

## ALD Fundamentals

### Room Evergreen Ballroom & Foyer - Session AF3-MoP

#### Growth Mechanisms and In Situ Studies Poster Session

**AF3-MoP-1 Langasite Crystal Microbalance (LCM) for In-situ Process Monitoring of ALD up to 440 °C, Masafumi Kumano,** Tohoku University, Japan; *K Inoue,* Piezo Studio, Japan; *K Hikichi,* Technofine co. Ltd, Japan; *M Shimizu, S Tanaka,* Tohoku University, Japan

A quartz crystal microbalance (QCM) is often used as an in-situ monitoring tool for ALD process. The piezoelectric constant of quartz crystal starts to decrease at 300 °C and disappears at 573 °C. In addition, its temperature coefficient of frequency (TCF) around the turn over temperature increases above 300 °C. Therefore, QCM is generally limited in use under 300 °C. In a higher temperature range, GaPO<sub>4</sub> is only a material practically used for a microbalance<sup>1</sup>. However, the crystal growth of GaPO<sub>4</sub> is not industrially established like quartz, and the crystal size is limited.

Langasite Ca<sub>3</sub>TaGa<sub>3</sub>Si<sub>2</sub>O<sub>14</sub> is a new candidate for a high temperature microbalance. It keeps piezoelectricity in a wide temperature range without any phase transition, and a large crystal can be potentially grown in an industrial scale. Around the turnover temperature range, a Langasite crystal microbalance (LCM) shows a much smaller TCF than the conventional QCM (Fig. 1).

The Langasite has a dielectric constant about 5 times as larger as that of quartz. This must be taken into account of to use an available QCM oscillator circuit. As shown in Fig. 2, the active area of the LCM, i.e. the center part where the electrodes on both sides overlap, is smaller than that of the QCM. Fig. 3 shows the resonance impedance characteristic of the LCM. The resonance frequency is 6 MHz, and the electromechanical coupling factor is 2.6%. A weak spurious mode remains in Fig. 3, but it can be swept out by polishing the crystal surface to a convex shape.

The LCM was applied for TMA/H<sub>2</sub>O cycle up to 440 °C. The inside of a LCM holder is purged by pulsed pressure synchronized to the ALD cycle to avoid internal deposition. Transient temperature fluctuation is repetitive and reproducible over the ALD sequence and can be separated from a mass change by averaging over sequence numbers. The measured LCM frequency change by a mass change of each cycle is 1.6 Hz at 395 °C and 2.2 Hz at 280 °C, which is smaller than that of the QCM (3.5 Hz/cycle at 285 °C). The sensitivity is improved using a larger active area of LCM in conjunction with a dedicated oscillator circuit.

1) J. W. Elam and M. J. Pellin, *Anal. Chem.* 77 (2005) 3531-3535

**AF3-MoP-2 In-Situ Process Monitoring of Precursor Delivery Using Infra-Red Spectroscopic Method, Robert Wright, T Baum,** Entegris, Inc.

ALD processing is an increasingly critical deposition method for conformally coating high-aspect ratio features in advanced logic and memory devices. Accurate, consistent and controllable delivery of precursor materials to the deposition system is a necessity. To achieve reliable, low-cost deposition processes, a sensitive and non-destructive real-time method for monitoring the precursor concentration is increasingly important. An IR method offers chemical specific information for both the reactant and the reaction by-products. An IR based system was developed and used to measure the 'direct' flux from a solid source in real time. The real-time measurement of precursor concentrations in the gas-phase can be applied to process monitoring, process control and towards the detailed characterization of key variables in the precursor delivery. Further, this method can be used to characterize ampoule performance under different pressure, temperature and flow conditions for a specific chemical precursor.

**AF3-MoP-3 Quantitative Analysis of High-k ALD Precursors for Trace Elemental Impurities by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS), Jinjin Wang,** Air Liquide Electronics – Balazs NanoAnalysis

The scaling of logic technology node following Moore's law has reached <10 nm. Consequently, high-k dielectrics are prevalent in modern microelectronic devices. They are insulating thin films of metal oxides, metal nitrides or other types of metallic compounds with much higher dielectric constant k ranging from 8 to 32, in contrast to SiO<sub>2</sub> with 3.9. These thin films are deposited from high-k dielectric precursors, which are organometallic or inorganic compounds, via atomic layer deposition (ALD) technology. The ALD allows growth of thin films of high conformity and uniformity downscaled to single nm. In order for these thin films to function in micro devices, the films must be free of contamination, especially elemental impurities that causes defects of microelectronic

devices. Therefore, for quality control of the ALD process, all high-k precursors used must be completely free of elemental impurities. As a result, each batch of high-k precursors is now analyzed for elemental impurities before it can be used in the ALD process.

