Tuesday Morning, October 31, 2017

Thin Films Division
Room: 20 - Session TF-TuM

Advanced CVD and ALD Processing, ALD Manufacturing and Spatial-ALD
Moderators: Halil Akyildiz, Uludag University, Turkey, Paul Poodt, Holst Centre / TNO, Netherlands

8:00am **TF-TuM1 Aluminum-Doped Zinc Oxide via Spatial ALD: Process Impact on Film Morphology, Electrical Conductivity and Stability**, *S.F. Nelson*, ***Lee Tutt***, *C.R. Ellinger*, Eastman Kodak Company

Aluminum-doped zinc oxide (AZO) is an attractive transparent conductive material because of to its nontoxic, earth-abundant material composition. A wide range of electrical properties have been reported for AZO deposited using a variety of techniques and a range of process conditions. This talk will focus on the AZO grown using spatial atomic layer deposition (SALD), and the impact of process conditions on the electrical, optical and crystallographic properties of the resultant AZO films. We will report primarily on those AZO films deposited using a co-flow of dimethyl aluminum isopropoxide (DMAI) and diethyl zinc (DEZ) as the metal precursors, and water as the oxygen source.

We will share our current understanding of the mechanisms responsible for the interplay between process parameters and material properties, including the correlation of film properties such as doping-level and crystallographic structure to the end-use properties of conductivity and optical transparency. For reference, we have deposited AZO having a bulk resistivity of 2.7×10^{-4} Ω-cm and an average visible transmission of 85%, obtained from 204 nm thick AZO films deposited at 300°C. This compares well to commercially available ITO coatings having, for example, about 1.2×10^{-4} Ω-cm and 82% average visible transmission for film thicknesses between 150 nm and 200 nm.

In addition, the impact of passivating the AZO surface with very thin aluminum oxide (Al_2O_3) will also be reported. We have found that passivation with Al_2O_3 enhances conductivity through an increase in both mobility and carrier concentration. Improved thermal stability during elevated annealing conditions in air was also observed for alumina-passivated AZO samples

8:20am **TF-TuM2 Fast Pulsing of Precursor and Reactant to Merge ALD and CVD Processes: Example of Thick Al_2O_3 Deposition**, ***Fabien Piallat***, *L. Bonnet*, *J. Vitiello*, KOBUS, France

A specific pulsed-CVD reactor was developed for the chemically enhanced deposition of materials. In this specific reactor, both reactant and precursor can be pulsed or sent continuously to the deposition chamber. Thus, many materials can be deposited by one of the three following methods, Atomic Layer Deposition (ALD), Chemical Vapor Deposition (CVD) or pulsed-CVD.

In this presentation, an investigation of Al_2O_3 deposition will be presented, with detailed process comparison for each of the three techniques in order to highlight the variability brought by the process on the material properties. Al_2O_3 deposition was done with TriMethylAluminium (TMA) precursor and O_2 in-situ plasma.

Influence of the pulse length on the deposition rate shows a gap between the surface saturation growth mode of the ALD and the continuous growth of the CVD. Starting with pulse length in the order of seconds, in the case of the ALD mode, a reduction of the pulse length leads first to a reduction of the growth rate, because the precursor does not have enough time to adsorb at the sample surface to form a monolayer. Then, in a second time, for pulse time in the order of hundreds milliseconds, there is an increase of the growth rate, due to the change in the growth mode, from the surface saturation to the continuous growth. Further reduction of the pulse length, in the order of tens milliseconds, the growth can be assimilated to a CVD growth, with properties similar to the one of material obtained in continuous growth.

Additionally, extraction of the activation energy of the deposition reaction, using the Arrhenius law from deposition at temperature ranging from 100°C up to 450°C, will give some insight on the importance of the process on the favoring of the deposition reaction.

Finally, to address the photonic and MEMS applications, thick layers of Al_2O_3 will be deposited by the three methods and will be characterized by ellipsometry, Fourrier Transformed Infra-Red (FTIR), Raman measurement and X-ray Diffration (XRD). Pro and cons of each technique will be discussed based on these characterizations.

8:40am **TF-TuM3 Employing Atmospheric Pressure Micro-Plasma Printer for ALD of TiO_2 Thin Films**, ***Morteza Aghaee***, *J. Verheijen*, Eindhoven University of Technology, The Netherlands, *A. Stevens*, InnoPhysics B.V., The Netherlands, *W.M.M. Kessels*, *M. Creatore*, Eindhoven University of Technology, The Netherlands

A broad range of devices such as thin film transistors (TFTs), solar cells, sensors and microfluidic channels benefit from micron-scale patterns in their structure. These micron-scale patterns are often fabricated by means of costly methods such as (photo-)lithography. For this reason, there is a large interest in alternative simple and cost-effective approaches for micron-scale to sub-millimeter patterning that reduce the number of etch and lithography process steps.

