

Electrical characterization of thin Al_2O_3 films grown by atomic layer deposition on silicon and various metal substrates

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Abstract

Al_2O_3 films with thicknesses ranging from 30 to 3540 Å were grown in a viscous flow reactor using atomic layer deposition (ALD) with trimethylaluminum and water as the reactants. Growth temperatures ranged from 125 to 425 °C. The Al_2O_3 ALD films were deposited successfully on a variety of substrates including Au, Co, Cr, Cu, Mo, Ni, NiFe, NiMn, Pt, PtMn, Si, stainless steel, W, and ZnO. Electrical properties were characterized by current–voltage and capacitance–voltage measurements using a mercury probe. These measurements focused mainly on Al_2O_3 ALD films deposited on n-type Si(1 0 0) and on Mo-coated Si(1 0 0) substrates. Excellent insulating properties were observed for nearly all of the Al_2O_3 films. For a typical Al_2O_3 ALD film with a 120 Å thickness, leakage currents of <1 nA/cm² were observed at an applied electric field of 2 MV/cm. Fowler–Nordheim tunneling was observed at high electric fields and dielectric breakdown occurred only at ≥ 5 MV/cm. Dielectric constants of $k \sim 7.6$ were measured for thick Al_2O_3 ALD films. The measured dielectric constant decreased with decreasing Al_2O_3 film thickness and suggested the presence of a thin interfacial oxide layer. For Al_2O_3 ALD films grown on n-type Si(1 0 0), capacitance measurements were consistent with an interfacial layer with a SiO_2 equivalent oxide thickness of 11 Å. Spectroscopic ellipsometry investigations also were in agreement with a SiO_2 interfacial layer with a 13 Å thickness.

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1. Introduction

Future advances in silicon microelectronics and thin film devices are dependent on the development of new materials and new deposition processes. In particular, the continuing drive to shrink silicon devices will soon require SiO_2 gate oxide layers with a thickness on the order of 1 nm [1–3]. Electron tunneling produces high leakage current and device instability at these low SiO_2 thicknesses [1–3]. Depositing such thin SiO_2 films uniformly and maintaining the insulating properties has also become increasingly difficult. In response to these problems, high k dielectric materials are currently being investigated to achieve higher capacitances with thicker films to minimize electron tunneling leakage currents [4,5].

Al_2O_3 is a technologically important material due to its excellent dielectric properties, good adhesion to many surfaces, and thermal and chemical stability. These properties make Al_2O_3 attractive in the silicon microelectronics and thin film device industry as an insulator, ion barrier, and protective coating. Al_2O_3 is being considered as a high k material to replace SiO_2 in microelectronic devices such as DRAMs and MOSFETs [4,6–9]. Applications for Al_2O_3 films are also being investigated in a variety of other areas including solar energy devices and magnetic read heads.

The growth of thin films by atomic layer deposition (ALD) is rapidly gaining acceptance in microelectronics processing. ALD produces films with excellent conformality and precisely controlled thicknesses. ALD techniques have been applied to deposit a wide variety of thin film materials [10,11]. ALD relies on sequential, self-limiting surface reactions to obtain atomic layer

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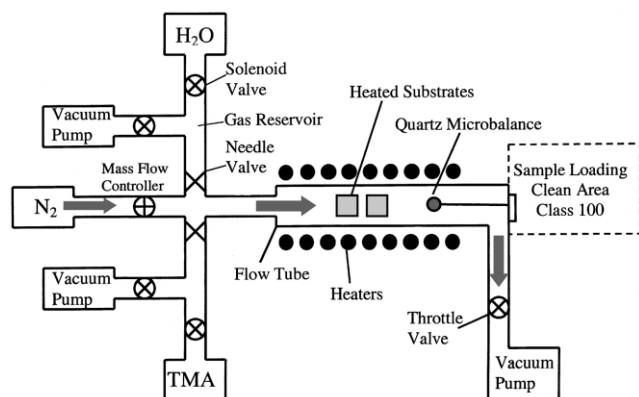
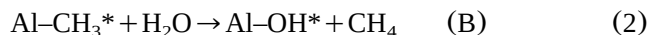
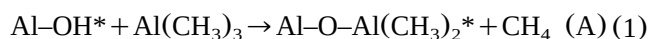


Fig. 1. Schematic diagram of the viscous flow ALD reactor.

control of deposition [10]. In addition to precise thickness control, ALD allows for excellent conformal growth. Many investigations have been performed to demonstrate the ability of ALD to coat uniformly high aspect ratio trench structures [12]. For atomic layer controlled and conformal deposition, ALD represents a significant advantage over other deposition techniques such as chemical vapor deposition (CVD) or molecular beam epitaxy.

Many promising applications result from combining the advantages of the ALD growth process with the excellent material properties of Al_2O_3 . Consequently, Al_2O_3 ALD growth has been studied extensively over the past few years. Al_2O_3 growth by ALD has been based on the CVD reaction: $2\text{Al}(\text{CH}_3)_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{CH}_4$. To perform Al_2O_3 ALD, this CVD reaction is split into two half-reactions [10,13–16]:



where the asterisks denote the surface species. Alternate precursors such as $\text{Al}(\text{CH}_3)_2\text{Cl}$, AlCl_3 and H_2O_2 have also been employed for Al_2O_3 ALD [17–20].

During Al_2O_3 ALD growth, trimethylaluminum (TMA) is introduced and allowed to react with hydroxyl groups on the surface. This reaction proceeds until the surface reaction reaches completion [14]. Subsequently, TMA is carried or pumped away. The same process is then performed with H_2O . The H_2O reacts with methyl groups on the surface until this surface reaction reaches completion. The sequential exposure to TMA and H_2O constitutes one AB cycle [14]. These AB cycles are repeated to achieve the desired film thickness. Previous studies have demonstrated the growth of $1.1 \text{ \AA}$ Al_2O_3 per AB cycle at 177°C [10,16].

Our previous studies of Al_2O_3 ALD films have been performed in high vacuum reactors under molecular flow conditions [14–16]. These investigations allowed

for a careful study of the surface reactions using well-defined exposure conditions. To grow the Al_2O_3 ALD films more rapidly, we have recently built a viscous flow reactor. This viscous flow reactor increases the Al_2O_3 ALD growth rates by over an order of magnitude [21]. Using this reactor, we have grown Al_2O_3 ALD films on a variety of substrates, including different types of Si, metals, and metal alloys. Al_2O_3 ALD films were deposited with thicknesses ranging from $30\text{--}3540 \text{ \AA}$ at growth temperatures from 125 to 425°C . This paper employs current–voltage (IV) and capacitance–voltage (CV) measurements using a mercury probe to examine the dependence of the electrical properties of these Al_2O_3 ALD films on film thickness, growth temperature and underlying substrate.