ICP-MS is the preferred technique for analysis of these high-k precursors for trace metals at ppb and sub ppb level. High-k dielectric precursors generally contain a metal atom bound to a ligand or other organic components, and often react violently with water and moisture in atmosphere. Both metal and organic components create various matrix effects and mass interferences, both of which affect the accuracy of the precursor analysis. One of the matrix effects is known as "space-charge-effects" due to high concentration of the metal atom present in the precursor sample. The "space-charge-effects" suppress the signal of many elements of interest and result in low spike recovery and analytical accuracy. Two types of mass interferences result from both metal matrix and organic components, caused by polyatomic molecular ions and isobaric ion species. The polyatomic molecular ions include and are not limited to metal oxide, metal argide and metal carbide, formed by high concentration metal ions reacting with organic components and other species in the plasma. Doubly charged ions are another form of mass interferences that affect the analysis.

ICP-MS methods have been developed to reduce and eliminate all these matrix effects and mass interferences. The methods are able to drive detection limits (DL) low. We will present these low DL that we have improved. Our method capability analysis (MCA) showed that our analyses have low DL, good repeatability and accuracy as demonstrated by spike recovery experiments. The MCA also showed that the matrix effects and the mass interferences have significantly been reduced or eliminated.

**AF3-MoP-4 Numerical Studies of the Fluid Dynamics and Chemical Kinetics of Spatial Atomic Layer Deposition of Al<sub>2</sub>O<sub>3</sub>, Dongqing Pan,** University of North Alabama

Low throughput is a major limitation for industrial level atomic layer deposition (ALD) applications. Spatial ALD is regarded as a promising solution to this issue. With numerical simulations, this paper studies an in-line spatial ALD reactor by investigating the effects of gap size, temperature, and pumping pressure on the flow and surface chemical deposition processes in Al<sub>2</sub>O<sub>3</sub> ALD. The precursor intermixing is a critical issue in spatial ALD system design, and it is highly dependent on the flow and material distributions. By numerical studies, it's found that bigger gap, e.g., 2 mm, results in less precursor intermixing, but generates slightly lower saturated deposition rate. Wafer temperature is shown as a significant factor in both flow and surface deposition processes. Higher temperature accelerates the diffusive mass transport, which largely contributes to the precursor intermixing. On the other hand, higher temperature increases film deposition rate. Well-maintained pumping pressure is beneficial to decrease the precursor intermixing level, while its effect on the chemical process is shown very weak. It is revealed that the time scale of in-line spatial ALD cycle is in tens of milliseconds, i.e., 15 ms. Considering that the in-line spatial ALD is a continuous process without purging step, the ALD cycle time is greatly shortened, and the overall throughput is shown as high as 4 nm/s, compared to several nm/min in traditional ALD.

**AF3-MoP-5 Mechanistic Understanding of Dicholasilane Thermal Decomposition during Atomic Layer Deposition of Silicon Nitride, Gyeong Hwang, G Hartmann,** University of Texas at Austin; *P Ventzek,* Tokyo Electron America Inc.; *T Iwao, K Ishibashi,* Tokyo Electron Ltd.

Silicon nitride (SiN) thin films have been widely employed for various applications including microelectronics, but their deposition presents a challenge especially when highly conformal layers are necessary on nanoscale features with high aspect ratios. Plasma-enhanced atomic layer deposition (PEALD) has been demonstrated to be a promising technique for controlled growth of SiN thin films at relatively low temperatures (< 400 °C), in which thermal decomposition of Si-containing precursors on a N-rich surface is a critical step. In this talk, we will present our recent findings regarding potential underlying mechanisms leading to facile thermal decomposition of dicholasilane (DCS, SiH<sub>2</sub>Cl<sub>2</sub>) on the N-rich SiN surface, based on periodic density functional theory calculations. Our study highlights the importance of high hydrogen content on the N-rich surface, rendering primary and secondary amine groups. When the N-rich SiN surface is fully hydrogenated, the molecular adsorption of DCS is predicted to be exothermic by 0.6 eV. In this case, DCS decomposition appears to be initiated by nucleophilic attack by an amine lone-pair on the electrophilic Si, leading to the formation of a DCS-amine adduct intermediate followed

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by release of a Cl<sup>-</sup> anion and a proton. The predicted activation barrier for the DCS decomposition reaction is only 0.3 eV or less, depending on its adsorption configuration. We will also discuss the formation and role of HCl, the subsequent formation and nature of Si-N bonds, and the interaction between adsorbed DCS molecules. While clearly demonstrating advantageous features of DCS as a Si precursor, this work suggests that thermal decomposition of Si precursors, and in turn the ALD kinetics and resulting film quality, can be strongly influenced by surface functional groups, in addition to product accumulation and precursor coverage.