A micro-plasma printer [1], which is based on a unique needle-to-plate micro-plasma dielectric barrier discharge (DBD), has recently been developed for spatially-resolved surface functionalization [2] and deposition of organic films [3] with sub-millimeter range resolution. In this contribution, the potential of the micro-plasma printer in delivering patterned, ultra-thin inorganic films at atmospheric pressure is addressed. Specifically, the setup is adopted to carry out thin film TiO_2 deposition in two configurations, namely plasma enhanced chemical vapor deposition (PE-CVD) and plasma-assisted atomic layer deposition (PA-ALD).

The properties of the TiO_2 layers as well as the patterning resolution have been investigated. The TiO_2 films deposited by PE-CVD mode have not shown satisfactory results in terms of purity and density of the layers (more than 5% C and refractive index of 1.8). However, the PA-ALD mode has been able to deliver patterns of amorphous TiO_2 films with low level of impurity and sub-nanometer thickness control. A growth rate of 0.15 nm/cycle has been obtained for 500 ms and 400 µs of TTIP and N_2/O_2 plasma exposures in each PA-ALD cycle, respectively. Rutherford backscattering spectroscopy (RBS) has revealed a growth rate of 2.4 Ti atoms per nm^2.cycle in saturation condition. Improvement of density and reduction of film impurities (H, C and N content) have been observed by prolonging the plasma exposure time. TiO_2 films with refractive index of 2 and less than 1% C have been deposited by 2 ms of plasma exposure. The width of the smallest features deposited by PE-CVD and PA-ALD modes have been determined by XPS line scan measurements to be 1.8 mm and 900 µm, respectively, for 7 nm thick layers.

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[1] T. Huiskamp, W. J. M. Brok, A. A. E. Stevens, E. J. M. van Heesch, and A. J. M. Pemen, IEEE TRANSACTIONS ON PLASMA SCIENCE, 40 (2012) 1913-1925.

[2] A. Mameli, Y. Kuang, M. Aghaee, C. K. Ande, B. Karasulu, M. Creatore, A. J. M. Mackus, W. E. M. M. Kessels, and F. Roozeboom , Chemistry of Materials, 29 (2017) 921-925.

[3] J.R.G Schalken, M. Creatore, P. Verhoven, A. Stevens, Nanoscience Nanotechnol. Letter, 7 (2015) 62-66.

9:00am **TF-TuM4 Large-Area Atmospheric Pressure Spatial ALD**, *C. Frijters*, *F. van den Bruele*, *F. Grob*, ***Paul Poodt***, Holst Centre / TNO, Netherlands

Atmospheric spatial ALD (sALD) is able to deliver high deposition rates while maintaining the advantages of conventional ALD, such as low defect density, high conformality and thickness uniformity. First industrial applications of Spatial ALD include passivation of c-Si solar cells and roll-to-roll manufacturing of flexible barrier foils. An emerging application for Spatial ALD are flat panel (OLED) displays. We have developed spatial ALD processes for making high mobility oxide semiconductors for the TFT backplane as well as thin-film encapsulation for the OLED front plane. As today's displays are fabricated using glass panels in the order of several square meters, a remaining challenge is the development of large-area sALD deposition technology that is able to combine high throughput with uniform performance across large areas.

As an intermediate step between the lab and the display fab, we have installed a large area Spatial ALD sheet-to-sheet tool which can handle up to 400x325 mm^2 sized substrates, able to deposit uniform films across a deposition width of 300 mm. The whole tool is operated under an atmospheric but inert N_2 atmosphere. We will present the basic deposition performance of the tool, where large-area thickness non-uniformities of less than 1% have been achieved for alumina on glass. Furthermore, we will demonstrate excellent compositional uniformity for binary oxides.

One of intended applications is thin-film encapsulation of OLED devices. In order to test the encapsulation performance of the films deposited by the large area spatial ALD tool, we deposited single layer and double layer alumina films, in combination with printed organic planarization layers, on PET foils laminated on 325 mm x 325 mm glass panels. The encapsulation performance was tested under damp-heat conditions. The deposited encapsulation stacks show excellent results, with virtually no visible defect appearing after more than 1000 hrs. at 60 ºC 90 %RH, corresponding to a potential device lifetime of at least 2.5 years. These results demonstrates the potential of spatial ALD for manufacturing large-area OLED devices.

