Suppressive Effect of Interface Reaction and Water Absorption by Al Incorporation into Pr-oxide Film

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Abstract. We have investigated the effects of Al incorporation into a Pr-oxide/Si gate stack formed by atomic layer deposition. The PrAlO\textsubscript{x} (PAO) layers show an amorphous structure by the incorporation of Al into the Pr-oxide. The PAO sample with 10%-Al shows good C-V characteristics without a hump, and the interface state density (D\textsubscript{it}) is as low as 5 \times 10\textsuperscript{10} cm\textsuperscript{-2} eV\textsuperscript{-1}. The amount of Si in the Pr-oxide film decreases by the Al incorporation. We deduce that Al incorporation into a Pr-oxide layer inhibits reaction at the interface of the PAO/Si substrate. We found that Al incorporation into the Pr-oxide is effective against the inhibition of moisture incorporation into the oxide film. The Pr(OH)\textsubscript{3} component, estimated by x-ray photoelectron spectroscopy, increases near the surface of the Pr-oxide and PAO films with 10%-Al after 300 days, while the SiO\textsubscript{x} component does not change. The Pr(OH)\textsubscript{3} component decreases with increasing Al incorporation. The D\textsubscript{it} of the PAO/Si sample with 10%-Al increases after 300 days. After post metallization annealing of the sample in N\textsubscript{2}, D\textsubscript{it} decreases with increasing annealing temperature.

1. Introduction

The thickness of a silicon dioxide (SiO\textsubscript{2}) layer for a gate insulator has decreased to the nanometer scale with shrinking of complementary metal-oxide-semiconductor (CMOS) transistors, and its leakage current increases significantly. Recently, Hf-oxide has been shown to be one of the most promising candidates for a high dielectric (high-k) gate insulator to reduce leakage current with increasing physical thickness. However, gate insulator materials having a higher dielectric constant than Hf-oxide (higher-k materials) are required for future CMOS devices. Rare-earth metal oxides such as praseodymium (Pr) - and lanthanum (La)-oxides are promising because their bulk dielectric constants are as high as 30 [1]. Moreover, it is expected that Pr-oxide has a large electron effective mass since the conduction band structures of Pr-oxide are very flat. The leakage current that can be attributed to the presence of such large electron masses in the Pr-oxide is very low (J\textsubscript{g}: 5 \times 10\textsuperscript{-9} A/cm\textsuperscript{2}, V\textsubscript{g}=1 V, EOT: 1.4 nm) [2].

Pr-oxide films have been grown by molecular beam epitaxy (MBE) [1], chemical vapor deposition (CVD) [3], and atomic layer deposition (ALD) [4]. Recently, we successfully deposited Pr-oxide films by CVD and ALD using a Pr(EtCp)\textsubscript{3} precursor by controlling the film thickness and its fluctuation [5-7]. However, an interfacial (IF) SiO\textsubscript{x} layer often forms between the high-k materials and Si substrate,
when high-k materials are deposited directly on Si [8-10]. The dielectric constant of the IF layer is usually low, which reduces the effective dielectric constant of the gate stack structure. Furthermore, the dielectric constant of the high-k oxide film decreases due to diffusion of Si into the high-k materials. It is thus important to prevent the formation of the IF layer. In addition, rare-earth metal oxides are highly hygroscopic in general. It is known that Pr-oxide tends to react with water vapor to form praseodymium hydroxides (Pr(OH)$_3$) [4,11].

The diffusion coefficient of oxygen in an Al oxide thin film is known to be smaller than those in the majority of oxides. There are some reports on the insertion of ultrathin Al$_2$O$_3$ film into the HfO$_2$/Si interface [12] and Al incorporation into La-oxide films [13-14]. The effects of the insertion of Al$_2$O$_3$ film include suppression of interfacial reaction, raising the thermodynamical stability of a high-k material on silicon, and modulation of the energy band gap and flatband voltage. Therefore, we focused on the incorporation of Al oxide into a Pr oxide layer in order to prevent formation of the IF layer and suppression of highly hygroscopic. Also, it is known that PrAlO$_x$ (PAO) has a high dielectric constant ($\varepsilon_r=18–25$) [15-16]. The PAO film can be deposited by CVD and ALD. However, the affect of the IF layer and hygroscopic properties on the electrical properties of the PAO film have not been clarified yet.

In this study, we examined the formation of PAO films by ALD using Pr(EtCp)$_3$, trimethylaluminum (TMA), and H$_2$O precursors. We also investigated the crystallinity and electrical properties of PAO gate insulators.