2. Experimental

2.1. Chemicals and substrates

Al_2O_3 ALD films were grown using H_2O (Fisher, Optima grade) and $\text{Al}(\text{CH}_3)_3$ (TMA) (Akzo-Nobel, Semiconductor grade, 99.9999%). The carrier gas was N_2 (Airgas, Ultra High Purity). Substrates included moderately doped n-type Si(1 0 0) wafers from MEMC Electronic Materials with a boron doping density $\sim 4 \times 10^{16}/\text{cm}^3$ and highly doped n-type Si(1 0 0). Metal-coated substrates were prepared by electron beam vapor deposition and by sputtering of $100\text{--}200 \text{ nm}$ thick metal films on highly doped n-type Si(1 0 0) wafers. The Au, Co, Cr, Cu, Mo, Ni, and Pt-coated Si(1 0 0) substrates were provided by ITN Energy Systems. Cu, FeNi, NiMn, PtMn and W-coated Si(1 0 0) substrates were prepared by Seagate Technology. Stainless steel foil and Mo foil were also employed as substrates for Al_2O_3 ALD. Conductive ZnO films on moderately doped n-type Si(1 0 0) were prepared using ZnO ALD [22] immediately prior to Al_2O_3 ALD. These ZnO films were $\sim 600 \text{ \AA}$ thick after 300 AB cycles of exposure at 177°C to the diethylzinc and water reactants.

Chemicals for etching and cleaning included 5% HF (General Chemicals Class 10 Water/HF (10:1) Mix), water (HPLC grade), sulfuric acid, hydrogen peroxide, and Micro cleaner/oxide remover (International Products Corp.). Silicon wafers were cut into $2.5 \times 2.5 \text{ cm}^2$ pieces, cleaned in a 60°C Piranha solution for 15 min, and then HF etched for 30 s. The etching and sample loading were performed in a class 100 cleanroom hood obtained from Terra Universal. Metal substrates were cleaned in a sonicator bath containing Micro cleaner. Metal foils were polished using $0.05 \text{ }\mu\text{m}$ diameter alumina particles before employing the cleaner.

2.2. Al_2O_3 ALD film growth in viscous flow reactor

Al_2O_3 films were grown by ALD in a viscous flow reactor. A simplified schematic of this viscous flow reactor is shown in Fig. 1. This reactor has been

described in detail in another publication [21]. Briefly, the N_2 carrier gas flowed at a rate of 200 sccm. An Alcatel 2010 mechanical pump with a maximum pumping speed of 3.2 l/s was used to pump the flow tube. The flow tube was a stainless steel tube with an inside diameter of 3.6 cm. Given the N_2 flow rate, conductance and throttle valve opening to the mechanical pump, the N_2 pressure was ~ 1 Torr in the flow tube. The N_2 carrier gas velocity was ~ 2.5 m/s.

H_2O and TMA were alternately entrained in the N_2 carrier flow using gas switching valves [21]. Fig. 1 shows the location of the gas switching valves and the gas reservoirs. With H_2O and TMA pressures > 10 Torr, the baratron on the flow tube measured pressure transient increases of ~ 0.1 Torr when the reactants were introduced into the N_2 carrier flow. The gas switching valves allow for a rapid turn on and shut off of the reactant gases for short ALD cycle times. This short time is facilitated by pumping the gas reservoirs with separate mechanical pumps after the reactant exposures. In addition, variable conductance needle valves are employed that control the reactant flux into the N_2 carrier gas and allow a 'gas window' to shut off the reactant quickly after the reactant exposure.

The time for one complete Al_2O_3 ALD cycle was typically 12 s. This cycle time was defined by (*a*, *b*, *c*, *d*) where *a* is the TMA exposure time, *b* is the N_2 purge time following the TMA reactant exposure, *c* is the H_2O exposure time and *d* is the N_2 purge time following the H_2O reactant exposure. Most of the Al_2O_3 ALD films were deposited using (1, 5, 1, 5) for a total ALD cycle time of 12 s. Cycle times as short as 3 s could be obtained before the Al_2O_3 growth rates displayed evidence of Al_2O_3 CVD resulting from insufficient purge times.

Approximately two hundred Al_2O_3 ALD films were grown and tested through the course of this study. Al_2O_3 ALD films were grown with film thicknesses ranging from 30 to 3540 Å and growth temperatures varying from 125 to 425 °C. Al_2O_3 ALD growth was monitored in situ using a Maxtek TM400 Thin Film Deposition Monitor quartz crystal microbalance (QCM). The QCM crystal housing was sealed to prevent deposition on the backside and positioned horizontally in the flow reactor tube. Average Al_2O_3 ALD growth rates of 1.18 ± 0.04 Å/cycle were obtained at 177 °C.

2.3. Al_2O_3 film characterization

Electrical measurements were performed using a MDC 811 Mercury Probe from the Materials Development Corporation. The mercury probe makes contact to the front surface of the Al_2O_3 films by drawing up a well-defined column of Hg with a surface area of 0.437 mm². A schematic of this electrical test apparatus is shown in Fig. 2. IV measurements were obtained at a

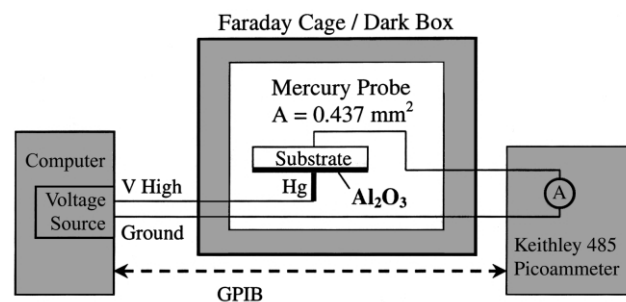


Fig. 2. Experimental setup for IV measurements using the mercury probe.

50 mV/s scan rate using a Keithley 485 Picoammeter and a ComputerBoards DAC02 ± 10 V voltage source. CV measurements were performed using a Stanford Research Systems SR720 LCR Meter. These CV measurements employed frequencies ranging from 0.1 to 100 kHz. Capacitance values were only accepted for large *Q* values typically *Q* > 10 . The experiments were computer controlled using Labview from National Instruments. To verify the capacitance values, additional measurements were conducted after depositing aluminum dots with smaller contact areas between 3.6×10^{-3} and 0.15 mm² on the Al_2O_3 films.

Al_2O_3 film thicknesses were measured using a J.A. Woollam M44 variable angle spectroscopic ellipsometer (VASE). Values of Ψ and Δ were obtained over the spectral range of 406–806 nm for an incidence angle of 75°. This incidence angle is close to the silicon Brewster angle of $\theta_B = 75.5^\circ$. Measured data were fitted using a least-squares algorithm from J.A. Woollam.

Al_2O_3 and SiO_2 have virtually identical optical constants. Consequently, a simple ellipsometric measurement yields only the sum of the Al_2O_3 and SiO_2 film thicknesses. To determine the true Al_2O_3 thickness and the thickness of any interfacial SiO_2 layer on Si(1 0 0), a procedure was employed that utilized simultaneous Al_2O_3 ALD growth on both an HF-etched Si wafer and a Si wafer with a native oxide. The thickness of the native SiO_2 layer was initially measured on the Si(1 0 0) wafer. Using the bulk SiO_2 refractive index and the Ψ and Δ values from the VASE analysis algorithm yielded a SiO_2 native oxide thickness of 31 Å.

