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Analysis of Leakage Current through Al/HfAlOx/SiONx/Si(100) MOS Capacitors

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We determined the energy band alignment of $HfAlO_x/SiON_x$ stack dielectric and Si(100) and analyzed the leakage current through the Al-gate MIS capacitors with dielectric stack structures by using a multiple-scattering theory which well-reproduces the tunnel current for the case of n^+poly-Si/SiO_2/Si(100). $HfAlO_x$ (Hf/(Hf+Al)=~0.3) in the thickness range of 3-7nm were formed on 1.2nm-thick SiON with an N content of ~20at.% prepared on p-Si(100) by an ALCVD method. From the onset of O1s energy loss spectra and the analysis of the valence band spectra, the energy band gap and valence band offset between $HfAlO_x$ and Si(100) were 6.50eV and 3.60eV, respectively. With 3.0nm-thick $HfAlO_x$, the calculated tunnel current agrees with the measured current if the effective mass of electrons tunneling through $HfAlO_x$ is assumed to be ~$0.5m_0$. In contrast, with 5.0 and 7.0nm-thick $HfAlO_x$, the measured leakage current was markedly larger than the calculated tunnel current level. Frenkel-Poole conduction is responsible for this extra leakage current because the current at oxide voltages higher than 1V is proportional to the square root of the oxide field and the permittivity derived from the slope of the Frenkel-Poole plot is almost equal to the value obtained from the accumulation capacitance.
Key words: tunnel current, direct tunneling, energy band alignment

1. INTRODUCTION

The implementation of a gate dielectric with high dielectric constant (high-k) is currently one of major technological challenges for the continuous scaling of complementary metal-oxide-semiconductor (CMOS) devices to sub-100nm technologies [1]. Although the use of a physically thicker high-k gate dielectric for the same electrically equivalent SiO_2 thickness (EOT) is an efficient way to achieve a reduction in the gate leakage to some practical limit under a required capacitive coupling between the gate and Si(100), there are formidable difficulties regarding interface issues and electrically active defects in most high-k dielectrics [2]. With a systematic consideration of the required properties of gate dielectrics such as favorable energy band alignment to Si(100), high thermal stability and process integration compatibility, attention has focused on Hf-silicates and Hf-aluminates as the most promising replacements for conventional SiON gate dielectrics [3, 4]. In fact, a significant reduction of leakage current through Hf-silicate or Hf-aluminate in comparison with SiO_2 has been reported and the scalability to 1nm in EOT has been claimed [3, 4]. However, a quantitative explanation on the leakage current through the gate dielectric or its mechanism was not found. In targeting EOT below 1nm, there are two key issues. First, minimization of the interfacial layer formation between high-k dielectric and Si(100) during the deposition of a high-k dielectric layer and during post-deposition anneal (PDA) in oxidizing ambient, which reduces the leakage current. The physical properties of the interfacial layer have a strong effect on leakage. Second, the replacement for poly Si-base gates with metal gates, which eliminates carrier depletion effect [5] and Fermi level pinning [6] but faces a new set of formidable challenges on manufacturing and reliability. Because the metal has continues filled electronic states below Fermi level, an increase in the gate leakage is of particular concern compared with poly-Si gate.

In this work, to characterize the leakage current through Al/$HfAlO_x$/$SiON_x$/Si(100) stack structures with different $HfAlO_x$ thicknesses, first we determined the energy band alignment of the stack structures by x-ray photoelectron spectroscopy. By applying a multiple-scattering theory, which well-reproduces the tunnel current for the case of n^+poly-Si/SiO_2/Si(100) [7], to the energy band profile, we simulated the ideal current-voltage (I-V) characteristics and compared them with the measured results. The conduction mechanism involving traps is also discussed.