2. Experiments

N-type Si(001) wafer was used as the substrate. Prior to the oxide film deposition, the Si substrate was cleaned with the conventional RCA solutions. Then, the native oxide on the substrate was removed and a hydrogen (H)-terminated surface was formed with a diluted HF-solution. We deposited PAO films on the hydrogen terminated n-type Si substrates by ALD using a SUNALE$^\text{TM}$ R-150B reactor (Picosun). Pulsed supply of Pr(EtCp)$_3$ and TMA was repeated alternately in an ALD chamber. The compositions of Pr and Al (Al/(Al+Pr)) were controlled by changing the duration of their subcycle values (x,y) in the [TMA/H$_2$O]$_x$/[Pr(EtCp)$_3$/H$_2$O]$_y$ ALD sequence. The subcycle values (x,y) used were (0,54), (1,8), (1,1), and (100,0). The composition ratio Al/(Al+Pr) was estimated from each deposition rate of TMA/H$_2$O and Pr(EtCp)$_3$/H$_2$O. Samples with Al/(Al+Pr) composition of 0%, 10%, 60%, and 100% were prepared. The ALD process was carried out at a substrate temperature of 300$\degree$C. After the ALD, top and back Al electrodes were formed by vacuum evaporation. Crystalline structures were determined using transmission electron microscopy (TEM). X-ray photoelectron spectroscopy (XPS) was carried out to analyze the chemical bonding states and elemental composition. Capacitance-voltage (C-V), deep level transient spectroscopy (DLTS), and current-voltage (I-V) measurements were performed for the Al/PAO/Si MOS capacitors.

3. Results and Discussion

Figures 1(a)-(f) show TEM images and transmission electron diffraction (TED) patterns of PAO films on Si(001) substrates with an Al composition of 0% [Fig. 1(a), Fig. 1(d)], 10% [Fig. 1(b), Fig. 1(e)], and 60% [Fig. 1(c), Fig. 1(f)]. The thickness of PAO films with Al composition of 0%, 10%, and 60% were estimated to be 8.4, 6.1, and 5.9 nm, respectively, from the TEM observations. In the sample without Al, many diffraction spots appear as shown in Fig. 1(d). This indicates the formation of polycrystalline cubic Pr$_2$O$_3$. On the other hand, only diffraction patterns related to the Si substrate are observed for the samples with Al/(Al+Pr) of 10% and 60%. This indicates that the structure of the oxide is amorphous. These results mean that the crystalline structure of the oxide film changed to an amorphous structure by Al incorporation during deposition.

Figure 2 shows the C-V characteristics of Al/PAO/Si MOS capacitors for various Al ratios at RT with a measurement frequency of 1 MHz. The PAO films were deposited with ALD at 300$\degree$C. All C-V
Al/(Pr+Al): 0% 10% 60% 5 nm glue Si (001) Pr-oxide 8.4 nm PAO 6.1 nm 5 nm glue Si (001) Si 002 c-Pr2O3 222 Si 002 Si 220 Si 220

Figure 1. TEM images and TED patterns of PAO films with an Al composition of 0% [Fig. 1(a), (d)], 10% [Fig. 1(b), (e)], and 60% [Fig. 1(c), (f)] deposited on a Si(001) substrate.

Figure 2. C-V characteristics of Al/PAO/Si MOS capacitor with various Al compositions.

Figure 3. Interface state density (Dit) of Al/PAO/Si MOS capacitor with various Al compositions measured by the conductance method and the DLTS method.

curves were measured from the inversion to accumulation conditions, and then these were continuously returned to the accumulation condition. In the C-V curves of all samples, a hysteresis loop was observed. The hysteresis loop direction was always clockwise (the direction is shown by an arrow). This indicates carrier injection into traps near the PAO/Si interface from the Si substrate. Also, a hump in the C-V characteristics can be observed in the sample without Al, which indicates a large interface state density (Dit). In contrast, in the PAO samples, no such hump is observed in the C-V curves. Figure 3 shows the Dit values estimated using the conductance method and DLTS as a function of the energy from the conduction band edge. The energy distribution of the interface state density shows a general U-shape, as shown in the DLTS results. The interface state densities of the PAO samples were smaller than that of the Pr-oxide sample without Al. In particular, a Dit value of $5 \times 10^{10}$ cm$^{-2}$ eV$^{-1}$ was achieved for the sample with Al/(Al+Pr) of 10% by the conductance method. This indicates that the interface state density can be decreased by the incorporation of Al into the Pr oxide/Si structure.

