

ALD Applications

Room Van Rysselberghe - Session AA2-TuM

ALD for Batteries and Energy Storage I & II

Moderators: Arrelaine Dameron, Forge Nano, Neil Dasgupta, University of Michigan

9:00am **AA2-TuM-3 Ultrathin TiN by Thermal ALD as Electrically Conducting Li-ion Diffusion Barrier for Integrated 3D Thin-Film Batteries**, *Jan Speulmanns, A Kia, S Bönhardt, M Czernohorsky, W Weinreich*, Fraunhofer IPMS, Germany

Upcoming autonomous microelectronic devices for the Internet-of-Things require ultralow power consumption enabling on-chip energy storage. Integrated 3D thin-film batteries (TFB) are a promising solution to meet these demands [1]. Enhancement and an in-depth understanding of Li-ion diffusion barriers are crucial factors to enable these devices. The diffusion of Li-ions into the Si substrate would damage surrounding components, detach the battery, and lead to a loss of capacity.

Titanium nitride (TiN) is an excellent Li-ion diffusion barrier and current collector [2]. Thin films manufactured by plasma-enhanced atomic layer deposition (ALD) proved superior blocking properties compared to sputtered layers, e.g., the insertion of around 0.02 Li per TiN formula unit was achieved for a 32 nm thick film [3]. Additionally, a sufficient specific resistivity of 200 $\mu\Omega$ cm as a current collector was shown. Orientation with low surface energy and reduced film contents of oxygen and chlorine were key factors for the performance. However, the employed remote plasma ALD was challenging for a conformal coating of structured substrates. Further thickness reduction of the barrier could increase the active volume fraction in 3D TFB.

In this work, we compare ultrathin 10 nm TiN films by thermal ALD and pulsed chemical vapor deposition (pCVD). The depositions are executed at 400-450 °C using titan(IV)-chloride and ammonia as reactants. The ALD film demonstrates excellent blocking capability. Only 0.03 Li per TiN formula unit are inserted exceeding 200 cycles at 3 $\mu\text{A}/\text{cm}^2$ between 0.05 and 3 V vs. Li/Li+. The low specific resistivity of 115 $\mu\Omega$ cm allows the application as a current collector. In contrast, a partial barrier breakdown is observed for the 10 nm pCVD film. We identify that the surface quality is critical for the excellent performance of the ALD TiN. The superior surface is quantified by the lowest roughness, the highest ratio of the TiN-component, and the lowest Cl-content. Conformal deposition of TiN with thermal ALD is demonstrated in a newly designed electrochemical test chip with high aspect ratios of up to 20:1. First results of the barrier performance in 3D substrates are discussed.

10 nm TiN ALD films are an ideal candidate to enable increased energy density of integrated 3D TFB to power upcoming autonomous sensors.

References

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- [2] H. C. M. Knoops, et al., J. Electrochem. Soc. 2008, 155, G287.
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9:15am **AA2-TuM-4 Atomic Layer Deposition of Nitrogen Doped Al- and Ti-Phosphate for Li-ion Battery Applications**, *Lowie Henderick*, Ghent University, Belgium; *H Hamed*, University of Hasselt, Belgium; *F Mattelaer*, *M Minjauw*, Ghent University, Belgium; *J Meersschaut*, IMEC, Belgium; *J Dendooven*, Ghent University, Belgium; *M Safari*, University of Hasselt, Belgium; *P Vereecken*, KU Leuven – University of Leuven/IMEC, Belgium; *C Detavernier*, Ghent University, Belgium

Phosphates have shown to be promising materials for Li-ion battery (LIB) applications. Their applications vary from protective coatings (Al-phosphate^[1,2]) to potential cathode materials (Ti-phosphate^[3]). Using ALD to tune the ionic and/or electronic conductivity through in-situ N-doping could make these materials even more interesting. In order to, for example, decrease the ionic and electronic blocking effect of the protective Al-phosphate coating, a new plasma enhanced atomic layer deposition (PE-ALD) process has been investigated. This new process is based on reports on PE-ALD of metal phosphates using a combination of trimethyl phosphate plasma (TMP*), oxygen plasma (O₂*) and a metal precursor (TMA or TTIP)^[3,4].

In combining a nitrogen-containing phosphorous precursor, i.e. diethyl phosphoramidate plasma (DEPA*), with nitrogen plasma (N₂*) and TMA/TTIP, a large GPC of 1.5 nm/cycle for N-doped Al-phosphate and 0.5

nm/cycle for N-doped Ti-phosphate was obtained. For both phosphates, self-limited growth is observed (figure 1, 2), and N-doping of respectively 7.9 at.% and 8.6 at.% for Al-phosphate and Ti-phosphate was found with Elastic Recoil Detection (ERD) (figure 3).

