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Effects of Oxidizer Dose and Temperature on Interfacial Silicate Formation and Flatband Voltage in Atomic Layer Deposition of Al_2O_3

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1. Introduction

This study reports on the role of ALD growth temperature and oxidizer dose on film properties relevant to gate dielectrics. Both variables influence gas-surface chemical equilibria, affecting the density of surface sites that undergo reaction. Mateor[1] has reported that oxidizer dose changes film growth rate but not density, film quality, nor electrical properties. However, extending this conclusion to gate dielectrics is not yet clear.

The purpose of this paper is, therefore, to clarify the role that oxidizer dose and temperature have on: (1) electrical properties of Al_2O_3 films in MOSCAP structures; and (2) suppression of silicate interfacial films that frequently appear when depositing Al_2O_3 on Si by ALD. Particular attention is given to manipulating interfacial silicate in this study since its formation seems to be most influenced by deposition variables.[2,3]

2. Experimental

ALD films were grown on H-terminated Si(001) using $Al(CH_3)_3$ and H_2O. Ar was used as a carrier gas to transport precursor vapors to the wafer surface and purge the reactor after each reaction half-cycle. Annealing was performed 1% O_2 in Ar at atmospheric pressure for 30 sec. MOSCAP structures were formed by evaporating gold contacts and aluminum/gold backside electrodes. Film thickness was measured optically by ellipsometry.

3. Results and Discussion

FTIR and EELS of as-deposited films formed at 300°C and standard oxidizer dose indicate the presence of an interfacial silicate layer. EELS data given in Fig. 1 shows AlO_x and Si^{4+} present together at the same spatial position. FTIR results show a silicate signal appearing at 1087 cm^{-1} (Fig. 2). XPS corroborates the presence of silicate. As shown in Fig. 3c, a silicate peak appears at a binding energy of 101.7 eV. The thickness of this interfacial silicate was calculated to be 1.11 nm by assuming the escape depth of Si 2*p* photoelectrons through the silicate layer is approximately the same as that through SiO_2. Annealing at temperatures as high as 750°C did not measurably affect the silicate layer. As shown in Fig. 4a and 4b, despite the formation of a separate SiO_2 layer, the XPS peak for the silicate layer remained relatively unchanged before and after annealing.

Reducing oxidizer dose while keeping the temperature constant at 300°C suppresses silicate formation. As shown by the XPS data in Fig. 3a, the intensity of the silicate peak relative to that of Si has been reduced compared to that of Fig. 3c. Using the same calculation methods as above, the silicate thickness is estimated to be 0.70 nm, a reduction of about 0.4 nm. Total film thickness is unchanged as the reduction in dose at 300°C has little effect on the film growth rate. Growth rate is 0.9-1.0 Å/cycle for both the low and standard dose conditions.

Similarly, reducing the ALD temperature from 300°C to 200°C while maintaining the same the oxidizer dose suppresses silicate formation, reducing its thickness to 0.58 nm. Comparing Fig. 3b to 3c, a reduction in the silicate peak intensity relative to that of Si is apparent. Deposition rate is affected slightly, decreasing by 5% to 0.85 Å/cycle.

Perhaps not surprisingly, operating at low dose and 200°C simultaneously yields even less interfacial silicate. As shown in Fig. 4c, an XPS signal at 101.7 eV is very weak. Overlap of the Si and SiO_2 peaks makes it difficult to determine if any silicate has formed. In the extreme case, one could assume that the entire signal at this binding energy is attributed to a silicate layer to calculate the maximum possible thickness. However, even in this case, the layer would be only 0.11nm, or 1/10th of that formed at standard dose and 300°C. The total film thickness is affected slightly, owing to a reduction in growth rate to 0.6 Å/cycle

C-V measurements were made on films grown at various doses and temperatures and annealed at 600°C. As shown in Fig. 5, the samples grown at 300°C/standard dose, 300°C/low dose, and 200°C/standard dose have different capacitance at negative biases. However, these C-V curves converge and produce about the same flatband voltage (ca. 0.9V). Such results have been previously observed and attributed to the presence of negative fixed charge.[4] On the other hand, when both the temperature and oxidizer dose are reduced together, changes in the flatband voltage persists even in the annealed film. As shown by the curve for the film grown at 200°C and reduced dose, the C-V curve shifts to negative biases, producing a flatband voltage and hysteresis of 0.33 V and 30 mV, respectively.

Origins of this shift may lie in structural differences in the as-deposited films and chemical changes that take place

during annealing. Simultaneous reduction in growth temperature and oxidizer dose reduces the reaction efficiency of H_2O at $-Al(CH_3)_2$ surface sites. Lower dose reduces conversion of methyl groups, shifting gas-surface reaction equilibria to lower saturation levels.[1] Decreasing the temperature also reduces the reaction conversion of surface sites after each H_2O pulse.[5] While the complementary half-reaction between $Al(CH_3)_3$ with Al-OH sites would also be affected by temperature, the rate constant of the oxidation half reaction is more sensitive to reductions in temperature as its calculated activation energy is 0.70 eV, nearly 0.2 eV higher than for the reaction between $Al(CH_3)_3$ and Al-OH sites.[6]

To confirm the presence of carbon in the low dose/low temperature films, as well as to investigate structural changes related to carbon content during annealing, we performed TDS from 25°C to 950°C. Results show that carbon, in the form of CH_3 fragments, volatilizes. Compounds with mass numbers of 28 and 44 were also observed which could represent ethylene and propane, respectively. However, these mass numbers also correspond to CO, N_2, and CO_2, making it difficult to confirm desorbed carbon species beyond CH_3 at this time.