Because of high tunneling and leakage currents, ultra-thin SiO_2 layers can exhibit a different refractive index, *n*, than the bulk oxide. The corrected refractive index for a SiO_2 layer with a thickness, *T_{ox}*, ranging from 1.4 to 8 nm can be obtained using [23]:

$$n_{ox} = 2.139 - 8.991 \times 10^2 T_{ox} + 1.872 \times 10^{-3} (T_{ox})^2 \quad (3)$$

With this new refractive index, another fitting was performed to determine a new thickness. This fitting

process was repeated until a nonvarying result was obtained for both the refractive index and the oxide thickness. The native oxide thickness was found to be 23 Å based on the corrected refractive index $n = 1.94$.

Subsequently, the Al_2O_3 thickness was measured for the Al_2O_3 ALD films grown on the Si(1 0 0) substrate with the native oxide. Using a native oxide SiO_2 layer thickness of 23 Å, the Al_2O_3 thickness was obtained by subtracting the contribution of the underlying SiO_2 film from the total measured thickness. Assuming the same Al_2O_3 ALD growth rate on both the HF-etched Si(1 0 0) and the native oxide SiO_2 layer on Si(1 0 0), the SiO_2 interfacial layer was determined on the HF-etched Si(1 0 0) after depositing Al_2O_3 . This analysis yielded a 13 Å thick SiO_2 interfacial oxide layer on a HF-etched Si(1 0 0) substrate after 100 AB cycles of Al_2O_3 ALD at 177 °C. Results from numerous samples revealed that a SiO_2 oxide layer thickness of 13 ± 2 Å was observed after 25–300 AB cycles of Al_2O_3 ALD at growth temperatures of 177 and 350 °C.

Very recent studies have compared Al_2O_3 ALD on HF-etched Si(1 0 0) and thin SiO_2 films on Si(1 0 0) [24,25]. Al_2O_3 ALD was observed to occur immediately and with a growth rate of ~ 1.0 Å/AB cycle at 300 °C on SiO_2 films on Si(1 0 0). In contrast, an induction period varying from ~ 5 AB cycles [25] to ~ 15 AB cycles [24] was monitored for Al_2O_3 ALD on HF-etched Si(1 0 0). These results on HF-etched Si(1 0 0) are different than the results of this study. We do not have evidence for a significant induction period on HF-etched Si(1 0 0). Quite to the contrary, we measure film thicknesses after Al_2O_3 ALD that are larger than expected from the Al_2O_3 ALD growth rate. These observations suggest that an SiO_2 interfacial oxide layer is formed easily during Al_2O_3 ALD on HF-etched Si(1 0 0) and support our assumption of equal growth rates on both HF-etched Si(1 0 0) and the native oxide layer on Si(1 0 0).

Al_2O_3 ALD growth rates were also measured on some of the metal substrates using ellipsometry. The Al_2O_3 ALD growth rates were the same within error as the Al_2O_3 growth rates measured on HF-etched Si(1 0 0) and on the native oxide SiO_2 layer. On Au and Pt substrates, ellipsometric data determined that there was no interfacial oxide layer after Al_2O_3 deposition. Although the electrical measurements suggested an interfacial oxide was present on Mo-coated Si(1 0 0) substrates, the ellipsometric measurements were inconclusive. Since Al_2O_3 ALD growth was often performed on n-Si(1 0 0) and Mo-coated Si(1 0 0) substrates simultaneously, the Al_2O_3 thicknesses measured on n-Si(1 0 0) were used to determine the Al_2O_3 thicknesses on the Mo-coated Si(1 0 0) substrates. An Al_2O_3 ALD growth rate of 1.18 Å/cycle was assumed if the Al_2O_3 thickness was not available from ellipsometric measurements.

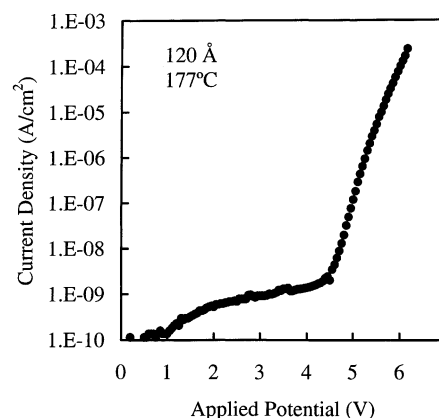


Fig. 3. IV plot for a 120 Å thick Al_2O_3 ALD film grown on n-Si(1 0 0) at 177 °C.

Atomic force microscope (AFM) images of the Al_2O_3 films and substrates were obtained using an AutoProbe CP Research scanning probe microscope instrument from ThermoMicroscopes. RMS surface roughness values were calculated based on $1 \mu\text{m}^2$ AFM scans. Transmission electron microscope (TEM) images were obtained at Seagate Technology using a JEOL 2010 TEM with a LaB6 filament and a Gatan Multi-Scan camera. Rutherford backscattering spectrometry (RBS) data were recorded by Charles Evans & Associates with a He^{2+} Ion Beam Energy of 2.275 MeV, a normal detector angle of 160°, and a grazing detector angle of $\sim 94^\circ$. Hydrogen forward scattering spectroscopy (HFS) and Auger depth profiling were also performed by Charles Evans & Associates.

3. Results

3.1. Electrical properties of a 120 Å thick Al_2O_3 ALD film

The IV plot for a 120 Å thick Al_2O_3 film is shown in Fig. 3. This Al_2O_3 ALD film was grown on a HF-etched moderately doped n-type Si(1 0 0) substrate by running 100 AB cycles at a growth temperature of 177 °C. The IV plot shows very low currents on the order of ~ 1 nA/cm² at low applied potentials. This current is attributed to a combination of leakage current and charging current due to capacitive charging. The rise in current starting approximately 4.5 V can be identified as Fowler–Nordheim (FN) tunneling. Catastrophic breakdown was observed at 6.2 V. This voltage represents an electric field of 5.2 MV/cm. Similar IV results were obtained for films grown on most of the other substrates.

