# Atomic Layer Deposition and Characterization of MgO from Magnesium Bis(Di-secbutylacetamidinate) and Water

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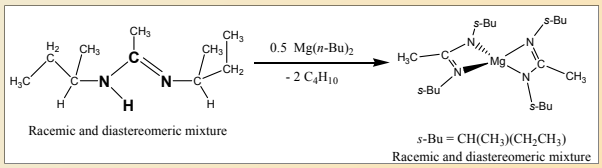
## INTRODUCTION

Magnesium oxide (MgO) is a moderately high dielectric constant material: 8-10, with a wide band gap: 7.8 eV. Potential applications include: gate insulator, buffer layer for superconductors and ferroelectrics, and high secondary electron emission film for plasma displays. MgO has been deposited via Atomic Layer Deposition using a variety of precursors[1], however the full electrical characterization of the material has yet to be published. This work introduces the ALD of MgO from Magnesium Bis(Di-secbutylacetamidinate) and water. In addition to the known applications, ALD of MgO is an important component of Arradiance high gain microchannel plate amplifiers and channeltron technology.

## Precursor Synthesis and Properties

The magnesium precursor is readily synthesized by the reaction of commercially available dibutyl magnesium with the free amidine. The product is a colorless liquid which may be distilled at 80 °C and 14mTorr. The amidinate and precursor are a racemic and diastereomeric mixture with one dominant diastereomer visible in the 1H NMR.




Racemic and diastereomeric mixture

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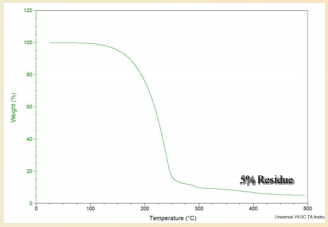
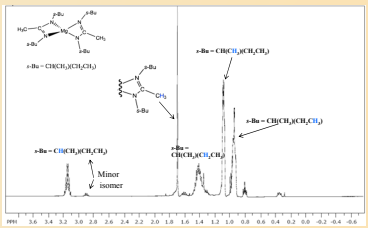



Thermogravimetric analysis of the crude Mg(secButAMD). Temperature ramp rate of 10 K min$^{-1}$ in an $N_2$ flow at 1 atm. Sample size is 50mg. TGA shows very low residue for the crude product and <1% residue for the precursor after distillation.

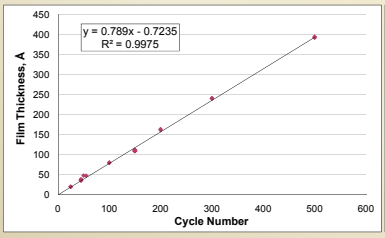



The $^1$H NMR spectrum indicates the distilled material is free of any organic impurities and also shows that the precursor is a mixture of isomers and diastereomers. The different conformations should show similar surface reactivity.

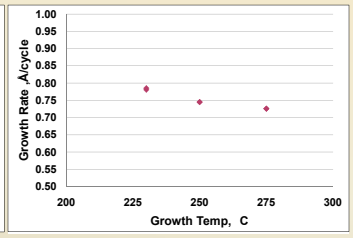
## ALD Growth Characteristics

- All film depositions performed in an Arradiance GEM-D2 ALD system
- Films grown in a temperature range of 225 – 275 C
- Magnesium Bis(Di-secbutylacetamidinate) was used in a temperature range of 105-118 C and was directly dosed from a 150cc precursor delivery bottle
- $H_2O$ was used as the oxidant at room temperature and was directly dosed to process chamber


| Precursor | Nominal Precursor Temp | Dose Time | Exposure Time | Purge Time |
|---|---|---|---|---|
| $H_2O$ | 28 C | 20ms | 0.5s | 70s |
| Mg(secButAMD) | 109 C | 1s (x2) | 1.5s | 30s |



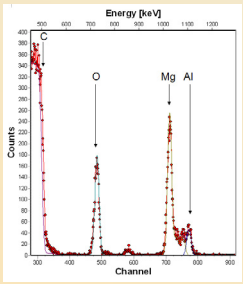

Film thickness determined using spectroscopic ellipsometer . Index of refraction=1.74; Extrapolated growth rate = 0.8Å/cycle. No growth delay on UV-ozone treated Si.



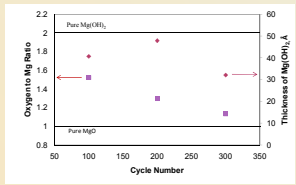

Growth rate is relatively stable over the temperature range of 225 – 275 C. Examination of of a larger temperature range is currently underway.