A clear effect of the nitrogen doping on the effective transversal ionic and electronic conductivities is observed (figure 4a). For both phosphates, a significant increase in the effective electronic conductivity is found. This is important, as phosphates (such as Fe-phosphate) typically suffer from poor electronic conductivity. The effective ionic conductivity shows a small increase for the Al-phosphate, but a slight decrease for Ti-phosphate. To study the possibilities of N-doped Al-phosphate in particular, a lithium nickel manganese cobalt oxide (NMC) powder was coated with (N-doped) Al-phosphate. An improved energy density at high discharge rates (w.r.t. uncoated NMC) was observed after only one deposition cycle of N-doped Al-phosphate, while the blocking effect of the undoped Al-phosphate coating (with a similar thickness as N-doped Al-phosphate) showed to hamper the battery performance at high rates (figure 4b). This shows that N-doping of phosphates with a high GPC was achieved by a new PE-ALD process, opening up opportunities for improving different types of phosphate coatings for LIB applications.

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[2] Cho, J. et al., Angewandte Chemie International Edition, 1618-1621 (2003).

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[4] Dobbelaere, T. et al., Chem. Mater. 6863-6871 (2014).

9:45am **AA2-TuM-6 Passivation of Lithium Metal Anodes with ALD Aluminum Fluoride**, *John Hennessy, J Jones, K Billings*, Jet Propulsion Laboratory

Lithium metal anodes are a key component of various next-generation battery technologies. However, the reactivity of the lithium surface can lead to battery cycling issues that are often associated with the formation of a solid electrolyte interphase (SEI) layer on the lithium surface. Here, we report on the use of ALD AlF₃ coatings deposited directly onto commercial lithium metal foils in order to engineer the stability of this SEI layer. ALD films are deposited at various substrate temperatures (< 175 °C) by cyclic exposure to tris(dimethylamino)aluminum and anhydrous HF. Symmetric Li/Li cells were fabricated with various electrolyte solutions in order to gauge the chemical stability of the passivated lithium surface. For example, electrochemical impedance spectroscopy reveals a significant reduction in the impedance growth of ALD-coated symmetric cells fabricated with a liquid electrolyte solution of LiPF₆ in acetonitrile. The AlF₃-coated Li was also used to fabricate Li/S cells and more than doubled the specific capacity of test cells versus samples with unprotected Li. The increase in Li/S cell impedance during prolonged cycling was also reduced for the passivated samples, although not completely eliminated. Coated foils were also characterized with a combination of scanning electron microscopy, energy dispersive xray spectroscopy, and spectroscopic ellipsometry. Finally, progress in the development of lithium-ion conducting thin films of lithium aluminum fluoride is also presented as a building block toward solid-state battery systems.

10:15am **AA2-TuM-8 Next-Generation Li-ion Batteries Enabled by Large-Area Atmospheric-Pressure Spatial Atomic Layer Deposition**, *Mahmoud Ameen, I Beeker, L Haverkate, B Anothumakkool, F Grob, D Hermes, N Huijssen, S Khandan Del, F Roozeboom, S Unnikrishnan*, TNO/Holst Center, Netherlands

Li-ion batteries have emerged as a key energy storage enabler, not only in portable electronic devices but also in electric vehicles and grid-storage. A combination of high energy density anodes such as Si or Li, and Ni- or Li-rich cathodes^{1,2} is necessary to achieve the targeted energy density (>350 Wh/kg). However, many of such high-potential redox-chemistries lead to serious safety issues and degradation during cycling due to either oxidative or reductive instabilities³, especially occurring at the electrode-electrolyte interface⁴. Therefore, optimizing the interfaces with chemically and mechanically-stable Li-ion conductive passivation layers is crucial for any Li-ion battery chemistry in order to mitigate the non-compatibility of the individual cell components. The interfacial stabilization layers can be formed either in-situ using electrolyte additives or ex-situ via chemical and physical methods. One option here is offered by atomic layer deposition (ALD) which is the preferred technique to achieve superior quality and 3D-conformal coatings with atomic-scale thickness precision. However, conventional vacuum-based ALD is not compatible with the mainstay high-

