ALD for Manufacturing
Room On Demand - Session AM1

Equipment Design/Modeling/Large Format/Precursor Delivery

AM1-1 Closed Loop Control of ALD/ALE Precursor Dose Delivery, ***Jim Ye***, *J. Ding, V. Saptari,* MKS Instruments, Inc.

Consistent precursor delivery is needed in ALD/ALE processes for generating a stable and homogenous deposition. Unstable deposition will cause defects and create wafer to wafer and batch to batch variations. Further improvements in ALD/ALE process throughput and cutting the waste of precursors will require a tighter control on precursor dose delivery to the process chamber.

Previously, concepts of ALD/ALE precursor concentration control have been reported. However, there are two potential problems in this approach. First, tuning the concentration of precursor is a relatively slow process which can be accomplished by either varying the temperature of precursor container or adjusting the dilution/carrier gas flow. They do not have enough bandwidth to handle faster varying changes in the flow. The second problem is that a constant concentration will not guarantee a constant dose in each precursor pulse due to other factors such as a switch drift.

In this work, we present a concept solution involving a gas sensor and a pulse MFC. The gas sensor measures the precursor concentration out of the source in real time and feeds the readings to a pulsed MFC immediately downstream to the sensor. The pulse MFC generates ALD/ALE precursor pulses. It continuously adjusts the total flow rate (pulse height) or pulse duration for each precursor pulse to achieve a constant dose of the precursor to the processing chamber.

AM1-2 Efficiency Characterization of Reactor-Scale Gas Exchange by CFD, ***Anton Persson***, Linköping University, Sweden; *Ö. Danielsson,* Physicomp AB, Sweden; *H. Pedersen, M. Karlsson,* Linköping University, Sweden

To utilize the sequential surface chemical reactions essential to ALD processes, the gas mixture in the ALD reactor needs to be exchanged between the metal precursor pulse and reagent pulse. This is commonly done through a continuous flow of carrier gas (purge) between the pulses and is often vital for a successful ALD process. Insufficient exchange can lead to unintentional reactions, which in turn may cause poor film thickness uniformity or formation of structural defects. In contrast, excessive purging leads to prolonged process times and waste of carrier gas. While the optimal purge time can be obtained from extensive experimental work, such studies are seldom reported for new ALD processes or fully understood at the full wafer scale, and is reactor design specific. ALD process development therefore has a lot to gain from a simple, yet powerful modelling approach to study gas transport at the reactor scale.

This work implements methods common in e.g. ventilation modeling to investigate efficiency aspects in gas exchange. An ALD reactor for 200 mm substrates with six in-plane, symmetrically positioned gas channels was modelled using computational fluid dynamics (CFD). It was assumed that the precursor partial pressure is small in relation to the partial pressure of the carrier gas, such that changes in the overall velocity field between pulse and purge steps may be neglected. Several configurations were tested, where precursor and reagent entered from opposing or asymmetric directions, with different carrier gas flow rates equivalent to N2 in a range of 50-200 sccm per inlet.

Purge times were quantified by the residence time distribution (RTD). It was shown that RTD was primarily a function of total mass flow rate and reactor geometry, and less affected by pulse time.

Moreover, precursor usage efficiency was characterized by the local mean age (LMA) measure, which represents the mean time for a particle to reach a certain location in the reactor in a steady state situation, calculated from the inlet. It was seen that the constant carrier gas flow in some configurations caused “blocking effects”, obstructing the precursor to spread uniformly over the substrate. Thus, care should be taken to engineer the flow field for efficient precursor usage.

While the model is subject to simplifications, the general trends and relative performance among test cases are expected to be accurate. Once the main design frame is established, promising configurations could be analyzed further by extending the model, e.g. by taking reversible adsorption on reactor walls into account.

