## ALD for Manufacturing
## Room Premier Ballroom - Session AM-TuP
## ALD for Manufacturing Poster Session

**AM-TuP-1 Methods of Precursor Delivery for ALD Process and Studies on Possible By-product Issues Occurred in the Exhaust System and its Solutions***, **Ellis Lee**, C Lee, S Lee,* CSK, Republic of Korea

As the technology in semiconductor manufacturing develops, device characteristics like the density of the pattern and the aspect ratio are changing and according to the change in trends, many changes in the methods for thin films deposition are being required. Especially methods like the ALD(Atomic Layer Deposition) or the PE(Plasma Enhanced) ALD that are able to have more detailed process control are in demand. In order to improve the electrical characteristics of the device as well as the deposition method, various types of precursors used in the ALD method and new precursors are currently being actively pursued.

Currently, liquid precursors used in the ALD method are being used in various mass production processes. For example, TEOS is used in the gap fill, DIPAS is used in the multi patterning, ATARP is used for Low-K process

Generally, the overall concept of the ADL production tool that uses liquid precursors uses the PDS(Precursor Delivery System) to deliver precursors to enhance its tool reliability

The PDS, a liquid precursor delivery system for ALD processes, can be divided into two different types. This is divided according to the vapor Pressure trend of the precursor.

If there are residuals of precursor in the inner side of the tube where the precursor is being delivered, when air flows in, a chemical reaction easily occurs and these reactions will eventually be sources that arouse particles and contamination. Therefore, after all the precursor is used up and the before exchanging the empty canister, the inner sides of the tube must be cleaned due to air exposure.

If it's a precursor that relatively has high vapor pressure trend, the tube can be cleaned with using just inert gas such as Ar or N2. However, if it's a precursor that relatively has low vapor pressure trend, a purge gas and a solvent like N-Hexane will be needed to fully clean the inner sides of the tube.

The excess residuals of the precursor that do not participate in the process after it is flowed into the chamber will be exhausted out through the pump and abatement. During the exhaust process, not only the precursor but also the reactant gas will be exhausted out of the system but through this, various by-products from the reactant of the main precursor occurs in exhaust system.

These various by-products are the main causes for decreasing the up-time of the ALD tool. However, at Edwards, we hold a great history on precursors and the PDS and also, we manufacture pumps and abatement systems of the exhaust system which allowed us to hold various experiences with expected issues regarding by-products that occur in semiconductor process.

*** Keywords: ALD, Precursor Delivery System**

**AM-TuP-2 High Purity Hydrazine Delivery System for Low Temperature Thermal ALD of Silicon Nitride***, J Spiegelman, **Daniel Alvarez**, K Andachi,* RASIRC*; A Lucero, A Kondusamy, S Hwang, X Meng, H Kim, J Kim,* University of Texas at Dallas

The demand for faster, smaller and more energy efficient logic devices plus higher density, higher speed and increased reliability for advanced memory devices has led to challenges in Semiconductor device manufacturing. Novel metal materials, 3D architecture and increasing HAR structures are being used to address these challenges, placing additional constraints on film deposition methods. CVD and ALD of SiN is used in several applications including gates spacers, etch stops, liners, encapsulation layers and passivation layers.[1] Recently PEALD of SiN is taking on an increasingly important role due to new temperature constraints of <400C. However several challenges remain on HAR and 3D structures in applications where plasma approaches may not meet conformality requirements. Also, thermal ALD with NH3 may not be feasible due to the high temperature requirement (>500C) of these reactions.[2]

Our approach involves development and use of a novel hydrazine delivery system for thermal ALD of SiN at <400C. A hydrazine delivery system was developed to provide a stable flow of ultra-dry hydrazine gas from a liquid source in a sealed vaporizer. The liquid source combines anhydrous hydrazine and a proprietary solvent that acts as a stabilizer. The solvent is highly non-volatile. High purity hydrazine gas is generated in-situ and delivered to the deposition chamber but the solvent remains in the vaporizer. Testing confirms that hydrazine vapor pressure is maintained at levels viable for ALD (12-14 torr) even in the presence of the solvent. Oxygen contamination has plagued previous hydrazine studies. This study demonstrates high purity hydrazine delivery at <800ppb water contamination in gas phase. Delivery system safety and optimization versus conventional hydrazine will be addressed.

A study of silicon nitride deposition was conducted using hexacholorodisilane (HCDS) and hydrazine on a Si-H substrate. A custom thermal ALD reactor was used to deposit films from 250-400°C. Film growth per cycle (GPC) with hydrazine was 0.4-0.5 Å/cycle at 400°C with refractive index of 1.813. Film stoichiometry was confirmed with XPS. SiN films with low impurities were achieved for oxygen (<2%) and chlorine (<1%). Highly uniform films were obtained across a 4-inch wafer for 200 as well as 400 cycles. Results were similar to films deposited using PEALD at 360°C with HCDS and NH3. The presentation will compare film density and wet etch rate results at different temperatures for hydrogen terminated silicon, hydroxyl terminated silicon, and hydrazine treated silicon. Nucleation behavior comparing surface pre-treated hydrazine versus HCDS will also be discussed.

