

Monday Morning, October 31, 2011

Nanomanufacturing Science and Technology Focus

Topic

Room: 207 - Session NM+MS+NS+TF-MoM

ALD for Nanomanufacturing

Moderator: B. Lu, AIXTRON Inc.

9:00am **NM+MS+NS+TF-MoM3 Industrialization of Atomic Layer Deposition: From Design to Deposition**, J.S. Becker, A. Bertuch, R. Bhatia, L. Lecordier, G. Liu, M. Sershen, M. Sowa, R. Coutu, G.M. Sundaram, Cambridge NanoTech, Inc. **INVITED**

The demonstrated benefits provided by Atomic Layer Deposition (ALD) in producing films of exceptional uniformity, and conformality, has set the stage for its use in large area, batch processing, and Roll-to-Roll applications. In this work we discuss the use of Computational Fluid Dynamics (CFD) as a means of gaining insight into the system performance of such industrial instruments, but also as a technique for refining system design. Additionally we describe the basic underpinnings of design for ALD systems operated under atmospheric conditions, (for Roll-to-Roll use), along with the design factors which must be considered for zone separated ALD methods. Finally we will present film results taken from a zone-separated ALD system, and discuss the salient aspects of the deposition process.

9:40am **NM+MS+NS+TF-MoM5 Improved MOS Characteristics of CeO₂/La₂O₃ and MgO/La₂O₃ Gate Stacks Prepared by ALD**, T. Suzuki, M. Kouda, Tokyo Institute of Technology and AIST, Japan, K. Kakushima, P. Ahmet, H. Iwai, Tokyo Institute of Technology, Japan, T. Yasuda, AIST, Japan

La₂O₃ is one of the candidate materials for the next-generation high-k gate stacks because it can achieve sub-1 nm EOT by forming direct-contact La silicate with Si. There have been many ALD studies for La₂O₃, however, the performance of the MOSFETs incorporating ALD-La₂O₃ needs much improvement. Our previous studies using EB evaporation showed that capping the La₂O₃ dielectrics with an ultrathin layer of CeO₂ or metallic Mg (~1 nm) effectively improved the channel mobility [1,2]. In this paper, we report fabrication of CeO₂/La₂O₃ and MgO/La₂O₃ gate stacks by ALD/CVD for the first time, and demonstrate that these stacks show improved electrical properties (k value, channel mobility, etc.) as compared to single-layer ALD-La₂O₃.

The experiments were carried out using a multi-chamber ALD/CVD system which was capable of in-situ metallization and RTA. The CeO₂/La₂O₃ and MgO/La₂O₃ gate stacks were formed on H-terminated Si(100) using Ce[OCEt₂Me]₄, La(PrCp)₃, and Mg(EtCp)₂ metal sources. La₂O₃ and MgO films were formed by ALD using H₂O as an oxidant. The ALD temperature was set at a relatively low temperature of 175°C in order to ensure the self-limiting growth [3]. CeO₂ films were formed in the CVD mode via thermal decomposition of Ce[OCEt₂Me]₄ at 350°C. The gate electrodes were formed by sputtering of W. MOSFETs were fabricated by the gate-last process.

The effective k values for the CeO₂(1nm)/La₂O₃(3nm) and MgO(0.8nm)/La₂O₃(4nm) stack capacitors were approximately 16, which was significantly larger than those for La silicate without any capping layer (k=10~12). The k-value improvement by the CeO₂ capping is presumably due to the higher k value of CeO₂ (~23), whereas the improvement by the MgO capping is ascribed to suppression of excessive La-silicate formation.

We have also found that the CeO₂/La₂O₃ gate stack leads to excellent mobility characteristics. The mobility for the MOSFET with 1.43 nm EOT was 214 cm²/Vs at an effective field of 1.0 MV/cm, which was 85% of the Si universal mobility. The mobility improvement by the CeO₂ capping is attributed to the reduced fixed-charge density, since V_{th} approached to the ideal values by the CeO₂ capping. On the other hand, the MgO capping induced a negative shift in V_{th} and consistently degraded the mobility. These effects of ALD-MgO capping are qualitatively different from those observed for EB-evaporated Mg [2]. The mechanisms causing such a difference between EB evaporation and ALD are now under investigation.