ALD for Manufacturing
Room On Demand - Session AM2

Spatial/R2R/Fast ALD

AM2-1 Surface Modification and Stabilization of Photoluminescence Perovskite Nanocrystals via Atomic Layer Deposition, *Y. Jing,* Huazhong University of Science and Technology, China; *K. Cao,* ***Rong Chen***, State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China

Photoluminescence perovskite nanocrystals (NCs) have shown significant potential in optoelectronic applications in view of their narrow band emission with high photoluminescence quantum yields (PLQYs) and color tunability. However, their poor stability in light, heat and water environments still hinders practical applications in optoelectronic and bioimaging fields due to their ionic character. Atomic layer deposition (ALD) has been developed as an attractive method to stabilize the crystal structure of perovskite NCs through encapsulation and surface passivation. In this presentation, several stabilization methods through ALD are introduced. First, a low-temperature Al2O3 ALD process was developed to enhance the stability of CsPbBr3 quantum dots-silica sphere in light, water and heat, which originated from the crystal structure stabilization after ALD coating. Nonetheless, a significant photoluminescence (PL) quenching of NCs was typically observed upon Al2O3 ALD. Accordingly, a specially designed ALD reactor integrated a FTIR spectrometer was exploited, which enabled in-situ characterizations to investigate ligands exchange and evolution during deposition after each precursor dosing. It was found that the surface chemical reaction between ALD precursor and capping oleic acid (OA) ligands led to reorganization of OA ligands that increased surface trap sites, leading to PL quenching. Based on the reaction mechanisms observed, a hybrid passivation strategy was developed to simultaneously enhance the photoluminescence quantum yield and the stability of perovskite NCs by two-step modification with surface halogen replenishment and ALD. Consequently, the PL quenching was avoided and the perovskite NCs/Al2O3 nanocomposites exhibited exceptional stability against water, light and heat. Our work provides a versatile method for preparing ultrastable perovskite NCs through ALD method and significantly improves their potential in LED illumination and backlight displays.

AM2-4 Influence of Reactor and Pattern Geometry on Atomic Layer 3D Printing, ***Ivan Kundrata***, *M. Plakhotnyuk,* ATLANT 3D Nanosystems, Denmark; *J. Bachmann, M. Barr, S. Tymek,* Friedrich-Alexander Universität Erlangen-Nürnberg, Germany; *P. Brüner,* IONTOF GmbH, Germany

As additive manufacturing in its various forms is shifting the paradigm of traditional manufacturing, the same space opens in the field of thin film deposition. Atomic layer deposition is, due to its inherent separation of reactions, uniquely suitable for adaptation into a 3D printer. In fact, the concept of spatial atomic layer deposition, which can be considered as a precursor for 3D atomic layer printing, goes all the way back to 1974.[1] Despite the many challenges of creation and miniaturization of spatial ALD reactors, atomic layer 3D printing was successfully proved as a concept recently.[2,3]

However, for the best performance of atomic layer 3D printing, the influence of geometry of both the reactor and the pattern being printed has to be examined. Generally, due to the necessary spatial separation of precursor and reactant, edge effects are necessarily present. Moreover, deviations from the perfect printing geometry cause additional line edge effects and selectivity defects.

In this study, we created a general theoretical model of effects caused by spatial separation on the printed pattern. The theoretical model was then

confronted with experiments performed on the atomic layer 3D printer developed by ATLANT 3D Nanosystems.

The theoretical effects and samples analyzed include edges of lines, overlaps of lines including rastering and gradients, multiple paths overlaps during pattern printing and step pattern printing. To prove that these effects are independent of the specific material, the effects are explored for TiO_2, ZnO, and Pt.

[1] Tuomo Suntola, Jorma Antson.Method for producing compound thin films. US4058430A,United States Patent and Trademark Office, 29 November 1974.

[2] Ivan Kundrata, Maksym Plakhotnyuk, Maïssa K. S. Barr, Sarah Tymek, Karol Fröhlich, Julien Bachmann (2020, June 30) An Atomic-Layer 3D Printer [Conference presentation] ALD/ALE 2020

[3] Cesar Arturo Masse de la Huerta, Viet H. Nguyen, Abderrahime Sekkat, Chiara Crivello, Fidel Toldra-Reig, Pedro Veiga, Carmen Jimenez, Serge Quessada, David Muñoz-Rojas.Facile patterning of functional materials via gas-phase 3D printing [2020, Cornell University Condensed Matter, Materials Science]

AM2-7 Realization and Dual Angle In-situ OES Characterization of Saturated 10-100 ms Precursor Pulses in a 300 mm CCP Chamber Employing de Laval Nozzle Ring Injector for Fast ALD*, Abhishekkumar Thakur, S. Wege, S. Bürzele, E. Ricken,* Plasway Technologies GmbH, Germany*; M. Krug,* Fraunhofer IKTS, Germany*; J. Sundqvist,* BALD Engineering AB, Sweden