**AM-TuP-3 Spatial ALD for Semiconductor Manufacturing - Expanding the Process Space***, **David Chu**,* Applied Materials

The use of ALD in semiconductor manufacturing has accelerated, growing to nearly a $1.5B market. A number of the new ALD applications challenge the boundaries of conventional ALD processing, often requiring high quality films at reduced thermal budgets. Spatial ALD extends the process space within which the ALD process is viable for volume manufacturing. This presentation will focus on our spatial ALD solution and its advantages over conventional ALD processes.

**AM-TuP-4 RT Atomic Layer Deposition System with a 1 m Size Reactor***, **Fumihiko Hirose**,* Yamagata University, Japan

Room temperature (RT) atomic layer deposition has been attracting much attention in the field of coating for electronic parts and micro machines since thermal damages to the coating objects are effectively minimized. In the field of the organic electronics, the RT ALD is applicable for producing the gas barrier flexible films. In our laboratory, RT ALDs of various films [1-3] were developed by using plasma excited humidified Ar[1-3]. Since oxidizing species of O and OH from the plasma excited humidified Ar are delivered at a distance as long as 1m, we developed a mass production system of RT ALD with a 1m size reactor. For the electronic parts with sizes of ~5 mm, the batch processing of thousands of pieces of parts are possible to be treated at one time. In the conference, we introduce the newly developed 1m size reactor of RT ALD and its application for the anticorrosion coating for the metal parts and gas barrier film production.

**AM-TuP-5 High Conductance Precursor Delivery and Control Valves***, **Masroor Malik**, Y Jiang,* Swagelok

In today's semiconductor chip manufacturing processes, more low pressure precursors, which are often solid source, are being used. Employing these low pressure precursors requires very high chemical conductance and high temperature systems.

In both the Atomic Layer Deposition (ALD) and Atomic Layer Etch (ALE) processes, control valves are used to precisely meter the chemical dosing. Traditionally, springless diaphragm valves offered the best cleanliness and cycle life in these applications. However, the increased molar chemical delivery demand of low pressure processes requires high conductance delivery systems. Springless diaphragm valves designed to operate under these parameters require very large diameter diaphragms that exceed practical space limitations.

Emerging manufacturing techniques are enabling the design of new control valve solutions to handle these challenging chemistries in the production environment while meeting the required cleanliness and cycle life expectations.

In this paper, we will describe the challenges faced, the solutions considered, and the path chosen to best fulfill the needs for high conductance control valves in low pressure precursors.

**AM-TuP-6 Computational Fluid Dynamic Study of Spatial ALD: Mapping the Transition Between Transport, Diffusion, and Reaction Limited Regimes***, **Angel Yanguas-Gil**, J Elam,* Argonne National Laboratory

Spatial ALD provides the advantage of higher throughput compared to conventional ALD by eliminating the need for long purge times. In a recent study, we presented an analytic expression for the saturation curves in spatial ALD in terms of the velocity of the moving substrate, chamber geometry, precursor pressure and input flows, and the surface chemistry.[1]

In this work, we have performed computational fluid dynamic studies of spatial ALD. Momentum, energy, and mass transport equations are solved for a moving surface incorporating both self-limited and non-self limited surface chemistries. The models are solved assuming that ALD precursors are dosed in the presence of a background carrier gas flow. The results show that, at low pressures, the dependence of the surface coverage with the process variables matches extremely well the simple analytic solution. However, with increasing pressure the system reaches a starved, diffusion-limited regime and the validity of the analytic approximation breaks down.

Furthermore, we found that as pressures approached one atmosphere, the flows became unstable, consistent with a transition from laminar flow to a turbulent regime. This transition is not necessarily detrimental for the process: when the timescale of the fluctuations are much smaller than the residence time and the flow becomes fully turbulent, precursor mixing in the chamber is enhanced resulting in a higher effective diffusion.

[1] A. Yanguas-Gil and J. W. Elam, Analytic expressions for atomic layer deposition: Coverage, throughput, and materials utilization in cross-flow, particle coating, and spatial atomic layer deposition, J. Vacuum Sci. Technol. A 32, 031504 (2014).

**AM-TuP-7 Simulation and Measurement of Mass Evaporation Rate of Precursors inside Canister during ALD Process***, **Seung-Ho Seo**, Y Lee, D Kim, H Shin,* GO Element Co.,Ltd, Republic of Korea*; J Kim, W Lee,* Sejong University, Republic of Korea

The precursor for atomic layer deposition (ALD) should have excellent purity, thermal stability, and high evaporation rate to deposit a high-quality thin film with high productivity. In particular, since the evaporation rate of the precursor affects the growth rate of the thin film, a constant amount of precursor should always be supplied to the ALD reactor. Therefore, it is very desirable to predict the evaporation characteristics of the precursor in the real ALD systems depending on the structure and temperature of the precursor delivery system, including the canister, and the temperature and gas flow rate of carrier gas. In this work, we calculated the evaporation rates of precursors as a function of time using computational fluid dynamics (CFD) method and then compared them with the measured rates. The fundamental physical properties of precursors, such as boiling point, vapor pressures at different temperatures, heat capacity, and viscosity, were obtained by either literature survey or measurements. The turbulence model and the evaporation-condensation model were used to predict the evaporation rates, the distributions of temperature and pressure, and the flow streamlines. The evaporation rates were determined using a measurement system equipped with a real-time level sensor to confirm the calculation results. The results of this work are expected to be used to predict the precursor evaporation characteristics or to design the optimal structure of the canister.

Keywords: Mass evaporation rate measurement, computational fluid dynamics simulation, metalorganic precursor, canister

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