Desorption of CH_3 from the film structure is expected to leave a void at an aluminum atom where the CH_3 group had existed. The formation of such voids would be expected to move the flatband voltage to more negative biases based on simple charge considerations. As stated earlier, since the flatband voltage for Al_2O_3 films is typically shifted to positive biases owing to fixed negative charge, the production of voids could in principle move the flatband voltage back closer to neutral biases, depending on the number created. Since the concentration of $-CH_3$ groups in the films formed at low dose/200°C is higher than in films formed at higher dose and/or higher temperature, we would expect that, after annealing, the density of Al atoms with these voids will also be higher in the low dose/200°C film. The observed shift in flatband voltage reported in Fig. 5 for the low dose/200°C film would be consistent with such changes in the material structure.

4. Conclusions

Oxidizer dose can affect interfacial film and electrical properties pertinent to high-k gate films. Flatband voltage of annealed Al_2O_3 can be shifted by as much as 0.6 V toward more neutral biases. Formation of voids resulting from volatilization of CH_3 during post-deposition heat treatment is suggested as a possible reason for this behavior. Changes in oxidizer dose and temperature do not necessarily affect film growth rate but can suppress the formation of interfacial silicate. Low oxidizer dose together with a growth temperature of 200°C can suppress silicate formation to less than 0.1 nm.

Acknowledgements

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References

[1] R. Matero, et al., Thin Solid Films, 368, 1 (2000).

[2] W.-S. Jeon, et al., J. Electrochem. Soc., 149, C306 (2002).

[3] T. M. Klein, et al., Appl. Phys. Lett., 75, 4001 (1999).

[4] R. S. Johnson, et al., J. Vac. Sci. Technol., A19, 1353 (2001).

[5] A. Dillon, et al., Surf. Sci., 82/83, 460 (1995).

[6] Y. Widjaja, et al., Appl. Phys. Lett., 80, 3304 (2002).

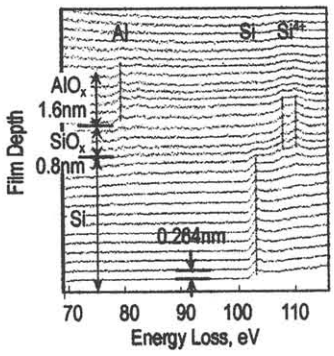

Fig. 1 EELS analysis of as-deposited Al_2O_3 by ALD at 300°C and standard oxidizer dose.

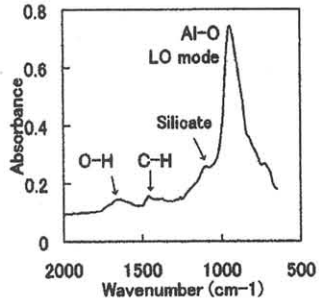

Fig. 2 FTIR analysis of as-deposited Al_2O_3 by ALD at 300°C and standard oxidizer dose.

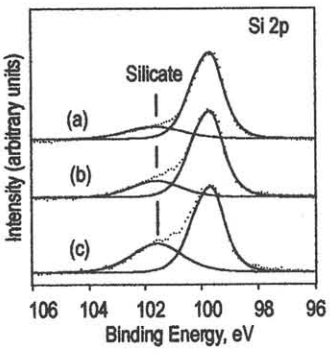

Fig. 3 XPS analysis of as-deposited Al_2O_3 film formed at: (a) 200°C, std dose; (b) 300°C, low dose; (c) 300°C, std dose.

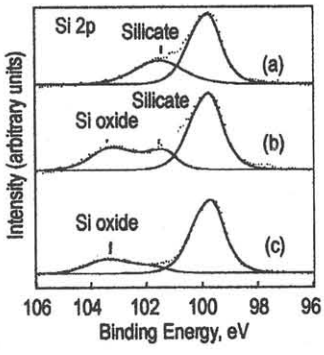

Fig. 4 Comparison of films by XPS analysis. (a) as-deposited Al_2O_3 film grown at 300°C/ standard dose; (b) Sample a) after annealing at 750°C in 1% O_2; (c) Al_2O_3 film grown at 200°C/ low oxidizer dose and annealed at 600°C in 1% O_2.

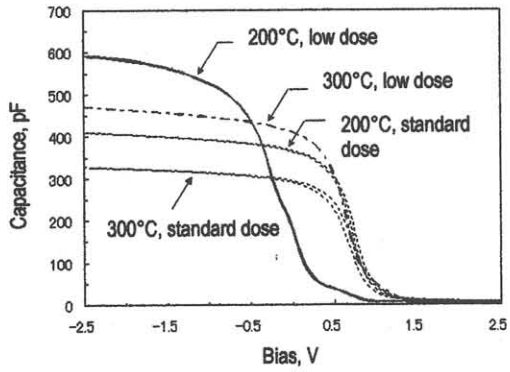

Fig. 5 C-V behavior at 100 kHz of Al_2O_3 deposited at various dose and growth temperatures. Samples were annealed in 1% O_2 in Ar at 600°C.