For Al_2O_3 films with thicknesses of ~ 120 Å, typically approximately 5 out of 10 locations tested using the Hg probe revealed good insulating behavior. The electrical properties of the Al_2O_3 ALD films were

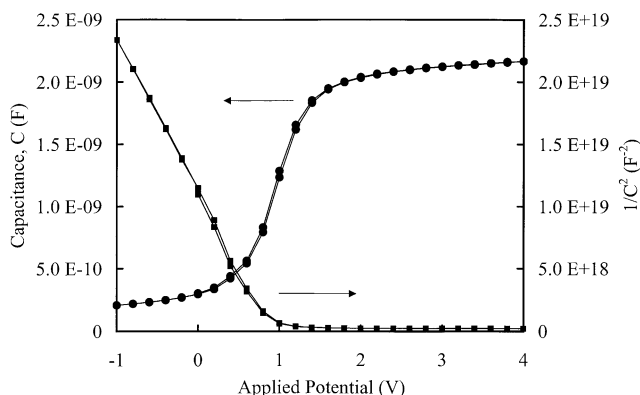


Fig. 4. CV and Mott–Schottky plot for a 120 Å thick Al_2O_3 ALD film grown on n-Si(1 0 0) at 177 °C.

dependent on sample preparation conditions. With the class 100 cleanroom hood in place over the viscous flow reactor, the samples could be cleaned and loaded in a near particle-free atmosphere. When samples were prepared outside of this cleanroom area, the percentage of locations exhibiting good insulating behavior was lower.

The CV plot for the 120 Å thick Al_2O_3 film is shown in Fig. 4. The variation in capacitance versus voltage is caused by changes in the space charge region of the moderately doped n-Si(1 0 0) semiconductor substrate. At large positive potentials where the silicon surface is in accumulation and there is no space charge region, the capacitance measured is the capacitance of the Al_2O_3 film. The dielectric constant can then be calculated using: $k = Cd/\epsilon_0 A$, where C is capacitance, d is thickness of the film, ϵ_0 is the permittivity of free space, and A is the area. For the CV data for the 120 Å thick Al_2O_3 ALD film shown in Fig. 4, the dielectric constant is $k = 6.7$.

The decrease in capacitance as the applied voltage becomes more negative is caused by the increase in thickness of the space charge region of the silicon substrate. The doping of the Si(1 0 0) wafer and the flatband voltage can be determined by this decrease in capacitance. The Mott–Schottky plot ($1/C^2$ vs. V) in Fig. 4 indicates an n-type dopant with a doping density of $5 \times 10^{16}/\text{cm}^3$. This dopant level is consistent with the specifications provided by the manufacturer. The flatband voltage was ~ 0.3 V. For Al_2O_3 ALD films grown on metal substrates and on highly-doped Si(1 0 0) substrates, capacitance values were constant with voltage.

3.2. Electrical properties versus Al_2O_3 film thickness

The electrical properties of Al_2O_3 ALD films grown at 177 °C were investigated vs. film thickness. Fig. 5 shows IV plots of Al_2O_3 films grown on the moderately doped n-Si(1 0 0) substrates for thicknesses ranging

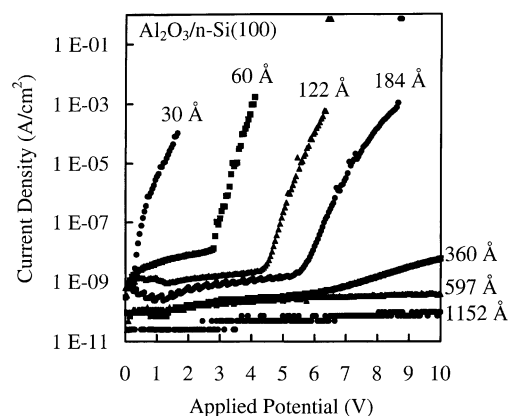


Fig. 5. IV plots for Al_2O_3 ALD films of different thicknesses grown on n-Si(1 0 0) at 177 °C.

from 30 to 1152 Å. These plots show a decrease in current density with increasing film thickness. This decrease is consistent with decreased leakage and tunneling currents for larger film thicknesses. In addition, part of this decrease is also attributed to smaller charging currents associated with the smaller capacitances of the thicker films.

Direct tunneling current is observed for Al_2O_3 ALD film thicknesses ≤ 40 Å. This direct tunneling is observed by the rapid rise of current in the IV plot for the 30 Å thick film in Fig. 5. Films with thicknesses ≥ 50 Å showed no significant direct tunneling. The excellent insulating behavior of these thicker films at low applied potentials corresponds to resistivities as high as $10^{16} \Omega \text{ cm}$. The voltage at which significant FN tunneling was observed also increased with film thickness. This onset voltage rose from ~ 3 V for the 60 Å thick film to ~ 5.5 V for the 184 Å thick film.

Fig. 6 shows similar IV plots for Al_2O_3 ALD films grown at 177 °C on the Mo-coated Si(1 0 0) substrates. Al_2O_3 ALD film thicknesses varied from 30 to 1180 Å.

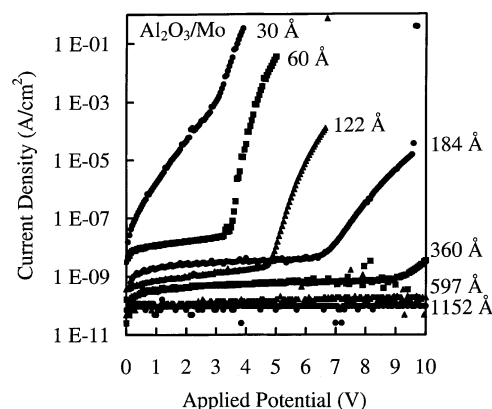


Fig. 6. IV plots for Al_2O_3 ALD films of different thicknesses grown on Mo-coated Si(1 0 0) at 177 °C.

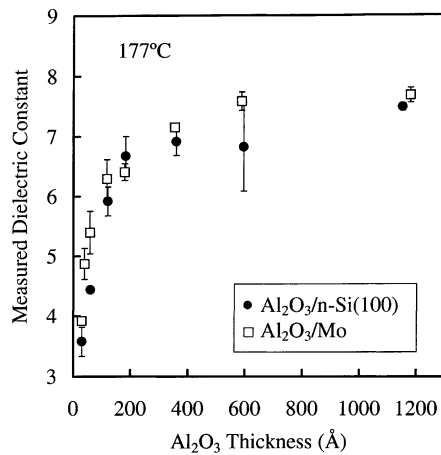


Fig. 7. Measured dielectric constant for Al₂O₃ ALD films of different thicknesses grown at 177 °C on n-Si(1 0 0) and Mo-coated Si(1 0 0).

Leakage currents are roughly the same as the leakage currents for the Al₂O₃ ALD films grown directly on n-Si(1 0 0). FN tunneling onsets occur at slightly higher potentials compared with the Al₂O₃ ALD films grown on n-Si(1 0 0).

The dielectric constants of the Al₂O₃ ALD films were measured versus film thickness. Results are displayed in Fig. 7 for Al₂O₃ ALD films grown at 177 °C on moderately doped n-type Si(1 0 0) and Mo-coated Si(1 0 0) substrates. For thick films ≥ 600 Å grown on the Mo-coated Si(1 0 0), the measured dielectric constant was $k \sim 7.6$. However, the dielectric constant decreases with Al₂O₃ thickness and a dielectric constant of $k \sim 4$ is measured for 30 Å thick films. Dielectric constants for the Al₂O₃ ALD films grown on moderately doped n-type Si(1 0 0) were slightly lower than the dielectric constants for the Al₂O₃ ALD films grown on Mo-coated Si(1 0 0). Note that the measured dielectric constants were determined using the deposited Al₂O₃ thickness.