2. EXPERIMENTAL

The substrates used in this study were 300mm p-Si(100) wafers. After wet-chemical cleaning, the wafer surface was nitrided at 700°C in pure NH_3 ambient and oxidized in NO, which resulted in a 1.2nm-thick $SiON_x$ layer [8]. Subsequently, $HfAlO_x$ (Hf/(Hf+Al)=~0.3) films in the thickness range of 3 to 7nm were formed on the $SiON_x$ layer by atomic layer controlled chemical-vapor-deposition (ALCVD), where $Hf[N(C_2H_5)CH_3]_4$, $Al(CH_3)_3$, and H_2O were used as precursors and remote plasma nitridation using pure NH_3/Ar was performed at each ALCVD cycle. Post deposition anneal at 1000°C for 1 sec in 0.2 % O_2 diluted with N_2 was carried out. The analysis of the stack structure in the thickness direction was made by x-ray photoelectron spectroscopy (XPS) using monochromatized AlKα (1486.6eV) radiation in combination with a wet-chemical etching in a 0.1% HF solution. For MIS capacitors with Al electrodes formed by thermal evaporation, the capacitance-voltage (C-V) and current-voltage (I-V) characteristics were

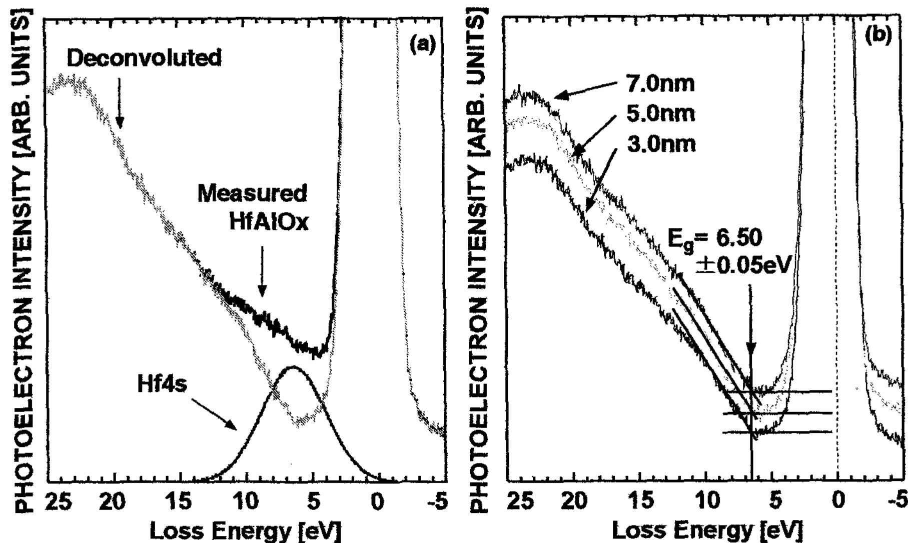

Fig. 1. O1s energy loss spectra for 3.0 nm-thick $HfAlO_x$ (a) and after subtraction of Hf4s contribution from the samples in the thickness range from 3 to 7 nm (b). The measured spectrum for 3.0 nm-thick $HfAlO_x$ was deconvoluted into inherent O1s energy loss signals and Hf4s signals in (a). The onset of the energy loss signals for each sample was determined with an accuracy of ±0.05eV.

measured at room temperature.

3. RESULTS AND DISCUSSION

No indication of crystallization was detected by transmission electron microscope (TEM) observations. Atomic force microscope (AFM) images confirmed a very smooth dielectric surface after PDA and a fairly uniform thinning of the dielectrics in the dilute HF-etching. The depth analysis of Si2p, N1s, O1s and Hf4f spectra showed a slight compositional intermixing in the dielectric stack. A few at.% of Si atoms were incorporated in $HfAlO_x$. The N content was ~1at.% in $HfAlO_x$ and ~20at.% in $SiON_x$. To evaluate the energy bandgap of the $HfAlO_x$ films, the energy loss signals of O1s photoelectrons from the $HfAlO_x$ layers were measured as shown in Fig. 1. Considering the fact that Hf4s signals overlap with the energy loss spectrum of the primary O1s core line signals [9], we first subtracted the Hf4s component expected from Hf4f signal intensity from the measured spectrum to obtain an inherent background of the O1s core line signals and then defined the onset with a linear extrapolation of a leading segment to the background level. The energy bandgap of $HfAlO_x$ film was determined to be constant at 6.50eV within an accuracy of 100meV, regardless of the $HfAlO_x$ thickness (Fig. 1 (b)). As for the energy band gap of the interfacial $SiON_x$ layer, the O1s energy loss spectrum was taken after complete removal of the top $HfAlO_x$ layer by dilute HF etching and compared to the spectrum for 1.6nm-thick thermally grown SiO_2 on Si(100) as represented in Fig. 2. Although a similarity in the spectral structure between the two cases was observable, the energy loss signals for the $SiON_x$ showed some remarkable tailing and the onset energy (7.5eV) was significantly shifted toward the lower energy side compared with that (8.95eV) for the SiO_2 case determined by line-fitting in the same energy region. The N2p non-bonding states are thought to be responsible for the measured bandgap shrinkage and band tailing. To determine the valence band offset

