

Investigation of ALD Dielectrics in Silicon Capacitors

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35th Annual Microelectronic Engineering Conference at RIT, 2017

Outline

- Project objectives and motivation
- Process flow of MOS capacitor fabrication
- Experimental Results and I-V characteristics
- Conclusions and future work
- Acknowledgments

Project Objectives

- Investigate material properties of aluminum oxide (Al_2O_3) for use as dielectric
- Characterize aluminum and molybdenum as gate metals for MOS capacitor fabrication
- Goal is to use analysis to scale Al_2O_3 for use in transistor fabrication with silicon
- Different metals offer varying work functions and impact gate control for transistor

Motivation for MOS Capacitors

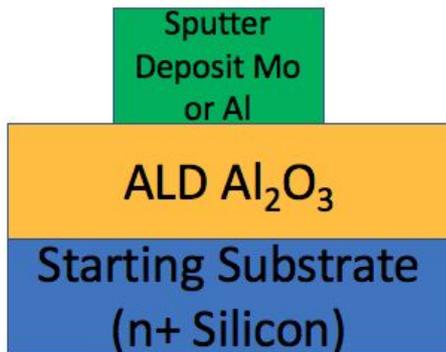
- Silicon-based CMOS technology dominates semiconductor industry due to scalability and incorporation of tried and tested SiO_2 as dielectric
- Why SiO_2
 - High breakdown electric field ($> 10\text{MV/cm}$) - great for short-channel devices and controlling field
 - Large melting point ($1,710^\circ\text{C}$) helps with drain/source implants as both a mask and subsequent processing (RTP anneal)
- Planar scaling of traditional CMOS technology becoming exponentially more difficult
- Compound substrates and stoichiometric channel devices can achieve similar operating frequencies and current densities as CMOS with easier constraints

Process Flow

- **Step 1:** 6-inch diameter silicon substrate degeneratively doped (n+) with Phosphorus (10^{15} cm^{-3})
- **Step 2:** Deposit Al_2O_3 using ALD
 - Precursors: Trimethylaluminium (TMA) and water - purge gas is N_2
 - Two thicknesses targeted - 15nm and 20nm
 - 200°C inner and outer ring deposition temperatures with 150 purge cycles for 15nm target
 - 200°C inner and outer ring deposition temperatures with 200 purge cycles for 20nm target
- **Step 3:** Static DC Sputter deposit gate metal - aluminum or molybdenum
- **Step 4:** Coat FujiFilm HPR 504 positive photoresist on SVG Wafer Track

Process Flow - (Continued)

- **Step 5:** Expose resist on GCA Stepper (g-line) and develop using CD 26 TMAH developer on SVG Wafer Track
- **Step 6:** Etch patterned metal
 - For aluminum, wet bath uses Fuji 16:1:1:2 (Mixture of Nitric Acid, Acetic Acid, Phosphoric Acid and water)
 - For molybdenum, use sulfur hexafluoride (SF_6) on Drytek Quad
- **Step 7:** Strip remaining photoresist
 - GaSonics Aura 1000 asher using oxygen plasma



Experimental Results - Metal Uniformity and Thickness

Molybdenum

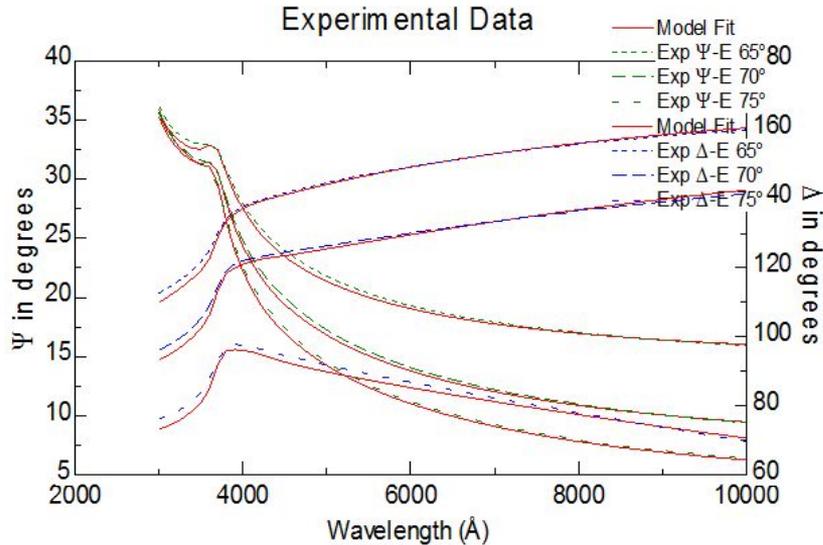
Measurement	Value	Units
Avg. Thickness	3785	[Å]
Thickness Non-Uniformity	18.438	[%]
Sheet resistance (ps)	563.16	[mΩ/square]
Sheet resistance Non-Uniformity (NU)	8.011	[%]
Resistivity (ρ)	2.223E-07	[Ω·m]
Good sites : Bad Sites	49:52	None

