Tutorials
Room Auditorium - Session TS-SuA
Tutorial I

Moderators: Christophe Detavernier, Ghent University, Belgium, Erwin Kessels, Eindhoven University of Technology, the Netherlands

1:00pm **TS-SuA-1 How I Learned to Stop Worrying and Love the Surface***,* ***Seán Barry,*** Carleton University, Canada **INVITED**

Surface chemistry is a main driving force in atomic layer deposition (ALD). Although this chemistry is mostly driven by Brönsted acid-base chemistry (using H^+), there are several examples – particularly on metal surfaces – where Lewis acid-base chemistry dominates. These surface reactions naturally depend on the precursor, and often on the ligands, which are often the first interaction that the precursor will have with the surface. This is most obvious in molecular layer deposition (MLD) and in the burgeoning field of small molecule inhibition (SMI), where non-metal "small" molecules nucleate at the surface as a component of a film growth process, or to alter the surface ch3emistry of film growth.

This tutorial will look at both classic and newer precursors and show the typical surface chemistry these undergo. Pulling examples from ALD and MLD, surface chemistry at either protonated nucleation points (e.g., -OH, -NH_2) or Lewis acid or base sites (e.g., metal surfaces) will be discussed. How ligands are lost, and how ligands interact with the surface will be highlighted. This will lead into a discussion of the nucleation of MLD precursors, and the specific surface chemistries of SMIs.

Effective surface chemistry will be featured, and design aspects of effective precursors, ligands, and SMIs will be examined.

1:45pm **TS-SuA-4 Combined Atomic/Molecular Layer Deposition for Designer's Metal-Organic Materials and Inorganic-Organic Multilayers***,* ***Maarit Karppinen,*** Aalto University, Finland **INVITED**

Atomic layer deposition (ALD) of high-quality inorganic thin films has been one of the cornerstones of microelectronics already for decades, while its counterpart for organic thin films, i.e. molecular layer deposition (MLD), remained nearly un-exploited for long. In recent years, the hybrid of these two techniques, i.e. ALD/MLD, has been strongly emerging as a state-of-the-art route for novel designer's metal-organic thin films.

Currently, the ALD/MLD literature comprises ca. 300 original papers covering processes for most of the alkali and alkaline earth metals, 3d transition metals, and lanthanides as the metal component and a variety of aliphatic, aromatic and natural organic components. Excitingly, some of these processes yield in-situ crystalline coordination polymer or metal organic framework (MOF) like structures. Another attractive aspect is that many of the metal-organics realized through ALD/MLD are fundamentally new materials, difficult if not impossible to access through conventional synthesis. Moreover, since both ALD and MLD cycles are modular, they can be combined into any arbitrary precursor cycling pattern to grow elaborated superstructures, to introduce multiple and even mutually contradicting properties into a single material.

In this tutorial lecture, my intension is to: (i) introduce the breath of the ALD/MLD processes developed, (ii) address the constraints/possibilities for growing in-situ crystalline metal-organic thin films, and (iii) highlight some promising ALD/MLD materials for their application potential in Li-ion batteries, flexible thermoelectrics and magnetics, as well as light-conversion and light-switchable materials.

2:30pm **TS-SuA-7 Plasma Assisted Atomic Layer Processing and Diagnostics***,* ***Sumit Agarwal,*** Colorado School of Mines **INVITED**

Plasmas play an important role in enabling atomic layer deposition (ALD) and atomic layer etching (ALE) processes for a wide variety of materials including dielectrics, semiconductors, and metals. In ALD of oxides, nitrides, and metals, plasmas of gases such as O_2, N_2, NH_3, and H_2 are typically employed in one half-cycle while the reaction in the other half-cycle is thermally activated. In ALE, a plasma may be used in both steps including surface modification and activation. The use of a plasma enables low temperature growth and anisotropic etching, but also adds complexity to these processes as the radicals, energetic ions, electrons, and ultraviolet photons influence the surface reactions, chemical composition, and microstructure. Additionally, in plasma-assisted ALD, achieving conformal growth in high-aspect-ratio structures can be challenging due to radical recombination on the sidewalls of the structures. In plasma-assisted ALE, an added challenge is to obtain material selectivity during anisotropic etching of nanoscale features across different aspect ratios over large areas. In this tutorial, I will first describe the key features of these plasma-assisted processes, and then discuss the associated technological challenges. Next, I will describe plasma diagnostic tools that can be used to measure key plasma parameters including the radical composition, the ion energy distribution function, and electron density. Finally, I will discuss *in situ* surface optical diagnostics tools used in ALD and ALE tools to better understand the chemical and physical processes occurring on the surface.