Because the capacitance measurements may be sensitive to the contact area of the electrode, the measurement of the dielectric constant was repeated for several Al₂O₃ film thicknesses using aluminum dots on the Al₂O₃ films with contact areas from 3.6×10^{-3} to 0.10 mm². These capacitance measurements displayed the same trend as the results obtained using the mercury probe shown in Fig. 7. The dielectric constants measured with the smaller aluminum dots were slightly higher but displayed the same dependence on Al₂O₃ thickness as the results shown in Fig. 7.

3.3. Electrical properties vs. Al₂O₃ growth temperature

Additional experiments investigated the effect of growth temperature on electrical properties. Al₂O₃ ALD films were grown at 125, 177, 225, 275, 325, 350, 375,

and 425 °C on both moderately doped n-Si(1 0 0) and Mo-coated Si(1 0 0) substrates. Earlier studies have examined Al₂O₃ ALD growth rates vs. growth temperature [16]. These growth rates were used to prepare a set of samples grown at different temperature that all had approximately equal Al₂O₃ film thicknesses. Subsequent ellipsometric measurements showed that the Al₂O₃ ALD film thicknesses varied randomly with growth temperature between 114 and 132 Å.

IV measurements did not reveal any significant trends with respect to Al₂O₃ ALD growth temperature. Leakage currents and FN tunneling onset voltages were similar for all growth temperatures. The percentage of tested locations that exhibited good insulating behavior varied over the temperature range. However, no obvious trends could be observed when comparing all the data.

Fig. 8 shows the measured dielectric constant of the Al₂O₃ ALD films with thicknesses of ~ 123 Å vs. growth temperature. The slightly different film thicknesses measured by ellipsometry are taken into account when determining the measured dielectric constant. The dielectric constant appears to increase slightly with growth temperature until a maximum dielectric constant is reached at ~ 350 °C. The measured dielectric constant was approximately $\Delta k \sim 0.5$ higher at 350 °C than at 177 °C for these Al₂O₃ ALD films. A similar trend was also observed for Al₂O₃ films with thicknesses of ~ 123 Å grown on moderately doped n-type Si(1 0 0) and for Al₂O₃ films with thicknesses > 1000 Å.

3.4. Chemical composition and impurity analysis

The composition of an Al₂O₃ ALD film grown at 177 °C was analyzed by RBS. The RBS analysis indicated $61 \pm 6\%$ O and $39 \pm 3\%$ Al. The O/Al ratio of 1.56 ± 0.19 agrees within experimental error with the expected stoichiometric ratio of 1.5. Auger depth profil-

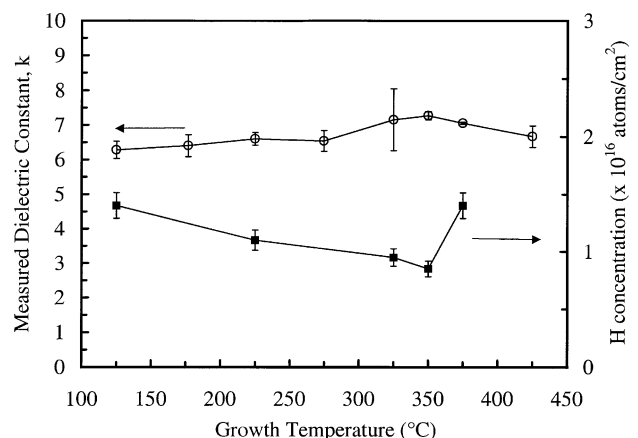


Fig. 8. Measured dielectric constant and hydrogen concentration for Al₂O₃ ALD films with a thickness of ~ 123 Å grown on Mo-coated Si(1 0 0) at various growth temperatures.

ing was performed to look for impurities in the Al_2O_3 film and at the $\text{Si}/\text{Al}_2\text{O}_3$ interface. No carbon or nitrogen was measurable given the 0.5% detection limit for these elements.

Another RBS study was performed on several Al_2O_3 ALD films grown at different temperatures. O/Al ratios averaged 1.48 ± 0.06 except for the 425 °C film which had a higher than expected O/Al ratio of 1.7. Hydrogen concentrations in these films measured by HFS are shown in Fig. 8. The hydrogen concentration decreases gradually as the growth temperature is raised from 125 to 350 °C. Subsequently, the hydrogen concentration increases for Al_2O_3 ALD films grown at 375 °C.

3.5. Properties of Al_2O_3 grown on other substrates

Al_2O_3 ALD films were also grown on many other substrates besides the moderately doped n-type $\text{Si}(100)$ and Mo-coated $\text{Si}(100)$ substrates. $\text{Si}(100)$ wafer substrates included n- and p-doped $\text{Si}(100)$ with a range of doping densities and $\text{Si}(100)$ wafers with and without the native SiO_2 oxide layer. Metal-coated $\text{Si}(100)$ wafers included Au, Co, Cr, Cu, Mo, Ni, Pt, W, NiFe, NiMn and PtMn. Other types of substrates included stainless steel foils, Mo foils and $\text{Si}(100)$ wafers coated with ZnO.

Based on electrical measurements, ellipsometry, and AFM data, Al_2O_3 ALD growth occurred on all of these substrates. The electrical properties of Al_2O_3 ALD films grown on most of these substrates were as good or almost as good as Al_2O_3 ALD films grown on the moderately doped n-type $\text{Si}(100)$ and Mo-coated $\text{Si}(100)$. There were a few notable exceptions. Al_2O_3 ALD films on Au, Pt, and Cu-coated Si wafers sometimes exhibited poor insulating behavior. Leakage currents were especially pronounced for Al_2O_3 ALD films thinner than ~ 150 Å on these substrates. In addition, the electrical properties of Al_2O_3 ALD films that were grown on $\text{Si}(100)$ wafers with a native oxide were generally not as good as the electrical properties for Al_2O_3 ALD films grown on HF-etched $\text{Si}(100)$.

4. Discussion

4.1. Current–voltage measurements

The rise in current observed in the IV plots in Figs. 3, 5 and 6 at higher applied potentials is consistent with FN tunneling [26]. This type of field-assisted tunneling can be described by charge carriers tunneling through a triangular barrier with:

$$J = AE_{\text{ox}}^2 \exp(-B/E_{\text{ox}}) \quad (5)$$

where

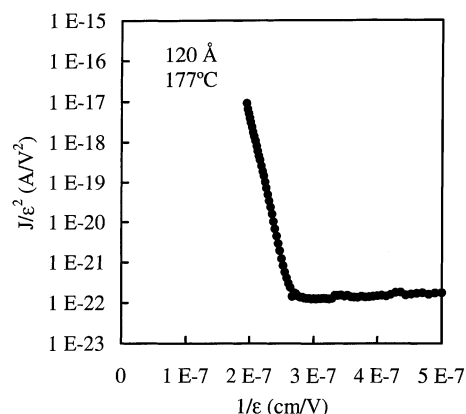


Fig. 9. FN plot of the IV data shown in Fig. 3 for a 120 Å thick Al_2O_3 ALD film grown at 177 °C.

$$A = 1.54 \times 10^{-6} \left(\frac{1}{m^* \Phi_B} \right) \text{ and} \\ B = 6.83 \times 10^7 (m^*)^{1/2} (\Phi_B)^{3/2} \quad (6)$$

E_{ox} is the oxide electric field, m^* is the effective mass of the charge carrier, and Φ_B is the barrier height.