Aluminum

Measurement	Value	Units
Avg. Thickness	1635	[Å]
Thickness Non-Uniformity	10.326	[%]
Sheet resistance (ps)	347.52	[mΩ/square]
Sheet resistance Non-Uniformity (NU)	9.546	[%]
Resistivity (ρ)	5.771E-07	[Ω·m]
Good sites : Bad Sites	51:52	None

Sheet resistance and non-uniformity measurements of Molybdenum and Aluminum from static DC sputter on 2-inch glass slides. Molybdenum process shows higher thickness non-uniformity than aluminum. Bulk resistivity of aluminum is higher than molybdenum.

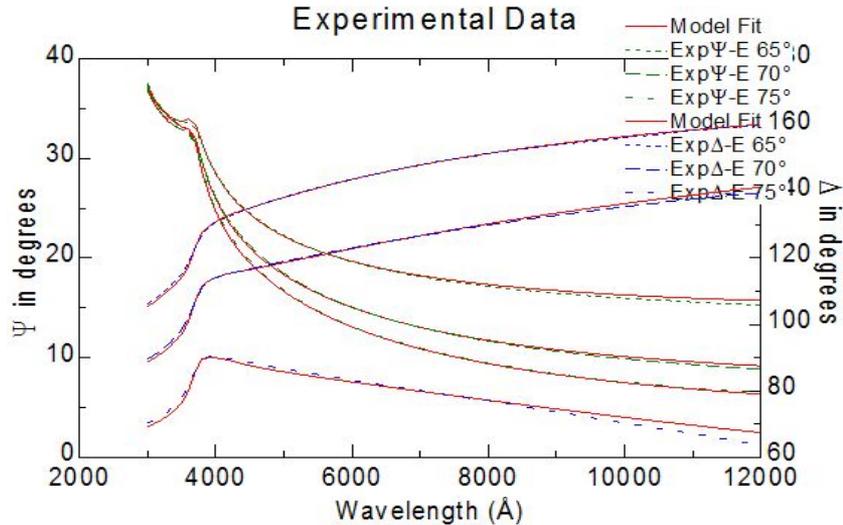
Experimental Results - Al₂O₃ Thickness Uniformity (15nm)



- Ellipsometry thickness measurement of 15nm target Al₂O₃ film using Cauchy model fitted to expected refractive index of aluminum (used $n=1.8$)
- Blue dashed line shows near-perfect match between thickness targeted and thickness measured
- Table shows extracted thickness and refractive index values

Thickness	15.642nm ± 0.105nm
Refractive Index (An)	1.744 ± 0.010

Experimental Results - Al₂O₃ Thickness Uniformity (20nm)



- Ellipsometry thickness measurement of 20nm target Al₂O₃ film using Cauchy model fitted to expected refractive index of aluminum (used $n=1.8$)
- Blue dashed line shows near-perfect match between thickness targeted and thickness measured
- Table shows extracted thickness and refractive index values

Thickness	20.391nm ± 0.115nm
Refractive Index (An)	1.613 ± 0.010

Experimental Results - Capacitance Measurements

	Hand-calculated Capacitance	Ideal ϵ_r (no units)	Experimental Capacitance	Experimental ϵ_r (no units)
15nm oxide with Area = 0.001cm ²	531 pF	9.00	489 pF \pm 58 pF (σ = 11.86%)	8.64 \pm 1.03
20nm oxide with Area = 0.001cm ²	395 pF	9.00	367 pF \pm 34 pF (σ = 9.26%)	8.45 \pm 0.78
15nm oxide with Area = 0.002cm ²	1063 pF	9.00	1001 pF \pm 105 pF (σ = 10.49%)	8.84 \pm 0.93
20nm oxide with Area = 0.002cm ²	797 pF	9.00	767 pF \pm 48 pF (σ = 6.26%)	8.83 \pm 0.55

$$C = \frac{\epsilon_r \epsilon_0 A}{t_{ox}} \rightarrow \epsilon_r = \frac{C t_{ox}}{A \epsilon_0}$$

