide, the activation energy of interlayer formation during air exposure was higher for a film deposited by NO than O_2, attributed to the reduced oxygen diffusion by higher nitrogen content.[8] The thinner interlayer by nitrogen incorporation can lead to a smaller equivalent oxide thickness, which is beneficial to device scaling.

Capacitance-voltage measurements were carried out for a postdeposition annealed *p*-type Si/ALD Ta_2O_5 (10 nm)/Al MOS capacitor (Fig. 3). Also, additional forming gas annealing was performed at 400 °C for 30 min in 5% H_2–95% N_2 to reduce the interface trap charge. While both ALD TaO_xN_y and Ta_2O_5 films have low hysteresis (<0.05 V), the latter was found to have a relatively thinner equivalent oxide thickness (4 nm) than the former (4.3 nm). The increase of dielectric constant with nitrogen incorporation is a general observation, which can be explained by reduced interface layer formation and higher dielectric constant of the film itself.[13] The interface state density (D_{it}) was measured by conductance method at various frequencies, from 1 kHz to 1 MHz. The midgap D_{it} values were measured to be 1.8×10^{12} cm^{-2} eV^{-1} for ALD Ta_2O_5 and

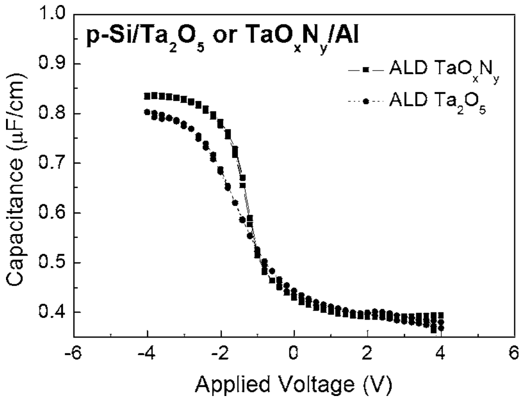

FIG. 3. Capacitance-voltage curves of MOS capacitors with 10 nm ALD Ta_2O_5 and TaO_xN_y as insulators.

1.4×10^{11} $cm^{-2}\,eV^{-1}$ for ALD TaO_xN_y. Thus, D_{it} near the midgap is almost an order of magnitude lower for ALD TaO_xN_y, indicating the significant improvement by *in situ* nitridation.

Figure 4 shows current-density–voltage measurement results of the same MOS capacitors. The leakage current density at 1 MV/cm was 7.6×10^{-6} A/cm^2 for ALD Ta_2O_5 and 4×10^{-7} A/cm^2 for ALD TaO_xN_y. Thus, by using NH_4OH as a single source for reactants, the leakage current is significantly reduced. The leakage current reduction by nitrogen incorporation has been commonly observed in previous reports. For example, two orders of magnitude reduction in leakage current density was reported by high density plasma N_2O annealing.[14] One of the plausible explanations for this phenomenon is that nitrogen passivates oxygen vacancies, which serve as an electron leakage path.[15] More noticeable improvement in electrical properties by using NH_4OH is the improvement in dielectric breakdown strength. Figure 4 shows that the dielectric breakdown occurs at 20 MV/cm for the ALD TaO_xN_y case, which is significantly higher than at 10 MV/cm for ALD Ta_2O_5.

For more unambiguous comparison on the improvement of reliability, time dependent dielectric breakdown measurement was carried out using a constant voltage mode measurement at 6.5 MV/cm of stress for postdeposition annealed samples. Figure 5 shows that the time to breakdown t_{bd} increases by about 700 times by *in situ* nitridation. This is almost comparable to other previous reports by employing a separate nitridation process. For example, t_{bd} of 4 nm ZrO_2 has been increased from 8 to 1000 s (Ref. 5) and 1000 times improvement was reported for 16 nm thick CVD Ta_2O_5 by NH_3 PDA.[5,16]

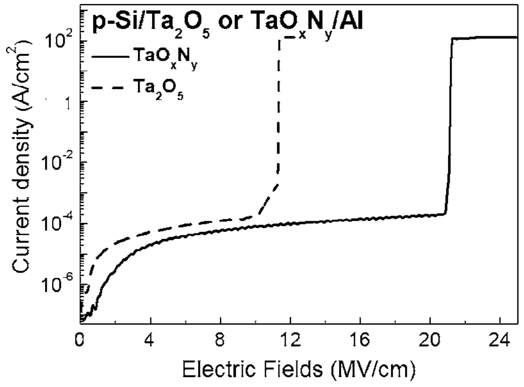

FIG. 4. Leakage current density–electric field curves with 10 nm ALD Ta_2O_5 and TaO_xN_y as insulators.

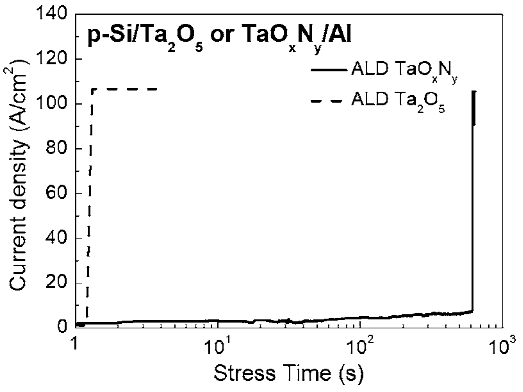

FIG. 5. Time dependent dielectric breakdown data for MOS capacitors with 10 nm ALD Ta_2O_5 (solid line) and TaO_xN_y (dotted line) as insulators. The voltage stress measurement was done at an applied voltage of 6.5 MV/cm.

Thus, by *in situ* nitridation using NH_4OH as a single source for reactants, considerable improvements in electrical properties can be made without a separate nitridation process. Moreover, by using this process, the nitrogen profile control is feasible, since ALD itself is beneficiated by atomic level control in thickness and composition. This would give additional degrees of freedom in reliablity control of gate oxide in future nanoscale device fabrication.

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