Process Notes on the Deposition of Al_2O_3, ZnO, and SiO_2 Thin Films

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Arradiance ALD experience ranges from high-k dielectrics such as HfO_2, Al_2O_3, ZrO_2, and Y_2O_3 to bulk conductive metals such as Pt and Ru. This document provides a sample of some of the process information aqcuired for various materials using the Arradiance 6" GemStar ALD system.

Growth of Al_2O_3 from trimethylaluminum (TMA) and water is the most cited and characterized ALD process known. The growth is characterized by both an ideal ALD response (self-limiting surface saturation of both precursors) and resulting high quality dielectrics. However, there are still process parameters that can impact the material properties and the extant of penetration of high quality alumina into high aspect ratio features. In order to facilitate the deposition of high quality films in aspect ratios in excess of 500:1, we utilize very high exposures of both precursors to the samples. High exposure, which is a measure of the duration and concentration of a compound above a feature, yields high penetration for ALD.[1] Figure 1 shows the growth rate of Al_2O_3 utilizing saturating doses of both TMA and H_2O as a function of temperature under high exposure conditions. The drop in growth rate above 200 °C can be attributed to the desorption of hydroxyl groups from the surface of the films prior to the TMA pulse. Figure 2 shows the growth rate as a function of purge time for a large dose of TMA (30ms). The precursor is fully purged from the chamber by 35s. For a normal saturating dose time of 20ms, the purge time flattens at 25s (which is the standard purge time for alumina process recipes installed on the GemStar). All alumina films deposited with Arradiance recipes show refractive indices > 1.65 at 632nm and have characteristic

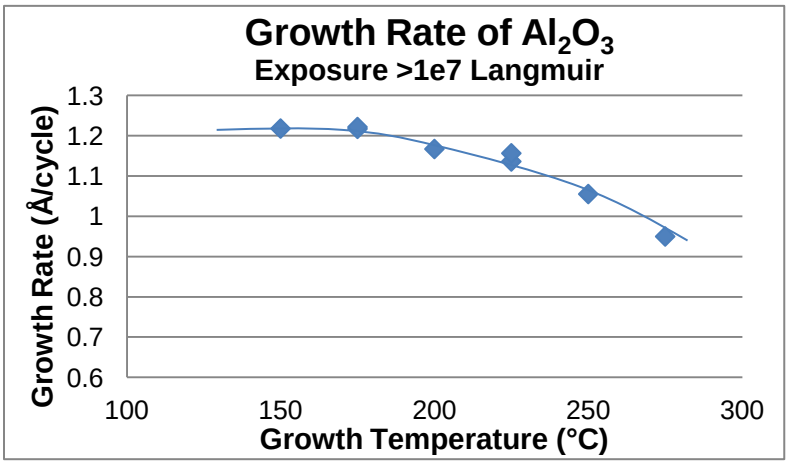

Figure 1 - Growth rate of Al2O3 as a funtion of temperature in GemStar

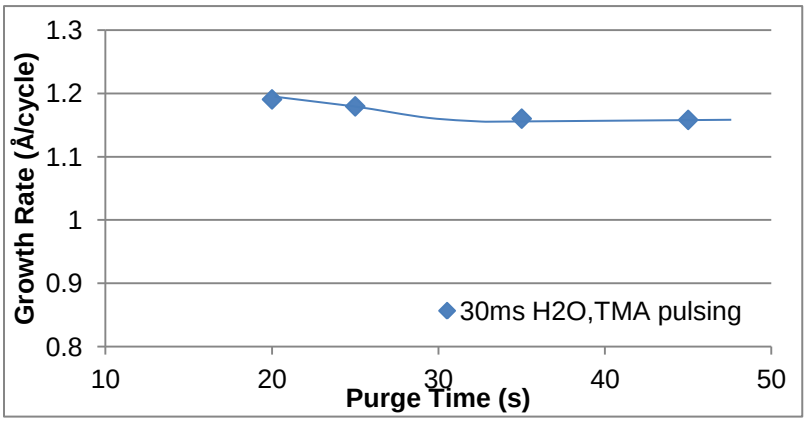

Figure 2- Growth rate as a function of Purge time at 200C

[1] **A Kinetic Model for Step Coverage by Atomic Layer Deposition in Narrow Holes or Trenches** Gordon et.al. Chemical Vapor Deposition (**2003**)9:73-78

resistivities/ low leakage. The resistivities of our ultra thin (<5nm) Al_2O_3 film are >1e15 Ω•cm, consistent with literature results.[2]