Fig. 9 shows a plot of J/E_{ox}^2 vs. $1/E_{\text{ox}}$ resulting from the data in Fig. 3. The plot has a slope of $-B$. This slope can be used to calculate the $\text{Si}/\text{Al}_2\text{O}_3$ barrier height. E_{ox} is the oxide electric field derived from the applied potential corrected for the flatband voltage, $V_{\text{fb}} = 0.3$ V, divided by the film thickness. The effective mass of an electron in Al_2O_3 is $m^* = 0.23$. This effective mass is an average based on previous analysis [27,28] of earlier measurements [29]. Using this effective mass, the $\text{Si}/\text{Al}_2\text{O}_3$ barrier height is $\Phi_B = 2.6$ eV based on the data in Fig. 9.

The CV data for some samples exhibited hysteresis and the V_{fb} values spanned a range of ~ 0 –1.5 V. However, the reproducibility of the IV data suggested that the effective V_{fb} values must have been fairly constant. The theoretical value of $V_{\text{fb}} = 0.5$ V [30,31] agrees fairly well with the experimental data. Therefore, this theoretical value for the flatband voltage was used for the determination of the barrier height. An average barrier height of $\Phi_B = 2.5 \pm 0.3$ eV was determined from several Al_2O_3 ALD films grown on n- $\text{Si}(100)$ using $V_{\text{fb}} = 0.5$ V.

A barrier height of $\Phi_B = 2.8$ eV was recently calculated for the $\text{Si}/\text{Al}_2\text{O}_3$ interface [8]. In addition, a barrier height of $\Phi_B = 2.78$ eV was measured at an n- $\text{Si}/\text{Al}_2\text{O}_3$ interface using ballistic electron emission spectroscopy [32]. At non-zero bias conditions, image force lowering decreases the barrier height [8]. This predicted decrease at non-zero bias might explain our slightly lower barrier height values.

The FN tunneling onset voltages for the Al_2O_3 ALD films grown on the Mo-coated $\text{Si}(100)$ substrates were

Table 1
Summary of the electrical properties for Al₂O₃ ALD films grown on silicon substrates

Reference	Al ₂ O ₃ thickness (nm)	Growth temperature	Resistivity (Ω cm)	Leakage current (A/cm ²)	Electric field (MV/cm)	Catastrophic breakdown (MV/cm)	Dielectric constant <i>k</i>	Electrode area (cm ²)	Alternate precursor
[9]	6.5	350		1 e−7	3.1		~8		
[13]	40	450	1 e17			6–8	7	5 e−4	
[17]	≥ 100	150	1.2 e16	6 e−10	3	6–7	7.1		H ₂ O ₂
[18]		300					8.4		AlCl ₃
[19]	114–118	200		5 e−8	4		7.3	0.294	Al(CH ₃) ₂ Cl
		500		1 e−5	0.5		8.5	0.294	
[31]	107	250		1 e−8	4	7–8	~7	1 e−4	
	101	350		1 e−7				1 e−4	
[32]	59–115	150–300				7.5(5)	5.3(2)		+ NO ₂
This study	115	177	1 e16	1 e−10	1		7.5	4.37 e−3	
	12	177	1 e15	2 e−9	3	5.3	5.9	4.37 e−3	
	57	350	5 e15	2 e−10	1		7.7	4.37 e−3	

higher than the onset voltages for the Al₂O₃ ALD films grown on moderately doped n-type Si(1 0 0). This trend is reasonable considering that the Mo work function of 4.6 eV is approximately 0.5 V greater than the Si electron affinity [30,31]. This work function would result in a larger barrier height and a higher FN tunneling onset voltage on the Mo-coated Si(1 0 0) substrate. In support of this explanation, the determined barrier heights for the Mo/Al₂O₃ interface were ~3 or ~0.5 eV larger than for the Si/Al₂O₃ interface.

The electrical properties of Al₂O₃ ALD films have been investigated by several other research groups [9,13,17–19,33,34]. Most of these studies were performed on Al₂O₃ films on the order of ~1000 Å thick. The electrical results for these thick films are summarized in Table 1. Comparing our IV results to the previous results for films of similar thickness reveals that our leakage currents are as low as any of the other measurements. Breakdown fields in our study ranged from 5 to 13 MV/cm and are slightly lower compared with films of similar thicknesses. However, breakdown fields are more difficult to compare since catastrophic breakdown is dependent on the voltage scan rate.

Post deposition annealing has been previously reported to improve the insulating properties of Al₂O₃ ALD films. Annealing at 900 °C was reported to cause a ~10% decrease in film thickness and decrease leakage currents at 4 MV/cm to ~1×10^{−10} A/cm² [33]. Contrary to this earlier report, annealing had a detrimental effect on the insulating properties of our Al₂O₃ films. After annealing at 800 °C in N₂, leakage currents increased by many orders of magnitude. Ellipsometry indicated a ~5% decrease in film thickness for one Al₂O₃ ALD film prepared using 300 AB cycles at 177 °C. In contrast, a thinner Al₂O₃ film prepared using 30 AB cycles was observed by ellipsometry to increase in

thickness after annealing at 800 °C. This increase in thickness may be attributed to substrate oxidation.

AFM images of our annealed Al₂O₃ films also revealed some large peaks and holes on the surface up to 1 μm tall and several micrometer wide. Even the relatively flat areas of the Al₂O₃ surface had very high RMS roughness values of 2–3 nm on annealed samples. This compares with RMS roughness values of <0.3 nm for non-annealed Al₂O₃ ALD films for thicknesses up to 1500 Å. A similar observation of voids by AFM was reported after annealing an Al₂O₃ ALD film at 1000 °C for 20 s [7].

4.2. Capacitance–voltage measurements

Published values of the dielectric constant of bulk Al₂O₃ range from <8 to 10 [35–37]. The higher values are consistent with Al₂O₃ samples with higher purity, density, and crystallinity. Our values of *k*~7.6 measured for film thicknesses >600 Å grown at 350 °C are at the lower end of this range. These lower values may be expected because of the lower density of amorphous Al₂O₃ ALD films. TEM studies have determined that our Al₂O₃ ALD films are amorphous. Earlier ellipsometric measurements have also revealed Al₂O₃ ALD film densities that are in agreement with amorphous Al₂O₃ densities [15].