## AF3-MoP-6 New Challenges of the Channeled Spectroscopic Ellipsometry for ALD Applications, *Gai Chin*, ULVAC Inc., Japan

The channeled spectroscopic ellipsometry is a snapshot method for the spectrally resolved polarization analysis. Two high-order retarders are utilized to generate a channeled spectrum carrying information about the wavelength-dependent multiple parameters of polarization of light. This method does not require mechanical or active components for polarization-control, such as a rotating compensator and electro-optic modulator. It can measure the thickness and optical constants of thin films at an ultra-high speed. Its data acquisition time is as short as 10 ms per measurement.

This innovative technology created great opportunities for new applications of the spectroscopic ellipsometry in which the compactness, the simplicity and the rapid response are extremely important. It can be integrated into many kind of deposition tools and successfully measured thin films *in-situ* and *ex-situ*. Obviously, ALD is one of the promising applications for this novel spectroscopic ellipsometry.

This paper describes the principle, system configuration and new challenges on developing this compact high-speed spectroscopic ellipsometry to satisfy daily increasing *in-situ* monitoring requirements from the ALD industrial and R&D users.

Some of the successful ALD applications will be introduced, such as measurement data obtained on Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, TiO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub> and TiN thin films etc. By acquiring thickness and optical constants data from this spectroscopic ellipsometry, the layer by layer growth and material properties of the films can be studied in detail. The growth rate per cycle was determined directly, and an automatic process control can be realized by feedback and feed-forward approach on the ALD tools.

## AF3-MoP-7 *In-situ* Ellipsometric Analysis of the Plasma Influence on Atomic Layer Deposited AlN Thin Films, *Necmi Biyikli, S Ithom, D Shukla, A Mohamad, B Willis*, University of Connecticut

In this report we have carried out real-time process monitoring to understand the impact of RF-plasma power and plasma exposure time on aluminum nitride (AlN) growth and film properties via *in-situ* ellipsometry. AlN thin films were grown on Si(100) substrates with plasma-enhanced atomic layer deposition (PE-ALD) using trimethyl-aluminum (TMA) as metal precursor and Ar/N<sub>2</sub>/H<sub>2</sub> plasma as co-reactant. Saturation experiments have been employed in the range of 25-200 W plasma power and 30-120 s plasma exposure time within 100 - 250 °C substrate temperature. *In-situ* multiwavelength ellipsometry provided the necessary sensitivity to identify single chemical adsorption (chemisorption) and plasma-assisted ligand removal events, as well as changes in growth-per-cycle (GPC) with respect to plasma power. Our real-time dynamic *in-situ* monitoring study revealed mainly the following insights about the plasma power influence on AlN growth: GPC and TMA chemisorption amount exhibited plasma-power dependent saturation behavior at 30 seconds of plasma duration. The amount of chemisorption saturated at ~2.25 Å for higher RF-power levels, while for 25 and 50 W it went to below 1 Å, which was attributed to insufficient ligand removal. Besides *in-situ* characterization, *ex-situ* measurements to identify optical, structural, and chemical properties were also carried out on 500-cycle AlN films as a function of plasma power. AlN samples displayed single-phase hexagonal crystal structure with (002) preferred orientation for 150 and 200 W, while the dominant orientation shifted towards (100) at 100 W. On the other hand, 50 and 25 W resulted in films with amorphous character with no apparent crystal signature. Furthermore, it was found that when the plasma exposure time was increased from 30 to 120 s for 25 and 50 W, the amount of chemisorption exceeded the thickness gain values recorded for 150-200 W: ~2.4 Å. However, such a recovery in chemisorption did not reveal crystalline material as the AlN films grown at sub-50 W both showed amorphous character.

## AF3-MoP-8 Reaction Mechanisms of Thermal and Plasma-Modified ALD Growth Studied by *In-Situ* Mass Spectrometry, *Thomas J. Larrabee, L Ruppalt*, U.S. Naval Research Laboratory

Mechanisms of gas-surface chemical reactions, and reactions caused by plasma-surface interactions, have been studied to understand different aspects of the atomic layer deposition (ALD) of zinc oxide (ZnO) and niobium oxide (NbO<sub>x</sub>) using a differentially-pumped, highly-sensitive *in-situ* quadrupole mass spectrometer to detect reactant and product gas species. Examination and comparison of the gaseous reaction products of these two ALD processes aid our understanding of how to use plasmas to modify ALD oxide growth, generally.