9:20am **TF-TuM5 High Speed ALD of Multifunctional ALD Ultrabarriers for Flexible OLED Encapsulation**, ***Jacques Kools***, Encapsulix, France **INVITED**

In recent years, Atomic Layer Deposition (ALD) has established itself as a viable technology for deposition of ultrabarriers on large area electronic devices such as photovoltaics, OLED's and organic electronics. As a first generation material, Alumina (Al2O3) has been established as the workhorse material to deliver excellent water vapor and oxygen barrier properties. However, many devices require protection from a multitude of invasive fluxes, such as UV light, salt water, electromagnetic radiation, ... etc. A nanoengineered synthetic barrier material allows to tune the different physical properties of the barrier.

In this paper we will describe our recent work on the development of hardware and process for industrial deposition of nanoengineered barriers, with properties that have been optimized to the specific device requirements. Leveraging the unique ability of ALD to control materials on the atomic scale, multilayered barriers are constructed atomic layer by layer from a set of up to ten precursor materials. In this way, it is possible enhance the flexibility (by the use alucone layers), the UV resistance (by the use of TiO2), the resistance to liquid water.. etc.

Process development and manufacturing experience in the OLED industry will be discussed.

11:00am **TF-TuM10 Simulation of Atomic Layer Deposition**, ***Paul Moroz***, TEL Technology Center, America, LLC, *D. Moroz*, Harvard University

Semiconductor industry overcomes many challenges by advancing materials processing to new levels of precision, accuracy, manufacturability, and reliability, while the role of numerical simulations grows. Here we present new results on Monte Carlo feature-scale simulations of Atomic Layer Deposition (ALD) conducted with a feature-scale simulator, FPS3D [1-5], as well as comparison of obtained simulation results with corresponding experiments. The ALD processes are often complex, involving large molecules and, to our knowledge, have not been addressed by other feature-scale simulations except via FPS3D [4-5]. ALD has a potential for conformal and precise deposition. However it requires definite conditions for being successful, and those conditions are very important to understand. The main factor of all of ALD schemes is the cyclic change of flux parameters and the corresponding chemistry, producing a single monolayer or, most typically, a fraction of a monolayer of the deposited film after application of a cycle. We consider two very different cases of SiN film deposition. The first one uses cycles of dichlorosilane and ammonia plasma, while the second one applies cycles of disilane and hydrazine. The SiN deposition rate for the former corresponds to a half of a monolayer per cycle, while for the later, it saturates at values close to a full monolayer per cycle. Steric hindrance was found to be an important factor in explaining those phenomena.

References:

[1] P. Moroz, IEEE Trans. on Plasma Science, **39** 2804 (2011).

[2] P. Moroz, D. J. Moroz, ECS Transactions, **50** 61 (2013).

[3] P. Moroz, D. J. Moroz, J. Physics: CS **550** 012030 (2014).

[4] P. Moroz, 15th Int. Conf. on Atomic Layer Deposition, Portland, OR (2015).

[5] P. Moroz, D. J. Moroz, to be published in Japan. J. of Appl. Physics (2017).

11:20am **TF-TuM11 Boron Nitride Film Growth at Room Temperature Using Electron Enhanced Atomic Layer Deposition (EE-ALD)**, ***Jaclyn Sprenger***, *H. Sun, A.S. Cavanagh, S.M. George*, University of Colorado Boulder

Electron-enhanced atomic layer deposition (EE-ALD) can drastically reduce the temperatures required for film growth. The temperature reduction occurs because electrons can desorb surface species by electron stimulated desorption (ESD) to create very reactive "dangling bonds". Precursors can then adsorb efficiently on the dangling bonds. EE-ALD lowers the thermal budget and enables the deposition of thin films on thermally sensitive substrates. EE-ALD has been demonstrated previously for the deposition of polycrystalline GaN [1] and amorphous Si [2] at room temperature.

BN film growth by EE-ALD was performed at room temperature on Si (111) substrates using alternating doses of borazine ($B_3N_3H_6$) and low-energy electrons. Borazine is a single-source precursor for BN deposition. *In situ* ellipsometry was performed during the BN EE-ALD. These ellipsometry measurements yielded a linear growth rate of ~3 Å/cycle for electron energies of 100 eV with an electron current of 300 μA for 240 s. This *in situ* growth rate was confirmed by *ex situ* spectroscopic ellipsometry. A BN film with a thickness of 150 nm was deposited after ~500 EE-ALD cycles (see supplemental Figure 1). *Ex situ* ellipsometry measurements show flat BN thickness spatial profiles (see supplemental Figure 2) which are consistent with self-limiting reaction conditions including hydrogen desorption.