Arradiance has also demonstrated controlled and high quality growth of the transparent conducting oxide, ZnO and Al:ZnO. Transparent conducting oxides are an important set of materials for many applications including: gas sensors, transparent electrodes for solar cell devices, ligh emitting diodes, laser diodes, and flexible electronics. ZnO in particular is a n-type semiconductor with a band gap of ~ 3.0 eV. The most common ALD sources for the deposition of ZnO and Al doped ZnO are diethyl zinc (DEZ) and water and TMA and water. All three precursors are high vapor pressure liquids that can be pulsed directly from the bottles at room temperature and still achieve enough of a dose to coat high surface area, high aspect ration devices. At Arradiance, the process response for ZnO is similar to that of ALD alumina. Utilizing a 20ms DEZ and water pulse, the purge time required to achieve perfect self-limited ALD growth is 25s as can be seen in figure 3. The growth rate of ZnO has a strong dependance on the deposition temperature as can be seen in figure 4.

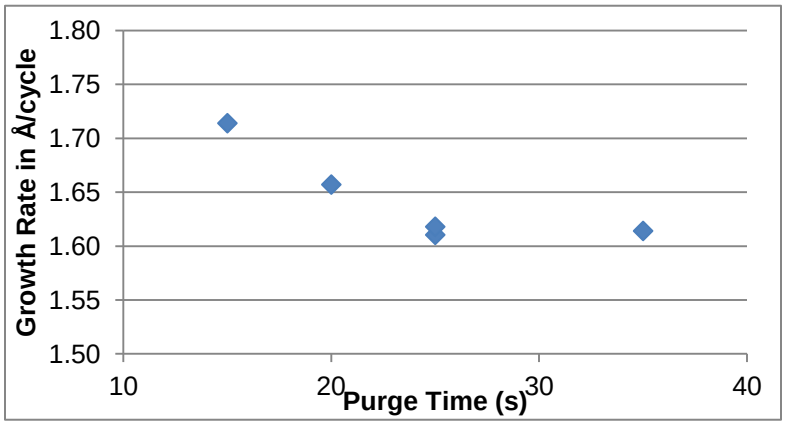

Figure 3 - ZnO growth rate as a function of DEZ purge time at 175C

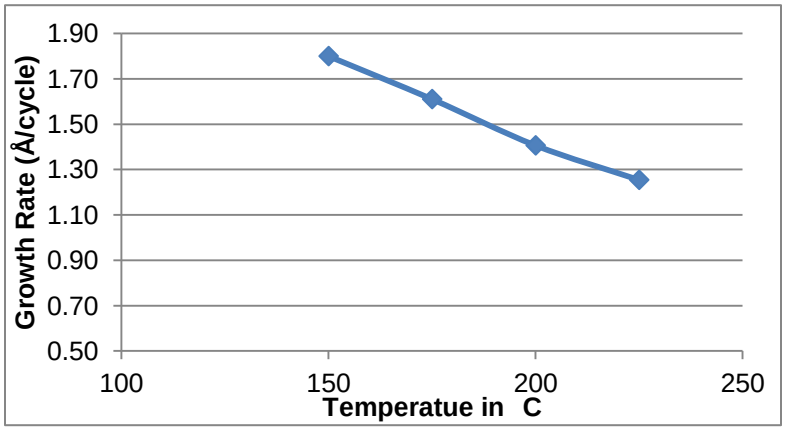

Figure 4 - GR of ZnO vs Temperature

[2] Alternative dielectric films for rf MEMS capacitive switches deposited using atomic layer deposited Al2O3/ZnO alloys Herrman et.al. Sensors and Actuators A 135 **(2007)** 262–272