ALD-based spacer-defined multiple patterning schemes have been the key processes to continued chip scaling, and they require PEALD or catalytic ALD for low temperature and conformal deposition of spacers (typically SiO_2) on photoresist features for the subsequent etch-based pitch splitting. Other SiO_2 applications in the logic and the memory segments include gap fill, hard masks, mold oxides, low-k oxides, hermetic encapsulation, gate dielectric, inter-poly dielectric ONO stack, sacrificial oxide, optical films, and many more. ALD is limited by low throughput that can be improved by raising the growth per cycle (GPC), using new ALD precursors, performing batch ALD or fast Spatial ALD, shrinking the ALD cycle length, or omitting purge steps to attain the shortest possible ALD cycle. Today's latest and highly productive platforms facilitate very fast wafer transport in and out of the ALD chambers. Current 300 mm ALD chambers for high volume manufacturing are mainly top-down or cross-flow single wafer chambers, vertical batch furnaces, or spatial ALD chambers. We have developed a Fast PEALD technology [1], realizing individual precursor pulses saturating in the sub-100 ms range. The key feature of the technology is the highly uniform, radial injection of the precursors into the process chamber through several de Laval nozzles [2]. To in-situ study (concomitantly from the top and the side of the wafer surface) individual ALD pulses in the 10-100 ms range, we use two fast scanning (≤10 ms acquisition time per spectrum ranging from 200 nm to 800 nm) Optical Emission Spectrometers with a resolution in the range of 0.7 nm. We present the results for PEALD of SiO_2 exhibiting substrate surface saturation for 30 ms of BDEAS pulse (Fig. 1) and 50 ms of O_2 plasma pulse (Fig. 2). All the processes were carried out in a 300 mm, dual-frequency (2 MHz and 60 MHz) CCP reactor in the temperature range of 20 °C to 120 °C and at ~1 Torr max. pulse pressure. The in-situ, time-resolved OES study of O_2 plasma pulse, indicating saturation ofO^* ($3p^5P à 3s^5S$) emission peak already at 50 ms pulse duration (Fig. 3, 4) and associated extinction of reactive O* within 161 ms (Fig. 5), suggest room for yet faster process. The mean GPC diminishes with the electrostatic chuck temp (Fig. 6). We will present a more optimized PEALD SiO_2 process and stacking of Fast PEALD SiO_2 on top of Fast PEALD Al_2O_3 in the same chamber without breaking the vacuum. The results will comprise XPS, TEM, film growth uniformity across 300 mm wafer, and residual stress investigation for the film stack.

Ref.

[1] AVSALD2020, Abstract# 2415, Oral Presentation AM-TuA14

[2] Patent US20200185198A1

ALD for Manufacturing
Room On Demand - Session AM4
ALD on Particles

AM4-1 Improvement of Mechanical Properties of Nanoparticles-Based Thin Films by Using Atomic Layer Deposition*, Fatma Trabelsi,* *M. Fivel ,* Univ. Grenoble Alpes, CNRS, Grenoble INP, SIMaP, France*; R. Salhi,* Laboratory of Advanced Materials, National School of Engineers of Sfax, University of Sfax, Tunisia*; F. Mercier, E. Blanquet ,* Univ. Grenoble Alpes, CNRS, Grenoble INP, SIMaP, France

Nanoparticle-based thin films are gaining interest in recent decades for catalysis, electronic or optical applications. However, their poor mechanical reliability and durability limit their industrial and commercial applications.

In this work, we report on a low temperature hybrid synthesis approach to insure the durability and encapsulation of photonic conversion films for its further integration in silicon solar cells. The proposed hybrid approach consists first on the synthesis of rare earths (Erbium and Ytterbium) codoped TiO_2 nanoparticles (size ~ 11 nm) fabricated by hydrothermal-assisted sol-gel method. Then, the nanoparticles are dispersed at the surface of silicon substrates using a spin-coating process (film thickness 750-900 nm). Finally, Er^{3+}-Yb^{3+}codoped TiO_2 upconversion nanoparticles in the powder phase are coated with an amorphous Al_2O_3 layer using atomic layer deposition technique (ALD) as a unique approach to reinforce mechanical properties of various photoluminescent nanoparticle porous thin films at a relatively low temperature without drastically changing their original structure.