Figures 4(a)-(c) show Si2p photoemission spectra from the Pr oxide sample with various Al ratios Al/(Pr+Al) of (a) 0%, (b) 10%, and (c) 60%. Samples were sputtered with Ar ions at an acceleration energy of 3 keV. The photoelectron spectra for various sputtering times of the samples are shown in the figures. In the case of Al/(Pr+Al) of 0%, a peak is observed at 102.5 eV for a sputtering time of 1000 s to 4000 s. This indicates that Pr silicate (PrSiO$_x$) and SiO$_x$ are formed [5]. In contrast, in the case of sputtering time above 5000 s, this peak is not observed. On the other hand, this peak is also observed in the PAO samples.
Figure 4. Si2p photoemission spectra of the Pr oxide sample with various Al ratios (Al/(Pr+Al)): (a) 0%, (b) 10%, and (c) 60% for various sputtering times.

Figure 5. The depth profiles of the area intensity of XPS spectra for each element of PAO samples with the ratio of Al to Pr of (a) 0%, (b) 10%, and (c) 60%, respectively.

Pr3d_{5/2}, O1s, Si2p, and Al2p core spectra were obtained by XPS. Figures 5(a)-(c) show depth profiles of the area intensity of each element core spectra for PAO samples with Al/(Pr+Al) of (a) 0%, (b) 10%, and (c) 60%, respectively. The existence of the SiOx component is observed through the films in all samples. This indicates that PrSiOx is formed. In other words, Si diffuses to the surface region during the ALD process. On the other hand, SiOx composition for Al/(Pr+Al) of 0%, 10%, and 60% samples was 5.4%, 1.8%, and 1.6%, respectively. The amount of Si in the PAO film decreases with increasing amount of incorporated Al. Thus, we deduce that Al incorporation into the Pr-oxide film inhibits interfacial reaction at the PAO/Si interface. The presence of Al is observed through the films in all samples. This shows that the Al atoms were mixed into the Pr-oxide films during the ALD process. In fact, the Al composition in the samples with the designed Al/(Pr+Al) composition of 10% and 60% was estimated to be 22% and 67%, respectively. We deduce that the difference between designed and practical values of the Al composition in the oxide is due to the difference in the surface condition of the Pr-oxide and Al2O3. The small value of the interface state density can be attributed to prevention of the formation of SiOx and PrSiOx at the interface by the Al incorporation. The Al incorporation into the Pr-oxides thus effectively improves the electrical properties of the Pr oxide MOS capacitors.

Next, we investigated the effect of Al on the hygroscopic characteristics of the Pr oxide film. We kept the PAO/Si samples in a vacuum desiccator for 300 days. We then performed XPS and C-V measurements. Figures 6(a)-(f) show O1s photoemission spectra for the Pr oxide sample with various Al ratios Al/(Pr+Al) of 0%, 10%, and 60%. We measured XPS spectra for the samples before and after Ar sputtering for 1000 s. These spectra were normalized by the area intensities of the Pr-oxide at the Pr3d_{5/2} core spectra for each sample. After 300 days without sputtering, the intensity of the peak around an energy of 532 eV increased in the samples with Al/(Pr+Al) of 0% and 10%. After sputtering, the peak intensity dramatically decreased. On the other hand, in the sample with Al/(Pr+Al) of 60%, the spectrum hardly changed after 300 days regardless of the surface sputtering. These results indicate that this component exists near the surface. Also, the peak intensity of SiOx in the Si2p photoemission spectra hardly changed after 300 days in all samples (not shown). Thus, we consider that this peak at
an energy of 532 eV in the O1s spectra is related to Pr(OH)$_3$ due to the hygroscopic properties of the Pr oxide. The area density of the Pr(OH)$_3$ peak decreased with increasing Al component in the Pr-oxide, as shown in Fig. 6(g). These results mean that hygroscopicity of the Pr-oxide film can be reduced by Al incorporation.

We also investigated the time degradation of electrical properties. Figures 7(a)-(c) show C-V characteristics of the Pr oxide sample with various Al ratios Al/(Pr+Al): 0%, 10%, and 60%, respectively. The flat band voltage, estimated from the C-V characteristics of the sample without Al, slightly changed to the negative voltage direction after 300 days compared to the as-deposited samples as shown in Fig. 7(a). In the C-V curve of Al/(Pr+Al): 10% sample, the hysteresis width increased after 300 days, as shown in Fig. 7(b). On the other hand, the C-V curve of the sample with Al/(Pr+Al): 60% hardly changed even after 300 days.
Figure 7(d) shows the interface state density value as a function of the surface potential energy for samples with the various Al ratios as-deposited and after 300 days. In the sample with Al/(Pr+Al): 10%, the $D_{it}$ value increased after 300 days. Meanwhile, the $D_{it}$ values for the samples with Al/(Pr+Al): 0 and 60% hardly increased even after 300 days. The variation in the $D_{it}$ value was too small in the sample without Al since $D_{it}$ is higher than for the sample with Al. Thus, we might not have observed a variation in $D_{it}$ after 300 days. In the low Al composition samples, the C-V characteristics changed. Thus, we deduce the degradation of electrical properties for the low Al composition samples by moisture.