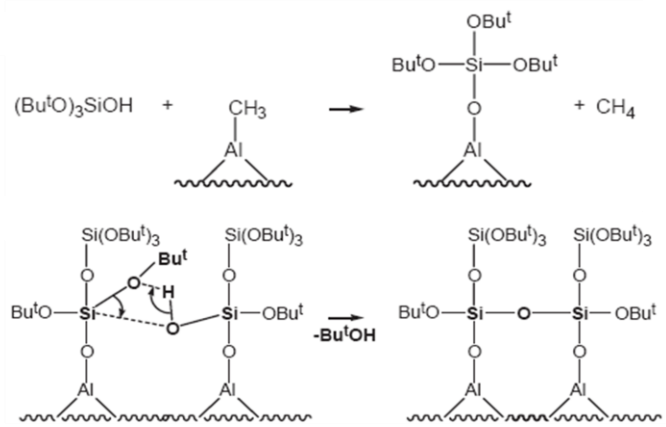

Figure 5 - Catalytic silica mechanism

Arradiance has also been working extensively with the catalytic ALD process for silica as developed originally at Harvard.[3] This process utilizes one of a class of silanol precursors (Tris-t-butoxy silanol or Tris(tert-pentoxy)silanol) combined with an aluminum source (usually TMA) that results in ALD silica films. The film growth rate can vary from 5.0nm /cycle to 20nm/cycle depending on the exposure of the silanol and the deposition temperature. These growth rates are roughly 50 to 200 X that of typical ALD processes. This can be useful when the user would like relatively thick silica films grown conformally over 3D substrates. This process is functional from 50 °C to 250 °C. Figure 5 shows a portion of the deposition mechanism for the silica process. The growth is controlled by the rate of cross linking of the precursors bound to the surface and the rate of insertion of each silanol monomer at the base of the growing polymer strands. During a single half cycle the film will eventually fully cross-link, preventing access of the silanol precursor to the aluminum catalyst center. This provides the self-limiting saturation necessary for ALD like behavior. The SEM cross-section of a tranch capacitor structure (figure 6) shows how this process can yield high quality, conformal silica growth. The trench has an aspect ratio >40:1 and the film thickness on the walls at the top of the feature is ~47nm and at the bottom is ~ 45nm (avg of both sides).

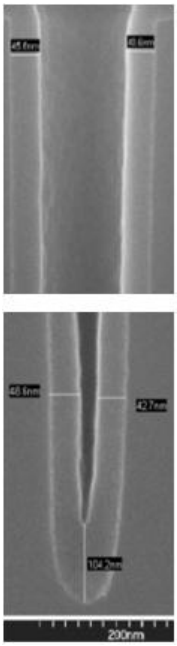

Figure 6 - SEM of silica coated trench

[3]Nanolaminates Rapid Vapor Deposition of Highly Conformal Silica Dennis Hausmann, *et al. Science* 298, 402 **(2002)**

Metal Deposition using Arradiance ALD Tools

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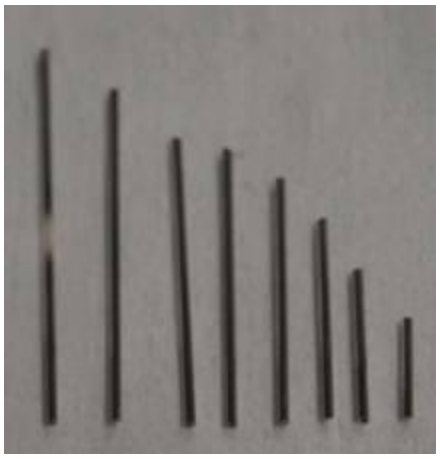
ALD can be used to deposit a wide class of materials including metals and conducting oxides. A large swath of the periodic table is accessible to varying degrees by ALD processes. Arradiance metal deposition capabilities should be considered to extend beyond those that are described in this document.

At Arradiance we have experience depositing the following conducting films.

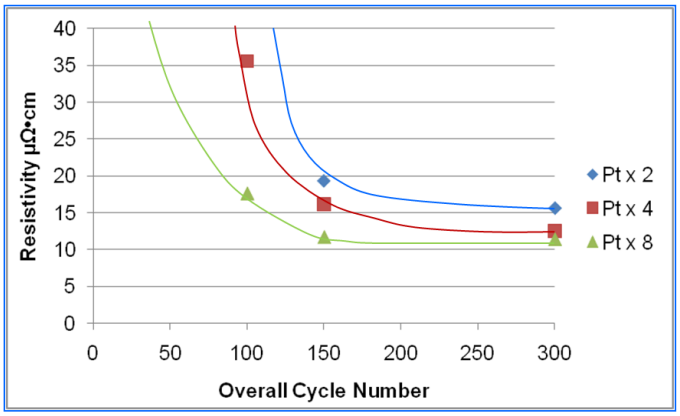
Materials	Precursors	Growth Rate Å/cycle	Lowest Resistivity Achieved
Al:ZnO	Trimethyl aluminum + diethyl zinc + H_2O	1.4 - 1.6	0.002 Ω•cm (literature[4])
ZnO	Diethyl zinc + H_2O	1.4 - 1.6	0.04 Ω•cm (71nm) 150°C
SnO_2	Tin (II) cyclic stannylene + H_2O_2	1.9	0.02 Ω•cm at 120°C
Pt	(methylcyclopentadienyl)trimethylplatinum + O_2	0.9 (250°C)	0.000018 Ω•cm (40nm)
Ru	Bis(ethylcylopentadienyl)ruthenium(II), 98% + O_2	~0.5 (290°C)	0.000022 Ω•cm (30nm)
Ru/RuO_2	Ruthenium Bis (Di-tbutylacetamidinate) dicarbonyl + H_2O	NA	In development
Ru	Ruthenium Bis (Di-tbutylacetamidinate) dicarbonyl + NH_3	1.5 (300°C)	0.000030 Ω•cm (7nm)[5]