In some of these cases, the ALD process was modified by inserting argon/hydrogen plasma steps, which has been shown to alter the stoichiometry of ZnO and NbO<sub>x</sub> (*i.e.* Nb<sub>2</sub>O<sub>5</sub> to NbO<sub>2</sub>), driving metal-enriched films and lower oxidation states. To date, it has been unclear what the mechanism of the plasma-surface reactions is in these processes or precisely how the thermal ALD growth has been altered by the insertion of argon/hydrogen plasma steps. By examining the reactant and product gas species detected by the *in-situ* quadrupole mass spectrometer, we are able to investigate the chemical reactions that occur during the ALD process, uncovering information not only about the impact of the plasma steps, but also the underlying mechanism of the thermal growth process, itself. Reagents used were diethylzinc for ZnO and (*t*-butylimido)tris(diethylamino)niobium(V) for NbO<sub>x</sub>, respectively, and water as the oxidant. In plasma experiments, capacitively-coupled plasmas of H<sub>2</sub>/Ar and Ar alone were used to alter surface chemistry.

Comparison was made between thermal reactions, and inserting plasma steps at different parts of an ALD sequence. Evidence for a mechanism involving metal-organic ligand desorption and possible further reaction with the plasma is to be presented for both the Zn and Nb precursors. No evidence demonstrating removal of oxygen atoms from the growing film, either by O<sub>2</sub> or H<sub>2</sub>O gas evolution was found for ZnO. The chemistry of the NbO<sub>x</sub> growth, both for thermal and plasma-modified reactions will also be presented. Results are relevant for the nearly ubiquitous alkyl-amino transition metal precursors.

Metal precursor saturation has been investigated, from which inference about physisorption vs. chemisorption may be gleaned. Relative abundances and the dynamics of reactant and product peaks are explored to clarify the problem of peaks appearing both as reactants and as products, which has previously obfuscated interpretation of mechanisms by examining QMS data alone.

## AF3-MoP-10 *In-situ* Quartz Crystal Microbalance Study of Poly(3,4-ethylenedioxythiophene) (PEDOT) by Oxidative Molecular Layer Deposition (o-MLD), *G Parsons, Jungsik Kim, A Volk*, North Carolina State University

Molecular Layer Deposition (MLD) has emerged as a promising vapor-phase deposition technique due to its self-limiting reactions and conformal film growth. This work investigates oxidative MLD (o-MLD) of poly(3,4-ethylenedioxythiophene) (PEDOT) by using a volatile liquid oxidant agent and 3,4-ethylenedioxythiophene monomer (EDOT). Traditionally, PEDOT growth has been synthesized through solution-based processes involving oxidation and deprotonation steps. Despite its simplicity, poor solubility of PEDOT requires a water-soluble polyanion, poly(styrenesulfonate) (PSS), often increasing the film resistivity. Alternative vapor-phase methods such as oxidative chemical vapor deposition (o-CVD) have been reported, but chemical additives/post treatments are necessary to obtain high conductivity. Previously, Atanasov et al. has reported an o-MLD process of PEDOT using molybdenum(V) chloride oxidant (MoCl<sub>5</sub>) and EDOT [1]. However, the low vapor pressure of MoCl<sub>5</sub> limits deposition temperature and facile dosing. Moreover, few basic growth analyses such as *in-situ* quartz crystal microbalance (QCM) have been carried out to understand PEDOT growth by o-MLD.

In this work, *in-depth* PEDOT growth behavior during o-MLD has been studied. The relationship between the film growth and various deposition conditions such as precursor dose/purge time, working pressure, and chamber/precursor temperature was investigated. The mass change per cycle is linear with the number of cycles for two different oxidant dose times. However, much longer purge times are required for the longer oxidant dose to remove the byproducts. QCM, X-ray photoelectron spectroscopy (XPS), spectroscopic ellipsometry (SE), and scanning electron microscopy (SEM) show that PEDOT film has been uniformly deposited at 100 °C, with a growth rate of ~1.5 Å/cycle. At higher chamber temperature, the growth rate decreases; above 150 °C, PEDOT growth is hindered by

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decomposition of precursors and monomer limited adsorption, resulting in rapid decrease of film growth. These QCM studies will play a pivotal role for understanding nucleation and growth mechanism of PEDOT via o-MLD and developing area selective MLD processes.

[1] S.E. Atanasov et al., Chem. Mater. 26, 3471–3478(2014)

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