Next, the samples after 300 days were annealed at 200-300°C in a N$_2$ ambient atmosphere to investigate the recovery effect of annealing for the time degradation sample. Figures 8(a) and (b) show the trap density near the interface and the flat band voltage ($V_{FB}$) estimated from the C-V characteristics as a function of the annealing temperature. In the samples with Al/(Pr+Al) of 0% and 10%, the trap density near the interface decreased with an increase in the annealing temperature. Meanwhile, the Al/(Pr+Al): 0% and 10% sample of the trap density near the interface increased with the annealing temperature. $V_{FB}$ hardly changed with annealing in the sample without Al while $V_{FB}$ of the PAO samples changed toward the ideal $V_{FB}$ value. The minimum value of $D_{it}$ at each temperature is shown in Fig. 8(d), which decreased with increasing annealing temperature.

4. Conclusions
We investigated the effects of Al incorporation into the Pr-oxide films for suppression of the formation of an IL layer as well as the hygroscopic properties. The amount of Si diffusing from the substrate into the Pr-oxide decreased with increasing Al composition. The interfacial reaction was effectively suppressed by the Al incorporation into the Pr-oxide. Good C-V characteristics without humps and a low interface state density as low as $5 \times 10^{10}$ cm$^{-2}$ eV$^{-1}$ were obtained in the PAO sample with the 10%-Al component. The Pr(OH)$_3$ component increased in the Pr-oxide with a low Al component after 300 days, while that in the PAO sample with the 60%-Al component did not change. The hygroscopic properties could be suppressed by Al incorporation into Pr-oxide that effectively improved the interfacial properties of the Pr-oxide/Si structure.

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References
[1] Osten H J, Bugiel E and Fissel A 2003 Solid-State Electron. 47 2161
[2] Osten H J, Dabrowski J, Müssig H J, Fissel A, and Zavodinsky V 2004 Predictive simulation of semiconductor processing: status and challenges (Berlin: Springer) p 259
[3] Nigra R L, Toro R G, Malandrino G, Raineri V and Fragalá I L 2003 Adv. Mater. 15 1071
[4] Kukli K, Rita M, Pilvi T, Sajavaara T, Leskelä M, Jones A C, Aspinall H C, Gilmour D C and Tobin P J 2004 Chem. Mater. 16 5162
[5] Kondo H, Sakurai S, Sakashita M, Sakai A, Ogawa M and Zaima S 2010 Appl. Phys. Lett. 96 012105
[6] Kondo H, Matsui H, Furuta K, Sakashita M and Zaima S 2010 Jpn. J. Appl. Phys. 49 04DA14
[7] Adachi M, Sakashita M, Kondo H, Takeuchi W, Nakatsuha O and Zaima S 2011 Jpn. J. Appl. Phys. 50 04DA08
[8] Watahiki T, Tinkham B P, Jenichen B, Shayduk R, Braun W and Ploog K H 2008 Appl. Surf. Sci. 255 758
[9] Müssig H J, Dąbrowski J, Ignatovich K, Liu J P, Zavodinsky V and Osten H J 2002 Surface Science 504 159
[10] Schmeißer D and Zschech E 2006 Materials Science in Semiconductor Processing 9 934
[11] Mullica D F, Milligan W O and Beall G W 1979 J. Inorg. Nucl. Chem. 41 525
[12] Park M, Koo J, Kim J, Jeon H, Bae C and Krug C 2005 Appl. Phys. Lett. 86 252110
[13] Arimura H, Brown S L, Callegari A, Kellock A, Bruley J, Copel M and Watanabe H 2011 IEEE Electron D’ev. Lett. 32 288
[14] Sivasubramaniam P, Kim M J, Gnade B E, Wallacea R M, Edge L F, Schлом D G, Craft H S and Maria J P 2005 Appl. Phys. Lett. 86 201901
[15] Rouffignac P and Gordon R G 2006 Chem. Vap. Deposition, 12 152
[16] Schroeder T, Lupina G, Sohal R, Lippert G, Wenger C, Seifarth O, Tallarida M and Schmeisser D 2007 J. Appl. Phys. 102 014103