One of these materials in particular we have quite a bit of experience with. We grow platinum thin films from 200 °C to 300 °C by atomic layer deposition (ALD) using (methylcyclopentadienyl)trimethylplatinum (MeCpPtMe3) and oxygen as precursors. We have extensive experience growing this material under varying conditions and on different types of substrates. We are also leaders in the field of conformal coatings on structures with aspect ratios greater than 20:1.



One way we examine the growth characteristics of conductors is by growing the films in fused silica capillary tubes and measuring the resistance from end to end through the interior of the tube after ALD. The image to the left shows an experiment where a Pt film was conformal over the first 7 tubes and doesn't quite connect with the 8th tube (far left). Electroding the tubes and then measuring the resistance produces a plot like the one below. We can examine how changing a parameter such as the Pt precursor cycling can affect the film growth and film properties.

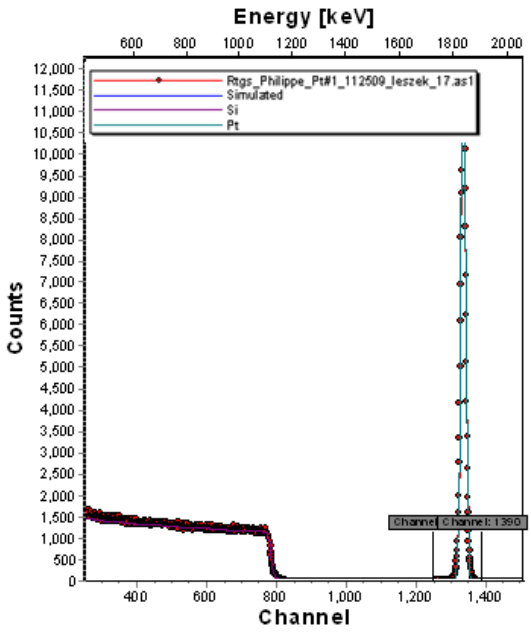
[4] *Journal of The Electrochemical Society*, **150** (6) G339-G347 (2003)
[5] *Journal of The Electrochemical Society*, **154** (12) D642-D647 (2007)



Resistivity as a function of cycle number for different Pt pulses all at 70 °C – AR ~ 25:1

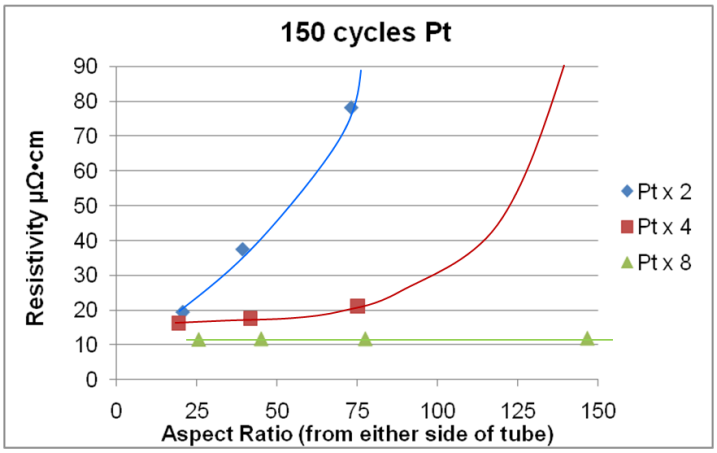
cycles (~7.5nm) and uniform phyically and electrically to AR >150:1 (see below).

Characterization of the Pt films using a technique such as Rutherford Backscattering, can yield important information on the composition and the purity. Arradiance Pt films show little to no carbon or oxygen and meet or exceed results published in the literature.



Increasing the exposure moves the resistivity vs. cycle curve to the left. It also extends the penetration depth where the resistivity is constant. So, a recipe with a double pulse of Pt will yield fairly conductive (<20µΩ•cm) Pt films after 150cycles, but the resistivity will increase significantly as the AR goes over 50:1.

A recipe where the Pt is exposed to the feature for 3 s x 8 pulses yields a film with bulk resistivity after only 150



Resistivity vs aspect ratio for different Pt pulse multiples