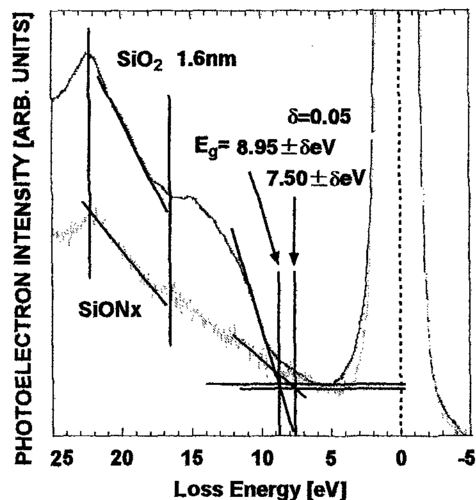

Fig. 2. O1s energy loss spectra for $SiON_x$/Si(100) after complete removal of the top $HfAlO_x$ layer and for 1.6nm-thick thermally-grown SiO_2.

(VBO) between $HfAlO_x$ and Si(100), the valence band spectra for $HfAlO_x/SiON_x$ stack structures on Si(100) were measured and first deconvoluted into two components as shown in Fig. 3. In the spectral deconvolution, the valence band spectrum measured after complete removal of the top $HfAlO_x$ layer, that is $SiON_x$/Si(100) as shown in Fig. 2, was used and the binding energy for each valence band spectrum was calibrated with the Si2p(3/2) core line peak due to the Si(100) substrate. From the energy separation of the tops of the deconvoluted valence band spectra, the VBO between $HfAlO_x$ and Si(100) was determined to be 3.6eV (Fig. 3). The result indicates that the conduction band offset (CBO) between $HfAlO_x$ and Si(100) is 1.78eV in consideration of the energy bandgap. From further spectral deconvolution of the valence band spectrum of $SiON_x$/Si(100) by using the

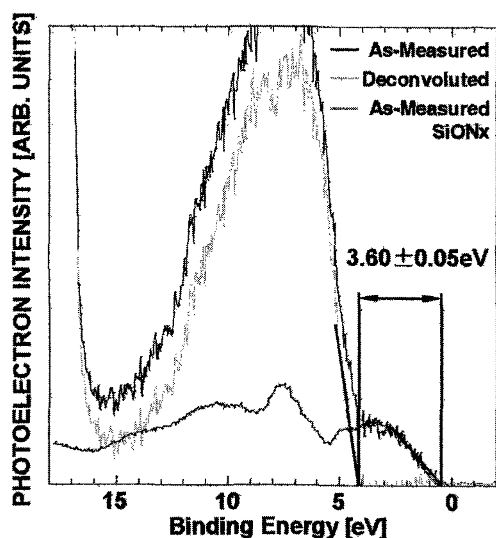

Fig. 3. Valence band spectrum for 3.0 nm-thick $HfAlO_x/SiON_x/Si(100)$ and spectral deconvolution using the spectrum measured for $SiON_x/Si(100)$ after complete $HfAO_x$ removal with the consideration of the binding energy of the Si2p core line peak. By the spectral deconvolution, the $HfAlO_x$ component (deconvoluted) was extracted from the measured spectrum of the stack structure.

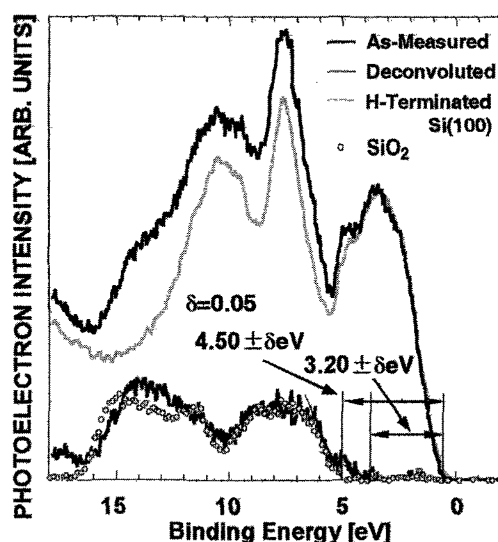

Fig. 4. Valence band spectrum for the $SiON_x/Si(100)$ shown in Fig. 3 and spectral deconvolution using the spectrum for wet-chemically prepared H-terminated Si(100) with consideration of the binding energy of the Si2p core line peak. By the spectral deconvolution, the $SiON_x$ component (deconvoluted) was extracted and compared with the reference valence-band spectrum of thermally grown SiO_2 (open circles).

