Comparison of Water Vapor to Ozone for growth of ALD Films

By Jeffrey Spiegelman and Jonas Sundqvist

ABSTRACT: The application of a backside passivation layer is an important step in the manufacture of crystalline solar cells. The ALD process involved requires an oxidation step using either water or ozone. Ozone is costly, equipment intensive, and hazardous, making water vapor more attractive. A new technology for generating and delivering water vapor at the high flow rate required was evaluated. Results from using this water vapor were compared to those using ozone. Al$_2$O$_3$ films grew 14.5% faster with water vapor when compared to films grown under the same conditions with ozone.

Introduction

A recent breakthrough in crystalline silicon solar cell efficiency has been achieved by adding a thin backside Al$_2$O$_3$ passivation layer using atomic layer deposition (ALD). This thin Al$_2$O$_3$ layer increases solar cell efficiency and enables the use of thinner wafers, thus reducing one main cost factor. The ALD process allows for the depositing of ultra-thin conformational films with Angstrom-level thickness control.

ALD entails two sequential, self-limiting reactions between gas-phase precursor molecules and a solid surface. The ALD process consists of a cycle of precursor and purge pulses that repeat until the desired thickness is achieved. Each cycle (Figure 1: A-D) begins with a precursor pulse, initiating a chemisorption of the precursor at the reactive substrate until saturation is achieved (Figure 1A). Following saturation, the chamber is purged, removing the remaining precursor from the chamber (Figure 1B). Next there is an oxidant pulse. This oxidant reacts with the chemisorbed precursor molecule and creates new reactive sites for the next precursor pulse (Figure 1C). The oxidant pulse is followed by another purge (Figure 1D). The deposition of Al$_2$O$_3$ from trimethyl aluminum (TMA) requires an oxygen source, typically water or ozone. While ozone can provide high quality films, it is costly, equipment intensive, and hazardous. Water vapor can be used as an alternative with similar results for most film thicknesses. From a mechanistic standpoint (Eq. 1-2), water has a well-defined reaction pathway and is expected to show faster reaction kinetics than ozone.

Equation 1: Al(OH)* + Al(CH$_3$)$_3$ $\rightarrow$ AlOAl(CH$_3$)$_2$* + CH$_4$
Equation 2: AlCH$_3$* + H$_2$O $\rightarrow$ AlOH* + CH$_4$

Delivery of water vapor is not as straightforward as it initially appears. Early studies that reported higher quality films using ozone versus H$_2$O may have been limited by unsophisticated water vapor delivery systems. Water bubblers, and other crude delivery devices, are highly variable with respect to mass transfer rates and may lack purity levels required for optimal film formation (Figure 2).

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<th>Vaporizer</th>
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<th>Membrane Technology</th>
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<td>Initial Cost</td>
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Figure 2. Water vapor generating technologies

Figure 1. Illustration of the ALD cycle process. (1A) Precursor Pulse, (1B) Purge, (1C) Oxidant Pulse, (1D) Purge

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During ALD, the reaction occurs on the wafer surface molecule by molecule to form a High-K film. Water vapor purity is a key component in this process. The technique requires the proper molecule be available and not replaced by competitive or contaminant species that will disrupt reaction pathways and lattice structure. In addition, stringent temperature control of both the carrier gas and water vapor are required for uniform mass delivery. Non-uniform mass delivery can lead to incomplete and non-stoichiometric reactions. In the case of water deficiency, these may result in Al-Al bonds. In the case of excess water, additional O-H bonds may be incorporated into the films unless the excess is completely removed by extended purge times.

For ALD processing, the total water vapor needed per pulse is very low. The typical delivery method is to store the water in a pressure vessel and then through valve cycling to vacuum pull water molecules from the head space. This technique is difficult for production use, as the water must be degassed typically for 24 hours before use and microdroplets can be entrained into the headspace, leading to chemical vapor deposition (CVD) instead of ALD, which generates particles and non-uniformity.

Microdroplets can also create cold spots where they land, leading to non-uniformity and warpage. In order for oxide films to work properly, film thickness and uniformity are critical. Water droplets also deposit on the surrounding chamber and internal delivery line surfaces. These water spots are very hard to evaporate in the limited cycle time available during the purge pulse. If these drops are not removed, they will react on the surface with the TMA leading to direct combination.