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throughput roll-to-roll battery electrode production. Here, the large-area atmospheric-pressure spatial-ALD (s-ALD) technology as established by TNO-Holst Centre several years ago can offer prime solutions for various applications including thin-film batteries⁵. A wide range of materials like metal oxides, nitrides, sulfides, and hybrid organic-inorganic materials are possible using s-ALD. In this work, we will demonstrate several s-ALD films such as Al₂O₃, TiO₂, and ZnO which are specifically tailored for dendritic Li-growth suppression, interface stabilization, and cathode degradation protection. Furthermore, we will discuss the latest results on our upscalable s-ALD grown thin film LIPON electrolyte having a Li-ion conductivity >10⁻⁷ S/cm, low electronic conductivity (<10⁻¹² S/cm) and high stability against Li-metal anode during cycling. Such electrolyte is also relevant for the development of protection layers in liquid and polymer electrolyte-based Li-ion batteries, as well as for enabling thin-film planar and 3D solid-state batteries with ultra-thin electrolyte layers.

References:

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10:30am **AA2-TuM-9 ALD Al₂O₃ and MoS₂ Coated TiO₂ Nanotube Layers as Anodes for Lithium Ion Batteries**, *H Sopha*, University of Pardubice, Czech Republic; *A Tesfaye*, Ecole de Mine, France; *R Zazpe*, University of Pardubice, Czech Republic; *T Djenizian*, Ecole de Mine, France; **Jan Macak**, University of Pardubice, Czech Republic

The miniaturization of Lithium ion batteries (LIBs) as a power source to drive small devices such as smartcards, medical implants, sensors, radio-frequency identification tags etc. has been continuously developed to meet the market requirements of portable applications.¹ In this direction, 3D microbatteries have been considered to satisfy the requirements of these portable devices. Anodic TiO₂ nanotube layers (TNTs) have been recently explored as anodes for LIBs due to their high surface area, low volume expansion, short diffusion lengths for Li⁺ ion transport and good capacity retention even at faster kinetics.^{2,3}

Recently, various coatings produced by Atomic Layer Deposition (ALD) on electrode materials have been explored extensively in LIBs. For example, Al₂O₃ and TiO₂ coatings act as a protective layer for the suppression of the solid electrolyte interphase (SEI) in various electrode materials.^{4,5} But their influence on increasing the electronic conductivity of the electrode material has not been explored in details. In addition, it is also possible to synthesize using ALD the main electrode materials, such as oxides⁶ and sulphides.⁷ However, high surface area and sufficiently conducting support would be beneficial for these ALD derived materials to support an excellent performance of the batteries. The door for various one-dimensional nanomaterials, such as TNTs, is therefore open

In this presentation, we will show ALD synthesis of Al₂O₃⁸ and MoS₂⁹ and their combination¹⁰ on TNTs as new electrode material for lithium-ion batteries. We show an influence of different coating thicknesses on the battery performance, in particular on the charging and discharging capacity.

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10:45am **AA2-TuM-10 Molecular Layer Deposition for Stabilization of Electrochemical Materials**, **Chunmei Ban**, University of Colorado - Boulder
INVITED

The inherent non-passivating behavior of electrode materials in the organic lithium-ion battery electrolyte results in large irreversible capacity loss and

gradual electrolyte consumption during operation. Such interaction between electrolyte and electrode becomes more pronounced for intermetallic alloy and lithium-metal anode materials and high-voltage cathode materials. When using decreased nano-size electrode materials, the chemical interaction and the formation of solid electrolyte interphase (SEI) lead to even more irreversible loss of lithium inventory. Surface modifications on both active particles and laminated electrodes—with the capability to modify the surface and interface through the control of composition, thickness and mechanical properties—would chemically or physically change the surface of electrode materials. The atomic layer deposition (ALD) technique has proven itself to be the best method to deposit continuous, conformal and pinhole-free films. Our recent work has proven ALD as an important tool in mitigating the parasitic side reactions between the electrolyte and the electrode surface, which results in the greatly improved performance of lithium-ion electrodes. Furthermore, to address the challenge of dramatic volumetric change associated with high-capacity intermetallic anodes, we have used molecular layer deposition (MLD) to modify the surface with a mechanically robust, flexible coating. Combining with the results from advanced characterization techniques, this talk will emphasize the unique chemical interaction between the electrolyte and the surface of intermetallic electrodes. Furthermore, the surface modification strategies will be introduced here and exploited, in order to dictate the interface chemistry and manipulating the chemical-physical properties of the electrode-electrolyte interphase for efficient electrochemical reactions.

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