spectrum separately measured for H- terminated Si(100), the spectrum due to the $SiON_x$ valence band is extracted and very similar to the valence band spectrum for thermally grown SiO_2 as shown in Fig. 4. Obviously, two threshold energies can be determined near the low energy edge of the $SiON_x$ valence band spectrum. The lower threshold (~3.2eV from the Si valence band top) is attributable to the band edge for the nitrogen-rich region and the higher one (~4.5eV from the Si valence band top) is identical to the band edge for the SiO_2 network. Thus, the CBO between the $SiON_x$ interfacial and Si(100) is estimated to be 3.18eV for VBO = 3.2eV or 3.33eV for VBO = 4.5eV (Fig. 5), being almost equal to the value for thermally grown $SiO_2/Si(100)$ interface [10].

High-frequency capacitance-voltage (C-V) characteristics of Al-gate MIS capacitors with different $HfAlO_x$ thicknesses were evaluated by a two-frequency C-V method [11] and, from the plot of the reciprocal values of accumulation capacitances as a function of the $HfAlO_x$ thickness, the dielectric constants of $HfAlO_x$ and $SiON_x$ were estimated to be $12.8\varepsilon_0$ and $4.1\varepsilon_0$, respectively, where ε_0 is permeability in the vacuum. From the measured flat-band voltage shift, net positive fix charge densities for 3nm-thick and 7nm-thick $HfAlO_x$ cases were obtained to be $3.8x10^{12}$ and $1.5x10^{12}$ cm^{-2}, respectively. A C-V hysteresis in the range of 30-40mV due to the electron injection into oxide traps was also measured. Figure 6 shows I-V characteristics for Al-gate MIS capacitors measured with negative gate biases, in which the voltage through the dielectric stack was determined from the C-V characteristics, and compared with simulated results for tunnel currents through the stack structures from the Al gate. In the simulation, a multiple-scattering theory [12] was applied to the measured energy band profile. The effective mass of electrons

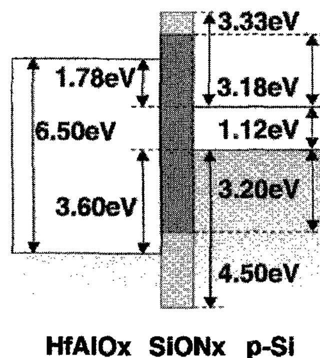

Fig. 5. Energy band alignment of HfAlOx (Hf/(Hf+Al) = ~0.3) to Si(100), including interfacial $SiON_x$.

tunneling through $SiON_x$ was set to be $0.35m_0$, where m_0 is the free electron mass. The effective mass of electrons tunneling through $HfAlO_x$ was set at $0.50m_0$ for the case of 3.33eV in CBO between $SiON_x$ and Si(100) and at 0.51m m_0 for the case of 3.18eV in CBO between $SiON_x$ and Si(100). For the case with 3.0nm-thick $HfAlO_x$, the measured leakage current at oxide voltages higher than 0.5V is well reproduced with the tunnel current calculation mentioned above. A significantly enhanced leakage current at voltages below 0.5V in comparison to the simulated result suggests that trap-assisted tunneling is dominant in the low electric-field. In contrast, for the cases with 5.0nm-thick and 7.0nm-thick $HfAlO_x$, the measured leakage current is markedly larger than the calculated tunnel current level. The plot of the leakage current vs. the square root of the oxide field indicates the field-enhanced thermal emission of trapped electrons, or so-called "Frenkel-Poole emission", becomes significant at oxide voltages