3:15pm **TS-SuA-10 Synthesis and Integration of 2D Materials Using ALD***,* ***Ageeth Bol,*** University of Michigan, Ann Arbor **INVITED**

2D materials have been the focus of intense research in the last two decades. For example, their ultrathin body, optical band gap and unusual spin and valley polarization physics make them very promising candidates for a vast new range of (opto-)electronics and catalysis applications. So far, most experimental work on 2D materials has been performed on exfoliated flakes made by the 'Scotch tape' technique. The major next challenge is the large-area synthesis of 2D materials with control over their properties by a technique that ultimately can be used in industry. This tutorial will focus on ALD for large-area synthesis of 2D transition metal dichalcogenides for application in nano-electronics and catalysis and will highlight the precise control over the thickness, morphology, composition and phase of the 2D-TMDs that can be obtained by ALD**.**

Another challenge in the 2D materials field is how to connect these materials efficiently to the outside world. For example, properly functioning contacts and dielectrics need to be fabricated on top of the 2D material to make functioning nanodevices. ALD is the method of choice for depositing ultrathin dielectrics, because of its ability to deposit high quality, ultrathin films at low temperatures. Furthermore, ALD could offer benefits for metal deposition, such as the formation of more intimate contact, as ALD is a chemical process. The second half of this tutorial will therefore focus on ALD approaches to deposit dielectrics and contacts on 2D materials without deterioration their properties.

4:00pm **TS-SuA-13 How Did (and Will) Atomic Scale Processing Change the Logic and Memory Industries?***,* ***Giuseppe Alessio Verni****, A. Illiberi,* ASM, Belgium*; P. Deminskyi,* ASM Microchemistry Ltd., Finland*; M. Givens,* ASM, Belgium **INVITED**

As the scaling of device density continues to follow Moore's law, industry has resorted to adopt increasingly more complex architectures and 3D geometries while simultaneously driving down most of the critical dimensions to the nanoscale. This tutorial aims at briefly reviewing the evolution of device scaling in Logic and Memory and outlining how future architectures such as Complementary FET (CFET) and 3D-DRAM are going to impact material and processing requirements. We will first present an overview of atomic scale processing technologies which have been in use in industry for the past 10 years, including atomic layer deposition (ALD) and atomic layer etching (ALE). Atomic Layer Processing (ALP) will then be discussed as the main technology capable of providing disruptive new materials to market while being compatible with advanced 3D geometries with tight space requirements such as Gate-all-around (GAA). The discussion will present examples of how ALP can overcome the integrations challenges arising with these architectures, enabling, for example, multi-Vt devices on the same substrate. To conclude, we will look at the future integration schemes and discuss what emerging opportunities and challenges will exist for ALD and ALE.

4:45pm **TS-SuA-16 Artificial Interphases for Interface Control in Li-ion Batteries***,* ***Philippe Vereecken,*** IMEC, Belgium **INVITED**

Energy density, charging time (C-rate) and Life time are the key figures of merit for Li-ion batteries. In this invited talk we will focus on the application of continuous closed thin films as artificial interfaces in large capacity batteries. We will deal mostly with the perspective of device performance where the ALD and MLD processes merely provide the films and enable their ultrathin, continuous and conformal nature. Nanoscale film thickness allows for a low interface and cell resistance even when the materials themselves are poor conductors. For example. LiPON (N-doped Li_3PO_4) is a solid electrolyte interesting because it is stable against metallic lithium but, because of its poor ionic conductivity ($<10^{-6}$ S/cm) only practically useful for thicknesses under few hundred nanometers. Materials which are not solid electrolytes by their own merit (e.g., TiO_2) still have ion-transparent properties up to several tens of nanometer and can be used as ion transparent artificial interfaces in contrast to, for example, alumina which is an insulator for Li-ions. However, solid-state reactions with the active material can form $LiAl_2O_4$ at the interface which is again a solid electrolyte. These thin solid electrolytes can provide protection against electrolyte decomposition when deposited in the porous powder composite electrode layer. However, for coating of the individual active material particles, ideally materials which have both electronic and ionic conducting (or transparent) properties. These dual conductors allow both good electronic contact with the conductive additive (carbon black) and with the electrolyte (liquid or solid).

Artificial interphase coatings are often seen only as a chemical buffer layer or electronic barrier. However, most active electrode materials are semiconductors and thus heterojunctions are formed for which the electron transfer can be engineered to one's advantage. In this paper, we will show how planar thin-film stacks can be used as a model system to study, understand and engineer these interfaces, which can then be translated into a solution for the actual powder composite electrode architectures.

Finally, volume changes during charge and discharge are limiting the cycle life-time of batteries, especially for rigid solid-state batteries. Also ALD thin-films suffer from the mechanical strain and the benefits of the "closed" protective film are lost. Therefore, MLD of hybrid organic/inorganic coatings is explored to enable more elastic coatings for improved cycle life time.

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