The measured dielectric constant for the Al₂O₃ ALD film on moderately doped n-type Si(1 0 0) decreased with decreasing film thickness as shown in Fig. 7. The decrease of the dielectric constant with decreasing Al₂O₃ film thickness can be attributed to interfacial layers and quantum mechanical effects [1,38–40]. The presence of an interfacial dielectric layer adds an additional capacitor. This arrangement lowers the measured dielectric constant because the two capacitors in series

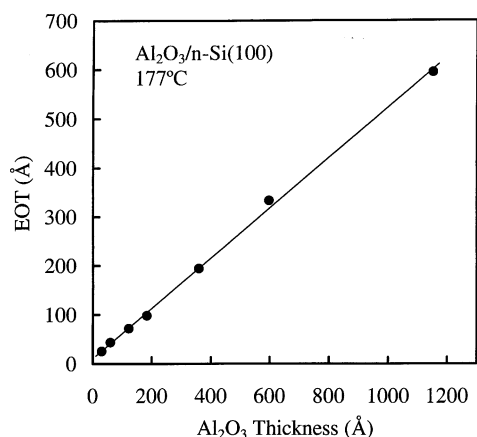


Fig. 10. EOT vs. Al₂O₃ thickness for Al₂O₃ ALD films grown on n-Si(1 0 0) at 177 °C.

increase the overall thickness and lower the capacitance as determined by $1/C_{\text{total}} = 1/C_1 + 1/C_2$.

Assuming that the interlayer at the Si/Al₂O₃ interface is SiO₂, the SiO₂ interlayer thickness can be obtained by plotting the equivalent oxide thickness (EOT) vs. Al₂O₃ thickness [38]. This plot for the data in Fig. 7 for the Al₂O₃ ALD film on moderately doped n-Si(1 0 0) is shown in Fig. 10. The Al₂O₃ thickness is determined by ellipsometry based on the procedure discussed in Section 2.3 using an interfacial SiO₂ oxide thickness of 13 Å. The EOT is obtained by taking the capacitance value measured for a film and calculating the thickness of SiO₂ with a dielectric constant of $k = 3.9$ film that would yield this capacitance value. This EOT vs. Al₂O₃ thickness plot takes the form:

$$\text{EOT} = \frac{k(\text{SiO}_2)}{k(\text{Al}_2\text{O}_3)} d(\text{Al}_2\text{O}_3) + d(\text{SiO}_2) \quad (7)$$

where $k(\text{SiO}_2)$ and $k(\text{Al}_2\text{O}_3)$ are the dielectric constants and $d(\text{SiO}_2)$ and $d(\text{Al}_2\text{O}_3)$ are the film thicknesses.

The slope of the plot shown in Fig. 10 yields an Al₂O₃ dielectric constant of $k = 7.6 (\pm 0.3)$. The y-intercept of the plot in Fig. 10 gives a SiO₂ thickness of 11 Å (± 3). The EOT was corrected for quantum mechanical effects due to the Si substrate accumulation (or inversion) layer [38,39]. The quantum mechanical effects have the effect of decreasing the EOT by approximately 5–10 Å. The quantum mechanical correction was obtained using a program on the IBM web site at <http://www.alphaworks.ibm.com/tech/tqm>. The SiO₂ thickness of 11 Å from the EOT vs. Al₂O₃ thickness plot is in excellent agreement with the interfacial oxide thickness of 13 Å used to determine the Al₂O₃ thickness.

A similar plot for the data in Fig. 7 for the Al₂O₃ ALD films grown on Mo-coated Si(1 0 0) substrates is shown in Fig. 11. The slope of this plot yields $k = 7.8$. The y-intercept gives an interfacial layer with an EOT

of 15 Å (± 2) assuming an interfacial oxide with the same dielectric constant as SiO₂. No quantum mechanical correction was applied for this metal substrate. Unfortunately, the stoichiometry and composition of this proposed interfacial oxide between Al₂O₃ and Mo are unknown. Attempts to characterize this interfacial metal oxide by ellipsometry using a three-layer model were not successful. However, there was evidence for interfacial complexity because the ellipsometric results for the Al₂O₃ layer on Mo could not be fit using a simple two-layer model.

The SiO₂ interfacial oxide thickness of 11 Å at the Al₂O₃/Si interface determined by the electrical measurements is consistent with the ellipsometric measurements that obtain a SiO₂ layer with a thickness of 13 Å. These thicknesses are slightly lower than the thickness of ~2 nm obtained from TEM images of Al₂O₃ ALD films grown on HF-etched Si(1 0 0). However, additional studies have indicated that the interfacial oxide following Al₂O₃ ALD on Si(1 0 0) has a dielectric constant of ~5.5–6 [36]. The suggestion was made that the interfacial layer may be an Al-silicate instead of SiO₂ [36]. Recalculating the interfacial oxide thickness with these higher k values results in an Al-silicate thickness of 15–17 Å.

The effect of a thin interfacial capacitor in series with the Al₂O₃ ALD film was also modeled using $1/C_{\text{total}} = 1/C_1 + 1/C_2$. These simulations confirmed that an 11 Å thick SiO₂ layer or a 15 Å thick Al-silicate layer yields a dependence of the dielectric constant vs. thickness that is very similar to our measurements. A comparison between the simulated results for the 11 Å SiO₂ layer including a quantum mechanical correction and the experimental measurements are shown in Fig. 12.

The change in dielectric constant with growth temperature may be caused by changes in the Al₂O₃ film density and/or hydroxyl incorporation. Studies have

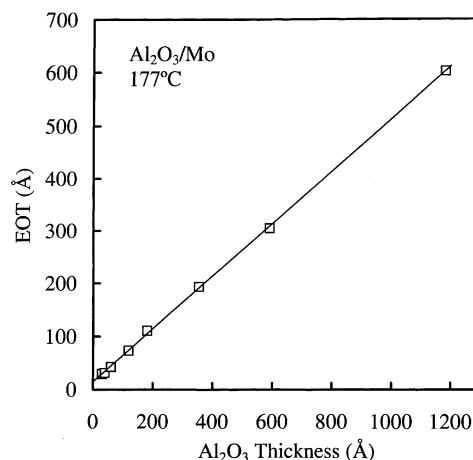


Fig. 11. EOT vs. Al₂O₃ thickness for Al₂O₃ ALD films grown on Mo-coated Si(1 0 0) at 177 °C.