The impact of different ALD-Al_2O_3 thicknesses and forming gas annealing step on the structural, compositional and mechanical properties ofEr^{3+}-Yb^{3+} codoped TiO_2 nanoparticles assembled on n-type Si (100) substrate are investigated. For that purpose, various analysis approaches involving automated crystal phase and orientation mapping in TEM (ACOM-TEM), scanning transmission electron microscopy–energy-dispersive spectroscopy (STEM-EDS), scratch test and nanoindentation are performed to understand the links between the structural properties and the mechanical properties.

The results indicate a clear increase in the adhesion of nanoparticle thin films to the Si substrate with increasing ALD-Al_2O_3 thickness followed by forming gas annealing treatment. This behavior is a consequence of the infiltration of Al_2O_3 layer within the porous matrix, as a result, effective interparticle bonding and filling of the pores are accomplished.

AM4-2 Three-Dimensional Conformal Coating of Particles *Resting* on a Surface by Vapor-Phase Infiltration*, Chang-Yong Nam,* Brookhaven National Laboratory

Three-dimensional (3D) encapsulation of micro- and nanoparticles by atomic layer deposition (ALD) can have broad applications but remains a technical challenge. Current ALD techniques for coating particles employ physical agitation to expose all surfaces of particles to precursors during the deposition process, requiring specialized chambers, such as fluidized bed reactors and rotary chambers and, therefore, only applicable to bulk powders in large volume and quantities. Achieving 3D encapsulation by directly applying conventional ALD on particles resting on a substrate without agitation would allow much smaller volumes and smaller sizes of particles to be used, but the conventional ALD on a particle stationary on a flat substrate yields a coating only on exposed surfaces, not on the bottom side directly in contact with the substrate. Here, we report a novel 3D conformal coating technique for individual particles on all sides while they are resting on an inert polystyrene (PS) film to enable the growth of inorganic films not only on the particle's exposed surfaces, but also on the bottom side that is in contact with the polystyrene [Liapis et al., *Adv. Mater. Interfaces***7**, 2001323 (2020)]. This technique repurposes vapor-phase infiltration (VPI), an organic-inorganic hybridization technique derived from ALD in which vapor-phase inorganic precursors perfuse into a polymer matrix and react with functional groups within it to form organic–inorganic hybrids. We exploit the inert nature of PS to use it as a substrate 'transparent' to vapor-phase ALD precursors. We demonstrate that the conformal coatings of alumina realized by this technique improve the stability in aqueous environments for two optically relevant particles: compound semiconductor laser microdiscs and lead halide perovskite nanocrystals, which have important optical tagging applications for *in vivo* and *in vitro* biomedical imaging.

AM4-5 Atomic Layer Deposition (ALD) of Ultra-Thin Diffusion Barriers on ZnSe Microparticles for Phase Stability in Chalcogenide Glasses for Mid-Infrared Optics*, Jaynlynn Sosa,* Nanoscience Technology Center, University of Central Florida*; M. Chazot ,* CREOL, College of Optics and Photonics, University of Central Florida*; C. Feit ,* Department of Materials Science & Engineering, University of Central Florida*; A. Kostogiannes,* Department of Chemistry, University of Central Florida, Orlando, FL 32816, USA*; M. Kang, C. Blanco , K. Richardson,* CREOL, College of Optics and Photonics, University of Central Florida*; P. Banerjee,* Department of Materials Science & Engineering, University of Central Florida

ZnSe embedded chalcogenide glass (ChG) composites are optically active in the mid-infrared (IR) and are ideal for niche applications in medical diagnosis, military missile heat-sensing, and chemical identification. The embedded ZnSe crystals play a critical role in providing lasing activity while the ChG - $As_2S_{3-x}S_{ex}$ matrix, acts as a host that can be drawn into fiber and provides the necessary mid-IR transparency. However, during synthesis, the ZnSe particles are prone to dissolution in the $As_2S_{3-x}S_{ex}$ matrix due to a high temperature (650 C) melting and homogenization process. Here we demonstrate that a thin amorphous barrier layer of Al_2O_3 deposited using atomic layer deposition (ALD) on ZnSe microparticles 5-10 µm in average diameter is successful to prevent ZnSe dissolution in the $As_2S_{3-x}S_{ex}$ matrix even after extended melting and homogenization at 650 C for 8 hours. This talk will highlight some of the key process innovations required to overcome challenges of ALD on powdered components for functionalizing and enhancing performance of multiphasic glasses for optical applications.