It is difficult to precisely control the delivery of ultrapure water to a process. Problems and dangers associated with direct reaction of hydrogen and oxygen to produce steam can be avoided by simply boiling de-ionized water. However, dissolved gases may remain in water vapor produced in this manner and removal of them requires multiple cycles of boiling and condensing within a
hermetically sealed environment. In addition, materials such as salts and metals can be generated during the boiling process, adding unwanted impurities. Bubblers, direct liquid injection (DLI) and vaporizers have all been used with limited success in the generation of ultrapure water vapor.

Bubblers are low cost but do not deliver a constant flow due to variations in temperature of the gas and liquid, operating pressure, liquid level, and thermal droop. They cannot prevent entrainment of dissolved gas, volatile molecular contaminants, and micro-droplets, which carry particulate and ionic molecular contaminants into the process. If the flow rate exceeds limited velocities, explosive bubbles blast the source liquid out of the vessel and into the downstream piping, forcing the use of phase separators that lead to increased particulates, condensation, and flow instability.

Direct liquid injection has limited flow control at low flow rates and at high flow rates bubbles can appear in the liquid, generating erratic values. DLI, which requires a metallic vaporizer or an additional metal hot plate to convert the liquid to gas, can vaporize only limited quantities due to thermal transfer rates, and has a potential for chemical decomposition. Most critically, it cannot provide any purification of the liquid being vaporized; everything in the liquid is vaporized into the process.

Vaporizers atomize the water and then try to combust the small droplets into molecular water. The heat of vaporization is very high and the ability to get the energy to the water molecule is limited by the heater transfer rate through the vaporizer plate and the carrier gas that is mixed in with the water vapor. In addition, the water is aggressive and can corrode the vaporizer’s internal components, leading to long term stability and reliability issues.

None of these technologies can deliver precise control of water vapor and at the same time remove particles, dissolved gases, and ionic impurities. In this study, a novel membrane delivery system that incorporates temperature, pressure, flow rate control, as well as water purification has been employed. The system adds controlled amounts of water vapor to any carrier gas. The unit operates in atmospheric and vacuum pressures and uses filtered deionized (DI) water as its source. The system utilizes a hydrophilic membrane that excludes organic and metal contaminants from the water vapor. Liquid water from the membrane system does not come into direct contact with the carrier gas, so the vacuum system, or reaction environment, is not exposed directly to the water source. For cost, simplicity, and safety pur-
poses, water is the preferred oxidant for Al₂O₃. To allow the successful use of ALD films in photovoltaic devices, the equipment will likely be configured as an inline atmospheric process as opposed to a vacuum-based process. An atmospheric process requires a high flow of humidified gas with single percent loading with water vapor. A new membrane technology that is capable of generating and delivering high flow rate ultrapure water vapor has been developed. The objective of this work is to determine the viability of this technology. A simple comparison with ozone was performed where films grown by both oxidants were compared for saturation rates, growth rates, uniformity, and particle formation.

Experimental

ALD: A 300mm vacuum ALD process tool was set up for deposition at 300°C and the process pressure of 0.5 Torr (Figure 3). A saturation dose of trimethyl aluminum (TMA) was predetermined using O₃ as reactant. Total cycle time was in the range of 2-3 seconds. Purge pulses with argon were in the range of 0.5-1.5 seconds.

Figure 7: Thickness versus pulse time shows saturation of water is 14.5% faster.

Figure 8 (left): Deposition data shows that the desired thickness was achieved with a small standard deviation.

Figure 9 (right): Particle map shows a small number of random particles added during deposition but not attributed to gas supply.

<table>
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<th>mean: 10.27 nm</th>
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<td>stddev: 0.05 nm (0.5%)</td>
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<td>full range: 0.22 nm (2.1%)</td>
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<td>thk. determined by spectral ellipsometry</td>
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- <40 particles added during deposition process
- random pattern
- not related to gas supply
A unit for generating and delivering water vapor to humidify
the process gas was placed in the gas cabinet (Figure 4). Pro-
cess parameters included a humidifier temperature of 70°C and
H₂O carrier flow of 300sccm. The humidified carrier gas flowed
through the unit at a constant rate and was pulsed into the
chamber by switching between final and evacuation valves. The
unit was a RainMaker® Humidification System (RHS) provided by
RASIRC. 100 ALD cycles of TMA/water and TMA/ozone precursors
were compared. A thickness of 10nm was expected after 100 ALD
cycles (1Å growth per cycle).