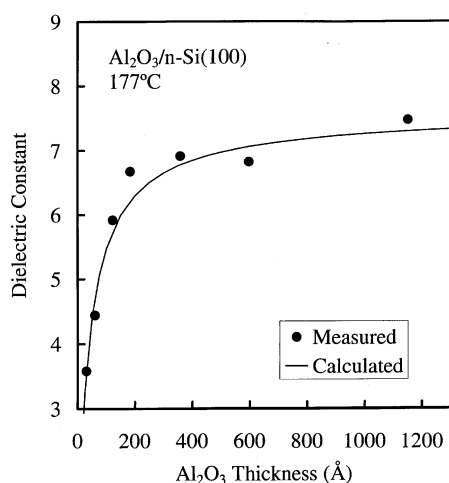


Fig. 12. Comparison of the measured and calculated dielectric constant for Al₂O₃ ALD films of different thicknesses grown on n-Si(1 0 0) at 177 °C.

shown an increase in density upon annealing [33]. Consequently, higher growth temperatures may lead to higher densities and higher dielectric constants. Earlier ellipsometric investigations of our Al₂O₃ ALD films grown at 177 °C yielded a density of 3.5 g/cm³ [15]. This density is at the lower end of the 3.5–3.7 g/cm³ range listed for amorphous Al₂O₃ and much lower than the α -Al₂O₃ density of 3.97 g/cm³.

Studies have also shown that higher temperatures lead to a decrease in incorporated hydroxyls in Al₂O₃ ALD films [14,41]. The loss of hydroxyls would be expected to increase the density and increase the dielectric constant. Fig. 8 shows that hydrogen concentrations obtained by RBS measurements mirror the dielectric constant trends vs. growth temperature. TMA decomposition has been previously reported to occur above 377 °C [42] and 450 °C [41]. This decomposition may explain the decrease in dielectric constant and increase in hydrogen concentration for Al₂O₃ ALD films grown at temperatures > 350 °C.

A comparison of the dielectric constants measured for various Al₂O₃ ALD films on Si substrates is given in Table 1 [9,13,17–19,33,34]. This comparison includes only Al₂O₃ ALD films thicker than 60 Å. Our measurements are fairly consistent with the previous results. A recent study reported a dielectric constant $k \sim 11$ for very thin (10–50 Å) Al₂O₃ ALD films [38]. This high dielectric constant was obtained by including the presence of a thin (~ 7.5 Å) interfacial SiO₂ layer and quantum mechanical effects [38].

An important issue for Al₂O₃ ALD films grown on HF-etched Si is the absence or presence of the interfacial oxide layer. An interfacial oxide can dramatically affect the electrical properties of the Al₂O₃ ALD film. Our capacitance, ellipsometry, and TEM data clearly show

the presence of the interfacial oxide. However, recent studies have reported Si/Al₂O₃ interfaces with little or no interfacial oxide using TMA and H₂O reactants for Al₂O₃ ALD. An abrupt Si/Al₂O₃ interface was observed by MEIS and TEM studies [6,25]. An interfacial layer SiO₂ layer of <2 Å was determined by XPS [24].

The formation of an interfacial oxide layer may occur during or after Al₂O₃ ALD film growth and may be dependent on growth parameters. Samples containing an abrupt Si/Al₂O₃ interface after Al₂O₃ ALD deposition have been exposed to air for 2 weeks at room temperature. These samples have revealed that up to 5 Å of SiO₂ interfacial oxide can grow under very thin Al₂O₃ ALD films. No additional SiO₂ interfacial oxide growth was observed for Al₂O₃ ALD films with thicknesses > 40 Å [24]. Another study has shown that a 25 Å thick Al₂O₃ ALD film does not hinder oxidation of the underlying Si substrate during low temperature annealing when compared with the oxidation of a HF-etched Si wafer under the same conditions [7].

We determined similar interfacial oxide thicknesses under Al₂O₃ ALD films of various thicknesses. This observation supports our belief that the interfacial oxide is formed during Al₂O₃ ALD film growth. As discussed earlier, some studies have reported an induction period for Al₂O₃ ALD growth on HF-etched Si(1 0 0) [24,25]. In contrast, we do not have evidence for a significant induction period for Al₂O₃ ALD. There may be a relationship between the induction period and the interfacial SiO₂ oxide. Perhaps our large TMA and H₂O exposures during the AB cycles promote the formation of an interfacial oxide and eliminate the induction period.

4.3. Al₂O₃ ALD nucleation and growth on various substrates

Given the surface reactions expressed by Eqs. (1) and (2), we initially believed that high quality Al₂O₃ ALD films could only be grown on hydroxylated surfaces. We suspected that there would be nucleation problems for Al₂O₃ ALD films grown on H-passivated HF-etched Si(1 0 0) surfaces and on the less reactive noble metal surfaces. However, our studies revealed that Al₂O₃ ALD film growth could be achieved on all of the substrates. These substrates include H-passivated HF-etched Si, Mo-coated Si, Au, Co, Cr, Cu, Mo, Ni, NiFe, NiMn, Pt, PtMn, stainless steel, W, and ZnO.

The electrical properties of most of these Al₂O₃ ALD films on the various substrates were quite good. The electrical properties for the Al₂O₃ ALD films grown on Pt, Cu and stainless steel may have suffered because of substrate roughness. Stainless steel was visibly scratched, Cu surfaces were visibly roughened by the cleaning procedure, and Pt substrates were shown by AFM to have a greater RMS roughness than the other

substrates. The RMS roughness for our Pt-coated Si samples was ~ 5 nm whereas the RMS roughness for the other substrates was generally < 2 nm.

The inconsistent electrical properties of Al_2O_3 ALD films grown on Au cannot be explained by surface roughness. The Au substrates were as smooth as most of the other metal substrates. Since Au oxide formation is thermodynamically unfavorable, we expected that there would be nucleation problems for Al_2O_3 ALD on Au because of the absence of hydroxyl groups. Ellipsometric results observed no interfacial layer at the Au/ Al_2O_3 interface. The ellipsometry investigations also suggested that Al_2O_3 ALD films growth rates were up to $\sim 15\%$ lower on Au than on the other substrates. These lower growth rates may be consistent with nucleation difficulties on Au. Additional studies are required to confirm this explanation.

5. Conclusions

Al_2O_3 ALD films were successfully grown on a variety of substrates, including H-passivated HF-etched Si, Mo-coated Si, Au, Co, Cr, Cu, Mo, Ni, NiFe, NiMn, Pt, PtMn, stainless steel, W, and ZnO. High quality insulating films with excellent dielectric properties were consistently obtained on most of the substrates. IV and CV data of Al_2O_3 ALD films grown on moderately doped n-type Si(100) and Mo-coated Si(100) were investigated in greater detail. For film thicknesses > 100 Å, the leakage currents were on the order of 1 nA/cm² at voltages prior to the onset of FN tunneling. Al_2O_3 ALD films were examined versus film thickness and growth temperature. Dielectric constants of $k \sim 7.6$ were obtained for the thick Al_2O_3 ALD films. Interfacial oxide layers were shown to be present and can account for the decrease in the dielectric constant with decreasing film thickness. Growth at 350°C was optimal for obtaining the highest dielectric constants. Differences in the electrical properties of Al_2O_3 ALD films grown on the many substrates were attributed to differences in substrate reactivity, substrate roughness, and interfacial oxide layers. In general, the Al_2O_3 ALD film grows remarkably well and is an excellent choice for an insulating or protective film on a wide variety of substrates.

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