Amorphous aluminum oxide (Al_2O_3) was deposited using alternate pulses of trimethyl aluminum and H_2O on 1 gm batch size ZnSe using a customized rotary barrel reactor inside a viscous-flow ALD furnace attached to a quadrupole mass spectrometer (QMS). The temperature of deposition was kept at 180 C and the number of cycles were varied from 100 to 300 cycles. The ZnSe particles were sieved to an average size of 5-10 µm and a maximum size ≤ 20 µm. The coated particles were characterized by x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The crystallinity of the ZnSe-$As_2S_{3-x}S_{ex}$ glasses were evaluated using x-ray diffraction (XRD) and their composition stability spatially mapped across individual ZnSe particles embedded in $As_2S_{3-x}S_{ex}$ matrix using Raman microspectroscopy.

Whereas 100 ALD cycles provide partial protection to dissolution for the ZnSe in $As_2S_{3-x}S_{ex}$, a 300 cycle ALD Al_2O_3 on ZnSe particles is sufficient to provide phase and composition stability to the ZnSe embedded $As_2S_{3-x}S_{ex}$ glass. Through our investigation, we exemplify the efficacy and potential of ALD of ZnSe powder in improving the stability of optical materials while still achieving optimal mid-IR lasing and transparency.

ALD for Manufacturing
Room On Demand - Session AM5
ALD for Manufacturing Poster Session

AM5-1 Development of MeCpPtMe3 Platinum Process by Rotary Type Reactor Atomic Layer Deposition on Powders*, Min Jong Kil, S. Yoon,* Korea Electronics Technology Institute, Korea (Republic of)*; S. Jung,* Gachon University, Korea (Republic of)*; H. Kim,* Korea Electronics Technology Institute, Korea (Republic of)*; T. Kim,* Gachon University, Korea (Republic of)*; H. Kim,* Korea Electronics Technology Institute, Korea (Republic of)

Atomic layer deposition has been widely studied to deposit materials with optimized usage and conformal coating on various applications such as semiconductor, energy storage/conversion devices, and catalyst. However, conventional atomic layer deposition is not suitable for powders or (nano)particles to coat materials with static processes. Therefore, atomic layer deposition for powders is developed in two types: fluidized bed reactor and rotary type reactor. At first, vertical fluidized bed reactor type atomic layer deposition was developed to conformally coat on (nano)particles. However, to develop the excessive usage of precursors in fluidization method, horizontal rotary type atomic layer deposition is developed to optimize the usage of precursor, especially noble metal precursors. To coat materials by powder atomic layer deposition, optimization of precursors and agglomeration/breakage of powders are required to achieve atomic layer deposition mode. In this study, process optimization and powder agglomeration/breakage are solved using rotary reactor type atomic layer deposition with MeCpPtMe3 platinum precursor and oxygen. For process optimization, each step pulse time is controlled with stop valve mode on silicon wafer. Using this optimized process, powder agglomeration/breakage is achieved by controlling ball type, size, and rotation speed. Platinum process optimization is achieved by X-ray reflectometry for thickness and density. Conformal coating on powders is confirmed by transmission electron microscopy and energy dispersive X-ray spectroscopy. This optimized process is applied to the biomass-derived graphene-based carbon to confirm the performance difference between conventional atomic layer deposition and powder atomic layer deposition. These results are expected to be valuable for atomic layer deposition on nanoparticles.