Capacitance model for parallel-plate capacitor

Hand calculations and experimental observations of capacitance and relative permittivity of silicon substrate MOS capacitors using aluminum as the gate metal. Dielectric constant and thickness depend on the deposition method, composition and microstructure of the material. For experimental calculations, $t_{ox} = 15.642\text{nm} \pm 0.105\text{nm}$ and $20.391\text{nm} \pm 0.115\text{nm}$. Error in die area was excluded and the area was held constant.

Conclusions and Future Work

- Variance in ϵ_f resulted from stoichiometry and microstructure of material
 - Non-uniformity of metals and modeling of film thickness
- Al_2O_3 has high band gap (9eV) and results in very conformal coat
 - Great for high aspect-ratio structures
 - DRAM supply voltages $<0.5\text{V}$ and needs capacitance values in 10^{-15}F range to store charge (memory) - need tall structures
- Silicon-Germanium samples difficult to come in standard 6-inch diameter
 - Requires molecular beam epitaxy (MBE) for compound substrates
 - Dramatically increases cost per wafer - needs pieces - difficult to standardize
- Future work - review different gate metals and dielectric materials to characterize capacitance-voltage response

Acknowledgements and References

- Special thanks to SMFL Staff (especially Patricia Meller!)
- Thanks to Dr. Pearson, Dr. Ewbank, and Dr. Rommel
- Ye, P.D., et al. “GaAs MOSFET with Oxide Gate Dielectric Grown by ALD.” IEEE Electron Device Letters 24.4 (2003): 209-211
- Lin, Jianqiang, Tae-Woo Kim, and Dimitri A. Antoniadis. “A Self-Aligned InGaAs Quantum-Well MOSFET Fabricated through Lift-off-free front-end process.” Applied Physics 5.6 (2012)
- Richard W. Johnson, Adam Hultqvist, Stacey F. Bent, A brief review of atomic layer deposition: From fundamentals to applications

Backup slides

Table of Relative Permittivity Values

	K	Gap (eV)	CB offset (eV)
Si		1.1	
SiO ₂	3.9	9	3.2
Si ₃ N ₄	7	5.3	2.4
Al ₂ O ₃	9	8.8	2.8 (not ALD)
Ta ₂ O ₅	22	4.4	0.35
TiO ₂	80	3.5	0
SrTiO ₃	2000	3.2	0
ZrO ₂	25	5.8	1.5
HfO ₂	25	5.8	1.4
HfSiO ₄	11	6.5	1.8
La ₂ O ₃	30	6	2.3
Y ₂ O ₃	15	6	2.3
a-LaAlO ₃	30	5.6	1.8

Overview of MBE

- Needs in-situ processing and ultra-high vacuum levels
- ALD can be done ex-situ and lower vac levels (rough vac)
- Limited throughput (1 wafer per time)
- Gets best abrupt heterojunction doping profiles of any growth technique
- Low thermal budget
- Constituents arriving @ surface (tetris model)
 - Arrive at substrate and then move in a pattern that is to minimize Gibbs Free Energy
 - Surface diffusion controlled by substrate temp
 - Nucleation of particles on surface described by Boltzman statistics
 - As nuclei coalesce into larger structures, free energy (ΔG_v) released to maximize free energy
 - To be stable nuclei, critical # of particles must have coalesced

Growth rate model for MBE

- n_0 to be the number of particles which have in the solid phase
- ΔG_{crit} : free energy change leading to the formation of embryos
- τ : average lifetime of the critical nuclei

$$R_n = \frac{n_0}{\tau} e^{-\Delta G_{\text{crit}} / KT}$$

Why use Molybdenum (Mo) - (1)

- Pd diffuses about 15 nm in InGaAs on annealing.
- Similarly, Pt contacts formed to InGaAs base in an HBT were found to diffuse and deteriorate device characteristics
- Fukai et al [22] have compared the reliability of emitter contacts formed by non-refractory metal (Ti/Au) and refractory metal (W) and show that device reliability greatly improves with the use of refractory metals.
- To improve the reliability by keeping the metal-semiconductor interfaces abrupt, it is important to use refractory metals, such as molybdenum (Mo)