This work was carried out in Leading Research Project for Development of Innovative Energy Conservation Technologies supported by NEDO.

References: [1] T. Koyanagi, et al., JJAP, **48**, 05DC02 (2009); [2] M. Kouda, et al., 2009 VLSI Symp., p. 200; [3] K. Ozawa, et al., 2010 ICSICT, p. 932.

10:00am **NM+MS+NS+TF-MoM6 Highly Uniform and Conformal Thin Film Metallization with Thermal and Plasma-Enhanced Atomic Layer Deposition**, M. Toivola, J. Kostamo, T. Malinen, T. Pilvi, T. Lehto, C. Dezelah, Picosun Oy, Finland

Ultra-thin, nanometer-scale metal or metallic films are a crucial component in e.g. several applications of modern MEMS/NEMS (Micro/NanoElectroMechanical Systems) and other advanced IC technologies, sensors, optical devices and catalyst manufacturing. When the component sizes keep diminishing and at the same time, the level of system integration increasing (for example the so-called "System-in-a-Package" multifunctional chip devices), it creates a drive from "conventional" 2D device architecture to 3D component integration. Through Silicon Vias (TSV) are a central structure in these 3D-stacked devices and there's often a need to produce highly uniform and conformal thin films of metals or otherwise conducting materials on the insides of the vias. Due to the often very high aspect ratio (AR) of the TSV structures, Atomic Layer Deposition (ALD) is one of the only methods with which reliably uniform and conformal material layers can be deposited on the via walls.

Industrially upscalable ALD processes were developed for several metals and metallic compounds, i.e. Pt, Ir, Ru, Cu, Ag, Au, TiN and TiAlCN. Deposition of metals can be done with thermal ALD and plasma-enhanced (PEALD). The main benefits of the PEALD technique are the possibility to use reductive processes instead of oxygen, lower deposition temperatures which decreases the thermal stress on the substrates, and a wider variety of precursor chemicals.

Inductively coupled remote plasma source system was further developed to reduce any possibility of plasma damage, which can often happen in the more conventionally designed, direct plasma devices. Instead of direct ion bombardment, our plasma system utilizes highly reactive radicals. Protective flows and separating metal precursor inlets shield the plasma source from getting short-circuited by films from precursor back-diffusion. E.g. N₂/H₂, H₂/Ar, O₂ and mixed gas plasmas can be generated with the system.

Structural design solutions were optimized for ALD reactors. Top flow delivery of the precursor gases ensures even distribution of reactive molecules inside the reactor vessel. This is beneficial especially in the case of non-optimal processes with precursor decomposition or etching or poisoning of reactive sites by reaction by-products. Less impurity and thickness gradient can be achieved with the top flow, compared to the side-flow (cross-flow) design since all the area reacts at the same time leaving less reactive sites left for reaction with the by-products. Therefore, it is possible to get more challenging reaction chemistries working with the top-flow design, and also a forced flow for through-porous samples is possible. With modified stopped flow design, extended reaction time inside the chamber can be reached while still keeping the protective flows from the inlets on to prevent any back-diffusion of precursor and subsequent particle formation in the inlet lines.

Upscalable structure was specifically designed to bridge the gap between R&D and production. Smaller ALD tools can be used for process and chemical precursor development at for universities and research labs, whereas the larger, ALD tools can be fully automatized, upscaled and clustered into full scale high volume throughput industrial production unit capable of coating even several thousands of wafers per hour.

10:40am **NM+MS+NS+TF-MoM8 Atomic Layer Deposition for Continuous Roll-to-Roll Processing**, S.M. George, P.R. P. Ryan Fitzpatrick, University of Colorado at Boulder **INVITED**

Atomic layer deposition (ALD) is currently being developed for continuous roll-to-roll processing. This development is significant because roll-to-roll processing would allow ALD to address many applications in a cost effective manner. This talk overviews the approaches and progress to date. The original idea of ALD with moving substrates and constant precursor flows was presented in a patent by Suntola and Antson in 1977. This scheme involved rotating the substrate between alternating precursor sources and vacuum pumping regions. One current approach under development is based on moving the substrate close to a gas source head. The ALD precursors continuously flow through slits in the gas source head that are separated and isolated by inert gas purging. A second version of this design involves using a gas bearing to set the gap spacing between the gas source head and substrate. Another ongoing approach is based on moving the substrate through separate regions of precursor pressure and inert gas purging. Limited conductance between the regions prevents the gas phase reaction of the ALD precursors. The talk examines the issues and prospects for achieving ALD for continuous roll-to-roll processing. Additional details

are presented for the dependence of precursor isolation on reactor parameters for a substrate under a model gas source head.