Water Delivery System: The carrier gas flows into the RHS where
water diffuses across the hydrophilic membrane and into the
carrier gas (Figure 5). The temperature of the humidified gas is
measured and fed back to a temperature controller to adjust the
humidification level. Internal pressure control maintains indepen-
dence from variations in downstream process pressures allowing
operation in atmospheric and vacuum pressure environments.

The RHS water vapor delivery system consists of a non-porous
membrane that excludes particles, micro-droplets, volatile gases,
and other opposite charged species from being transferred to the
carrier gas and ensures only water vapor is added. The membrane
is highly selective, preventing most carrier gases from crossing
over into the source (Figure 6). Selectivity of up to a million to
one water molecules over nitrogen has been found. Organic and
metal contaminants in the liquid source cannot permeate across
the membrane or enter the carrier gas stream, resulting in a water
vapor saturated product that is consistent and pure.

The RHS fully saturates the carrier gas based on the temper-
ature at the gas/water interface, providing accurate delivery
of water vapor (Table 1). With the addition of a back pressure
regulation device, low vapor pressure gases can be delivered
into sub-atmospheric processes. Because the RHS works on 100%
saturation of the carrier gas, the system can be cycled on and off
without significant effect on accuracy as long as the maximum
diffusion rate through the membrane is not exceeded.

Figure 10. Water pulse shown with quadruple mass spectrometry
Results

Initial ALD runs found that ozone saturation was observed with a pulse time of 1000 milliseconds (Figure 7). The growth rate for Al₂O₃ with ozone precursor was found to be ~0.9Å per cycle. In the water test, H₂O saturation was observed with a pulse time of 1000 milliseconds (Figure 7). The resulting film was measured by spectral ellipsometry (Figure 8). The growth rate for Al₂O₃ with water precursor was measured at ~1.025Å per cycle. The mean layer film thickness was 10.27nm with a standard deviation of 0.05nm (0.5%). The full range of film thickness was 0.22nm (2.1%). Particle mapping (Figure 9) indicated that <40 particles were added during the deposition process. These occur in a random pattern, which indicates that the particles are not related to the gas supply.

During the test, the water pulse was clearly visible by quadruple mass spectrometry. Consistent levels of water concentration were observed over multiple pulses (Figure 10). A very strong influence of the RHS temperature on the water peak was observed. Water concentration levels increased by a factor of 10 upon increasing temperature from 35°C to 70°C. This is consistent with the increase in water vapor pressure between 30°C and 70°C as would be expected and demonstrates versatility in the RHS water vapor delivery system with respect to water dosage concentration.

Discussion

ALD tests showed the replacement of ozone with water vapor increased the film growth rates by 14.5%. We believe this is due to the more straightforward reaction kinetics. Saturation pulse times were similar between the two oxidants as this is directly related to gas flow dynamics in the specific ALD process chamber. Film growth on the order of 1Å per cycle is similar to those reported in the literature for other water and ozone based systems. Expected layer thickness was achieved with no obvious particle issues due to water vapor supply by the RHS system.

Conclusions and Future Work

The average layer thickness of 1.025Å for water and 0.9Å for ozone are consistent with reported literature values. A higher growth rate for water is expected. The H₂O/TMA system is very efficient and self-limiting. The H₂O/TMA reaction highly favored thermodynamically, where the enthalpy of reaction ΔH = -376 kcal is one of the highest for any ALD reaction. Moreover, from a kinetic standpoint, this reaction can be viewed as a relatively straight forward proton transfer, versus that of ozone, where several reaction intermediates must be inferred in order to achieve the reaction product. In addition, the O₂ reaction product is likely to include Al-O-Al bonds which may lead to slower reactions with the subsequent TMA step. For ALD, less reactive surface sites may lead to lower average layer thickness per cycle.

The use of the RHS allowed for easy replacement of the existing ozone oxidant supply and eliminated the need for degassing water before use. In research environments, the one to two day delay is acceptable before putting a water bubbler on line, but in a production environment, this is a costly throughput requirement that the RHS can eliminate.

References


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