Film composition was studied with *ex situ* XPS (see supplemental Figure 3). The BN composition is consistent throughout the film with a B/N ratio of 1.3/1. The films are pure with C and O concentrations of only <3 at.% in the bulk of the film. A thin, self-passivating surface oxide resulting from atmospheric exposure is present. In addition, *ex situ* FTIR transmission was performed on the BN films. These FTIR measurements yielded an absorption peak at ~1370 cm^{-1} that is consistent with hexagonal BN.

[1] J.K. Sprenger, A.S. Cavanagh, H. Sun, K.J. Wahl, A. Roshko and S.M. George, "Electron Enhanced Growth of Crystalline Gallium Nitride Thin Films at Room Temperature and 100°C Using Sequential Surface Reactions", *Chem. Mater.* **28**, 5282 (2016).

[2] J.K. Sprenger, A.S. Cavanagh, H. Sun and S.M. George, "Electron Enhanced Atomic Layer Deposition (EE-ALD) of Silicon Films at Room Temperature", Presentation at ALD2016 in Dublin, Ireland.

11:40am **TF-TuM12 CVD of sp^2-BN on Si(111) Substrates**, ***Laurent Souqui***, *H. Pedersen, H. Högberg*, Linköping University, Sweden

Boron nitride (BN) is a wide bandgap semiconductor related to the other 13-nitrides (or III-nitrides), aluminium nitride (AlN) or gallium nitride (GaN). As BN is isoelectronic to carbon, it demonstrates graphite-like structure (sp^2-BN) in hexagonal BN(h-BN) and rhombohedral BN, (r-BN). In addition, BN exists as disordered phases such as amorphous (a-BN) or turbostratic (t-BN). Crystalline h-BN and r-BN films are promising materials for application such as UV-devices, power electronics and neutron detectors. Furthermore the similarities between graphene and sp^2-phases such as h-BN and r-BN make BN a commensurate insulating growth template for graphene.

Our previous works were focused on the CVD of epitaxial sp^2-BN films on Al2O3(0001) and 6H-SiC(0001) substrates [1] and found the optimal condition for BN growth to be around 1500°C. We now study the growth of boron nitride on silicon substrates (Si) as silicon is cheap, abundant and is a mature technology. However, due to its low melting point (1414°C), Si cannot withstand such high temperature processes. Because of the necessity of growing at lower temperature, CVD BN films grown on silicon usually show low crystallinity i.e. often a-BN, t-BN or nano-crystalline BN.

In this work, thin BN films were grown on Si(111) substrates in a horizontal hot-wall CVD reactor. Triethylborane (TEB) and ammonia (NH_3) were used as precursors and reacted at temperatures between 1200°C and 1300°C. The substrates were in-situ annealed in silane (SiH_4) and NH_3 before the deposition. Further, a small fraction of SiH_4 was also introduced during the growth as this has been shown to favour growth of crystalline sp^2-BN films [2]. Fourier-Transform Infra-Red spectroscopy (FTIR) confirms the presence of sp^2-BN. Adjustment of the SiH_4 concentration in the growth flux results in the deposition of crystalline films attributed to sp^2-BN in X-ray diffraction. In contrast, films deposited on Si at the same conditions but without SiH_4/NH_3 pre-treatment hardly nucleates and is amorphous to X-rays. This shows the importance of surface preparation in order to grow crystalline BN films on Si. In addition to growth of boron nitride, we observe the growth of SiC grains either due to a reaction between alkyl by-products from TEB and either the substrate or SiH_4 from the gas phase.

[1] M. Chubarov, H. Pedersen, H. Högberg, J. Jensen and A. Henry, Cryst. Growth Des. 2012, 12, 3215.

[2] M. Chubarov, H. Pedersen, H. Högberg and A. Henry, CrystEngComm, 2013, 15, 455.

12:00pm **TF-TuM13 Microcontroller-based Sequential Deposition Control Systems using Behavior Tree Algorithms: ALD for the "App Generation"**, ***Brandon Piercy***, *J. Crane, M.D. Losego*, Georgia Institute of Technology

A major challenge for researchers developing custom deposition equipment is the design and creation of the control software and electronics. While a simple loop-based control logic is often sufficient for sequential deposition applications like atomic layer deposition (ALD), it becomes cumbersome and difficult to reprogram when integrating more complex functionality or decision making. Furthermore, there are limited examples of publicly available control code or hardware schematics that can be easily integrated into an existing system. The "behavior tree" algorithm, developed in the robotics and artificial intelligence communities, is a highly adaptable and intuitive method to create complex behaviors. With behavior trees, we have created unique deposition recipes that would be challenging to implement using simpler control algorithms. We have written the core algorithm to run on widely available microcontrollers, making it possible to control equipment remotely using mobile “apps” or a centralized computer. In this talk, we will describe our microcontroller implementation and how it can be rapidly integrated into new or existing sequential deposition systems.

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