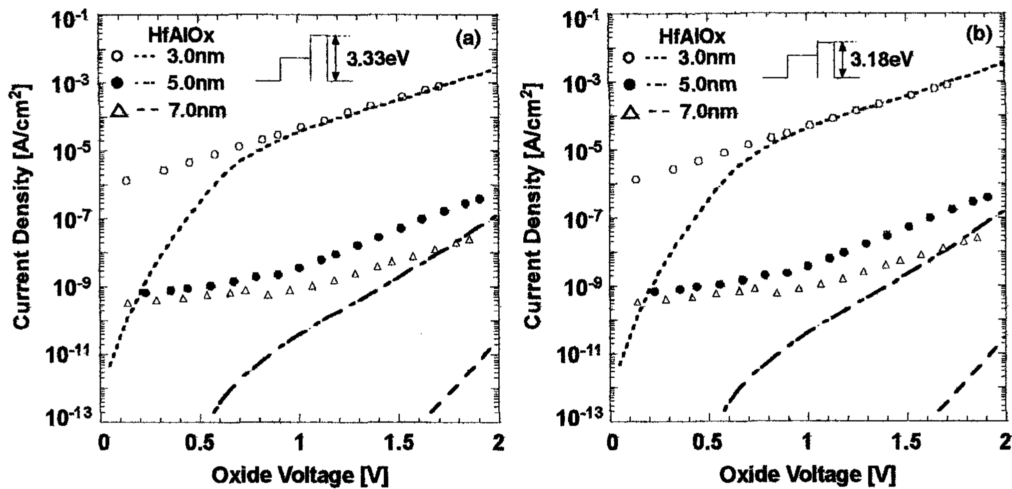

Fig. 6. The measured leakage currents (symbols) for Al-gate MIS capacitors with different $HfAlO_x$ thickness as a function of the oxide field in negative gate bias and comparison to the simulated I-V curves (lines) for the stack structures with an energy band profile shown in Fig. 5 using a multiple-scattering theory[12]. The simulated results are shown for each case with a conduction band offset between interfacial $SiON_x$ and Si(100) of 3.33eV (a) or 3.18eV (b), where the effective mass of tunneling electrons was set to be $0.5m_0$ (a) or $0.51m_0$ (b).

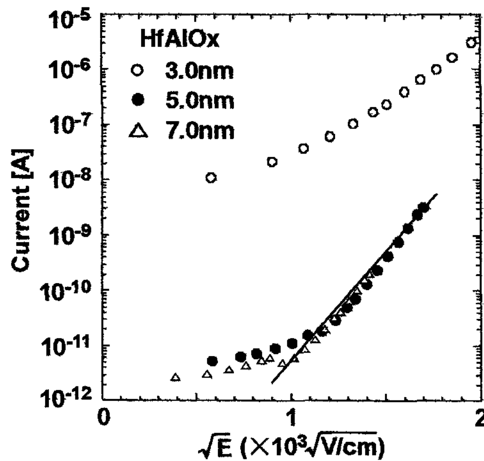

Fig. 7. The plots of measured leakage currents shown in Fig. 6 vs. the square root of the electric field in $HfAlO_x$.

higher than ~1V because the dielectric constant estimated from the slope of the Frenkel-Poole plot in the high electric field region is $\sim 10\varepsilon_0$ and fairly close to the value ($12.8\varepsilon_0$) obtained from the C-V measurements as described above.

4. CONCLUSIONS

The energy band alignment of the stack structure consisting of $HfAlO_x$ (Hf/(Hf+Al)=~0.3) and an interfacial $SiON_x$ layer with respect to Si(100) was determined by the analyses of O1s energy loss spectrum and valence band spectrum. By applying a multiple-scattering theory for electron tunneling through a dielectric stack structure to the experimentally determined energy band profile, the intrinsic leakage due to electron tunneling from Al-gate to Si(100) substrate with any assistance of traps was calculated and compared with the measured leakage current of Al-gate MIS capacitors with different $HfAlO_x$ thicknesses. The leakage current of the case with 3nm-thick $HfAlO_x$ is interpreted in terms of direct tunneling at oxide voltages higher than 1V and trap-assisted tunneling below 1V. The effective mass of tunneling electrons through $HfAlO_x$ was estimated to be $\sim 0.5m_0$. For $HfAlO_x$ thicker than 5nm, the enhanced leakage current in the oxide field higher than ~2MV/cm is attributed to Frenkel-Poole emission.

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