AM5-2 Nanoscale Film Thickness Gradients Printed in Open Air by Spatially Varying Chemical Vapor Deposition*, Jhi Yong Loke,* University of Waterloo, Canada

Nanoscale films are integral to all modern electronics. To optimize device performance, researchers vary the film thickness by making batches of devices, which is time-consuming and produces experimental artifacts. We present thin films with nanoscale thickness gradients that are rapidly deposited in open air for combinatorial and high-throughput (CHT) studies. Atmospheric pressure spatial atomic layer deposition reactor heads are used to produce spatially varying chemical vapor deposition rates on the order of angstroms per second. We printed ZnO and Al2O3 films with nm-scale thickness gradients in as little as 45 seconds and performed CHT analysis of a MIM diode and perovskite solar cell. By testing 360 Pt/Al2O3/Al diodes with 18 different Al2O3 thicknesses on a single substrate, we identified a thicker insulator layer (6.5 to 7.0 nm) for optimal diode performance than has been reported previously. An Al2O3 thin film encapsulation layer was deposited by atmospheric pressure chemical vapor deposition (AP-CVD) on a perovskite solar cell stack for the first time and a convolutional neural network was developed to analyze the perovskite stability. The rapid nature of AP-CVD enables thicker films to be deposited at a higher temperature than is practical with conventional atomic layer deposition. The CHT analysis showed enhanced stability for 70 nm encapsulation films.

AM5-5 Measurements and Prediction Model for the Evaporation of Bis(diethylamino)silane*, Seung-Ho Seo, E. Shin, Y. Lee, D. Kim, H. Shin,* GO Element, Korea (Republic of)*; C. Kim, W. Lee,* Sejong University, Korea (Republic of)

In ALD and CVD processes, the evaporation rate of the precursor affects the growth rate of the thin film. Therefore, a sufficient amount of the precursor must be continuously supplied to the reactor, and it is important to measure and predict the amount of precursor supply in an actual ALD system. The amount of precursor supply varies depending on the structure and temperature distribution of the precursor delivery system including the canister, the type of precursor, and the flow rate of the carrier gas. Recently, a nondispersive infrared (NDIR) gas analyzer was installed in the canister outlet pipe to measure the partial pressure of a Ta precursor, and the evaporation amount of the precursor was calculated [1]. However, in order to accurately predict precursor evaporation, it is necessary to measure the precursor partial pressure and temperature inside the canister.

In the present study, we measured the evaporation amount of a liquid silicon precursor, bis(diethylamino)silane (BDEAS), under various conditions and presents a model to predict the evaporation amount of the precursor. In order to accurately understand the evaporation characteristics, we measured the pressure and the temperature inside the canister were measured, not in the delivery line. We also measured the evaporation amount of BDEAS in real-time using an ultrasonic level sensor installed at the bottom of the canister. To predict the evaporation amount of the liquid precursor, the evaporation coefficient was calculated using the Hertz-Knudsen-Langmuir equation. The predicted evaporation amount of the precursor agreed well with the measurement result. The construction of the precursor evaporation prediction model is expected to be used to optimize the precursor delivery system design and the ALD process condition.

[1] B. A. Sperling et al., J. Vac. Sci. Technol. A 37, 060907 (2019).

AM5-6 Interface Modification of Bismuth by Atomic Layer Deposition: Enhanced Thermoelectrical Performance*, Shiyang He, A. Bahrami, K. Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany

Interfaces of phase boundaries play a critical role in the carrier/phonon transport in thermoelectric materials. It remains a big challenge to control over both chemical composition and dimension of interfaces precisely by traditional approaches. Herein, a strategy of interfaces modification based on powder atomic layer deposition (PALD) is introduced to accurately control and modify the phase boundaries of pure Bismuth (Bi). To

demonstrate the effect of this strategy, ultrathin layer of Al_2O_3 is uniformly deposited on Bi particles. It is observed that 5 cycles deposition of Al_2O_3 significantly scattered the phonons and 10% reduction on thermal conductivity in Bi-Al_2O_3 system can be achieved. Owing to the carrier scattering in the Bi-Al_2O_3 system, the electrical conductivity decreased from 5700 S/cm to 4500 S/cmfor 5 cycles coated Bi. However, the Seebeck coefficient increases from -69 μV/K to -78 μV/K which results in high power factor. Thanks to the precisely interface modification, a maximum *zT* of 0.13 with 5 cycles deposition of Al_2O_3 at 300 K is obtained, which is 11.2% higher compared with that of pure Bi. As a powerful interfacial modification strategy, PALD-based approach can be extended to other thermoelectric material system simply, which may contribute to the development of high-performance thermoelectric materials.