## Film Properties

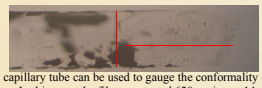
MgO was deposited on both Si and glassy carbon substrates. The composition of the films was measured using Rutherford Backscattering spectroscopy. A typical RBS plot is shown as well as a graph showing a decreasing O:Mg ratio with cycle number. Conformality was determined using fused silica capillary tubes and measuring the penetration of the film using an optical microscope




RBS of a 300cycle (24nm) MgO film on carbon. C and N <1%; composition is $MgO_{1.3}Al_{0.1}$
Film density is 3.06 g/cm$^3$ (similar to that reported by Burton et.al. of 3.07)[1]



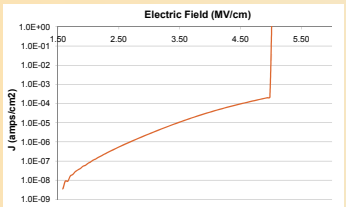

Increasing cycle number shows decreasing O:Mg. Assuming excess O is in the form of $Mg(OH)_2$, the thickness of the hydroxide layer seems to stabilize at ~4nm of the total MgO film thickness.



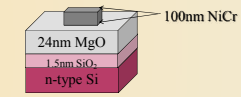
Glass capillary tube can be used to gauge the conformality of an ALD process. In this case, the film penetrated 620µm into a 14µm diameter tube, yielding an AR of **45**.

## Electrical Measurements

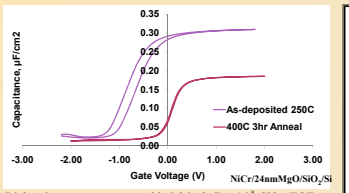
Electrical measurements made using NiCr contacts (4.5 x 10$^{-3}$ cm$^2$). IV measurements using a Keithley 2400 and Micromanipulator Probe station, CV measurements using HP 4275a LCR meter




MgO shows low leakage and a rel. high breakdown field of ~5MV/cm.



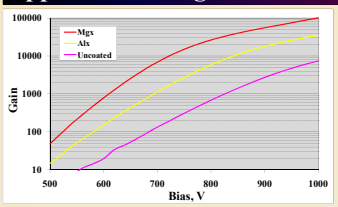

Contact evaporated from NiCr wire (80:20) yields an ohmic contact with good adhesion. Si back contact.

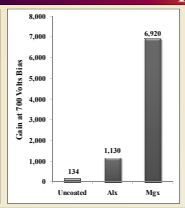



Dielectric constant pre-anneal is 9.8 including 16Å $SiO_2$ (EOT = 11nm) and decreases to 5.5 after anneal. $V_{FB}$ shifts from -0.7V to +0.15V. Hysteresis improves from 200mV to 20mV.

Electrical measurements of MgO thin films show a dielectric constant similar to that of $Al_2O_3$, as well as, low leakage current densities. The low leakage current densities are consistent with a material with a large band gap (7.8 eV). CV measurements show well defined behavior and both $V_{FB}$ and hysteresis are closer to the accepted ideal than corresponding $Al_2O_3$ films on Si. Future work will examine the electrical behavior of ultra thin (<10nm) MgO films within MIM and MIS devices.

## Application of MgO – Microchannel Plate Amplifiers





Microchannel plate amplifiers are electron multipliers that can directly detect charged particles, X-Rays, and UV. When coupled with a photocathode it can be used to detect visible light and is currently a critical component of night vision devices. They are also used extensively in mass spectrometers, imaging and spectroscopy in space, and ion and electron microscopy. MCP treatment with high secondary electron emission film leads to a substantial, 8-50X, gain increase over commercial lead glass MCPs. These devices exhibited extended lifetime and required a reduced scrubbing dose for preconditioning to stabilize gain. This treatment can be used to revive aged MCPs.

## Conclusion

ALD growth behavior of MgO was demonstrated using a novel volatile and liquid precursor, Magnesium Bis(Di-secbutylacetamidinate). The MgO films had undetectable levels of C and N, but showed a small amount of Al as a contaminant. Films exposed to air form a self-limiting hydroxide layer. Electrical measurements indicate the film is a good insulator with a dielectric constant of 8-10. Application of MgO to Arradiance microchannel plate amplifiers showed a substantial improvement in performance over existing commercial MCPs.

## References

[1] **Atomic Layer Deposition of MgO Using Bis(ethylcyclopentadienyl)magnesium and H2O; B. B. Burton, D. N. Goldstein, and S. M. George, *J. Phys. Chem. C* 2009, 113, 1939–1946**