11:20am **NM+MS+NS+TF-MoM10 High Rate Continuous Roll-to-Roll Atomic Layer Deposition**, *E. Dickey*, Lotus Applied Technology
INVITED

Atomic Layer Deposition (ALD) is a unique thin film deposition process, capable of producing coatings with unmatched quality and performance. Its unique attributes include high conformality and outstanding thickness precision, enabling the deposition of dense, continuous pinhole-free films, even when extremely thin, and even on highly imperfect substrate surfaces. These qualities have made the process attractive for applications on flexible substrates, including dielectrics and semiconductors for flexible electronics devices, and high performance gas diffusion barriers to encapsulate and protect environmentally sensitive devices such as OLED displays and lighting, and CIGS photovoltaic modules.

Until recently, ALD films have generally been deposited using conventional static processing, in which the individual precursors are sequentially introduced into and purged from a common volume containing the stationary substrate. This sequence, commonly called an ALD cycle, typically requires at least several seconds and results in the growth of approximately 0.1nm thickness. As a result, the time required to deposit films of reasonable thickness can be quite long. Furthermore, the static nature of the process makes roll-to-roll processing impractical. In this presentation, we discuss the development of a new ALD process based on substrate translation, with the ALD cycle elements enabled by transport of the flexible substrate back and forth between the precursor zones. Because no time is required for introducing, saturating, and removing precursors for each cycle, the deposition speed is dramatically increased. In addition, this configuration naturally provides the unique feature of film deposition only on the substrate itself, as it is the only surface which is exposed to both precursors. In turn, this allows the use of steady-state plasma as the oxygen source, enabling a new technique of precursor isolation; "precursor separation by radical deactivation", in which the oxygen gas precursor actually mixes with the metal precursor, but is only reactive in the region of the plasma source. Together, this technology set has allowed the deposition of high quality ALD films on polymer substrates, including ultra-barrier films, at substrate speeds in excess of one meter per second.

Authors Index

Bold page numbers indicate the presenter

— A —

Ahmet, P.: NM+MS+NS+TF-MoM5, 1

— B —

Becker, J.S.: NM+MS+NS+TF-MoM3, **1**

Bertuch, A.: NM+MS+NS+TF-MoM3, 1

Bhatia, R.: NM+MS+NS+TF-MoM3, 1

— C —

Coutu, R.: NM+MS+NS+TF-MoM3, 1

— D —

Dezelah, C.: NM+MS+NS+TF-MoM6, **1**

Dickey, E.: NM+MS+NS+TF-MoM10, **2**

— G —

George, S.M.: NM+MS+NS+TF-MoM8, **1**

— I —

Iwai, H.: NM+MS+NS+TF-MoM5, 1

— K —

Kakushima, K.: NM+MS+NS+TF-MoM5, 1

Kostamo, J.: NM+MS+NS+TF-MoM6, 1

Kouda, M.: NM+MS+NS+TF-MoM5, 1

— L —

Lecordier, L.: NM+MS+NS+TF-MoM3, 1

Lehto, T.: NM+MS+NS+TF-MoM6, 1

Liu, G.: NM+MS+NS+TF-MoM3, 1

— M —

Malinen, T.: NM+MS+NS+TF-MoM6, 1

— P —

P. Ryan Fitzpatrick, P.R.: NM+MS+NS+TF-MoM8, 1

Pilvi, T.: NM+MS+NS+TF-MoM6, 1

— S —

Sershen, M.: NM+MS+NS+TF-MoM3, 1

Sowa, M.: NM+MS+NS+TF-MoM3, 1

Sundaram, G.M.: NM+MS+NS+TF-MoM3, 1

Suzuki, T.: NM+MS+NS+TF-MoM5, **1**

— T —

Toivola, M.: NM+MS+NS+TF-MoM6, 1

— Y —

Yasuda, T.: NM+MS+NS+TF-MoM5, 1