AM5-9 Low Resistivity Titanium Nitride Thin Film Fabricated by Atomic Layer Deposition on Silicon*, **Cheng-Hsuan Kuo**,* UC San Diego, Taiwan*; V. Wang, z. zhang, H. Kashyap, A. Kummel,* UC San Diego

Titanium nitride (TiN) thin films areutilized as the diffusion barriers for Co and W metal layers as well as the gate metal barrier in CMOS and memory devices due to their low resistivity and good electrical conductivity. TiN is also used as a coating for hard disk drives[1].Low resistivity TiN has been deposited in commercial devices by plasma enhanced ALD (PEALD) and by physical vapor deposition. However, for high aspect ratio features, deposition by thermal ALD is needed because of the high conformality of the thermal ALD process and for back-end compatible deposition below 350 °C.Previously Wolf *et al.* demonstrated that at 400 °C, ALD of TiN with $TiCl_4$ and N_2H_4 resulted in a film with a resistivity of 500 mohm-cm[2].In this work, it is shown that the resistivity can be decreased below 200 mohm-cm when deposited at 300 °C - 350 °C by reducing the oxygen in the films.

Titanium tetrachloride ($TiCl_4$) and anhydrous hydrazine (Rasirc, Brute Hydrazine^{O}) were employed as the precursors with ultra-high purity nitrogen purge gas. To produce low resistivity films, a turbo molecular drag pump (Edwards EPX) was employed to maintain a high compression ratio during ALD pulsing. The TiN ALD chamber was connected to an *in-vacuo* Auger electron spectrometer (RBD Instruments), which was used to determine the atomic composition of ALD TiN after 50 cycles of deposition. Pulse lengths and purge times were optimized at sample temperatures of 300 °C and 350 °C on HF-cleaned Si (100) or degreased SiO_2; the optimized pulse times were 300 ms for $TiCl_4$ and 2400 ms for N_2H_4. Surface morphology was measured by *ex-situ* atomic force microscopy (AFM). To determine resistivity, four-point probe (Ossila) measurements were performed on TiN thin films on degreased SiO_2 substrates. Scanning electron microscopy (SEM), ellipsometry, and X-ray reflectivity (XRR) were used to measure TiN film thicknesses.

AM5-12 Morphology-Controlled MoS_2 by Low-Temperature Atomic Layer Deposition*, **Chengxu Shen**, M. Raza, P. Amsalem, T. Schultz, N. Koch, N. Pinna,* Humboldt-Universität zu Berlin, Germany

Two-dimensional (2D) transition metal dichalcogenides (TMDs) such as MoS_2 are materials for multifarious applications such as sensing, catalysis, and energy storage.[1] Due to their peculiar charge-transport properties, it is always desired to control their morphologies from vertical nanostructures to horizontal basal-plane oriented smooth layers.[2] Due to the high conformality, atomic layer deposition (ALD) exhibits promising potential in the precise control of the thickness and morphologies of the deposited layers, especially for the preparation of complex nanostructure.[3]

In this work, we established a low-temperature ALD process for MoS_2 deposition using bis(t-butylimino)bis(dimethylamino)molybdenum(VI) and H_2S precursors. Polycrystalline MoS_2 is conformally deposited on carbon nanotubes, Si-wafers, and glass substrates. Moreover, the morphologies of the deposited MoS_2 films are tuned from smooth film to vertically grown flakes, and to nano-dots, by controlling the reaction parameters/conditions and post sulfurization process. Noticeably, the deposited MoS_2 nanostructures show morphology-dependent optical and electrocatalytic properties, allowing us to choose the required morphology for a targeted application.

[1]T. Jurca, M. J. Moody, A. Henning, J. D. Emery, B. Wang, J. M. Tan, T. L. Lohr, L. J. Lauhon, T. J. Marks, *Angew. Chem. Int. Ed. Engl.***2017**, 56, 4991.

[2]C. Shen, M. H. Raza, P. Amsalem, T. Schultz, N. Koch, N. Pinna, *Nanoscale***2020**, 12, 20404.

[3]C. Marichy, M. Bechelany, N. Pinna, *Adv. Mater.***2012**, 24, 1017.

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