ALD Applications
Room Evergreen Ballroom & Foyer - Session AA4-TuP

Protective Coatings, Barrier Films, Membranes and Flexible Substrates Poster Session

AA4-TuP-1 ALD for Membrane Applications*, **Matthieu Weber,** M Bechelany,* Institut Européen des Membranes, France

Atomic layer deposition (ALD) is a technology allowing for the preparation of conformal ultrathin films with a sub-nanometer thickness control, a unique capability. Therefore, this route is particularly suited for the structural modification and pore tailoring of porous structures. ALD can be advantageously applied to the area of membranes by fine-tuning their surface properties, and by controlling the diameter and the aspect ratio of the pores with (sub)nanometer precision. The precise control over the chemical and physical nature of the pore surface provided by ALD makes this route extremely valuable for membrane science. Thus, ALD coatings have been prepared on a wide variety of membrane substrates, from inorganic templated substrates to porous polymers.

This presentation aims to provide a summary of the advances of ALD applied to membranes. Based on a wide literature data survey including some of our recent data,[1–3] the application of ALD for different types of membranes will be described and illustrated using relevant examples, and the main challenges and opportunities of the ALD route will also be assessed.

(1) Weber, M.; Koonkaew, B.; Balme, S.; Utke, I.; Picaud, F.; Iatsunskyi, I.; Coy, E.; Miele, P.; Bechelany, M. Boron Nitride Nanoporous Membranes with High Surface Charge by Atomic Layer Deposition. *ACS Appl. Mater. Interfaces***2017**, *9* (19), 16669–16678.

(2) Weber, M.; Iatsunskyi, I.; Coy, E.; Miele, P.; Cornu, D.; Bechelany, M. Novel and Facile Route for the Synthesis of Tunable Boron Nitride Nanotubes Combining Atomic Layer Deposition and Annealing Processes for Water Purification. *Adv. Mater. Interfaces***2018**, *5* (16), 18–56.

(3) Weber, M.; ALD for membranes: Basics, Challenges and Opportunities. *Chem. Mater.***2018**, 30, 21, 7368-7390.

AA4-TuP-2 Nano-Hardness of ALD Films*, **James Daubert,** W Sweet, J Kelliher,* Northrop Grumman

In this presentation, we will explore different films (Al_2O_3, ZrO_2, Ta_2O_5) deposited using atomic layer deposition (ALD) to compare how the processing conditions (i.e. deposition temperature, material interfaces, and annealing temperatures) effect hardness. The mechanical and electrical performance of materials used in microelectronics are often dependent on the processing conditions of material, but extensive testing after device manufacturing is often required to determine these relationships. Bulk, macroscale measurements, such as thickness, index of refraction, and sheet resistance can easily be measured, but often do not translate well to the performance of the final device, because the devices are often dependent on nanoscale properties of the materials (i.e. defects). If the nanoscale properties of the materials can be measured before final device fabrication, then correlations can be established linking material processing conditions with device performance.

One method to measure nanoscale properties of materials is through nano-identation. Nano-indentation is a method to measure the hardness of materials using atomic force microscopy (AFM) that allows one to see differences in hardness on the nanoscale. Measuring the hardness of a material on the nanoscale allows you to elucidate variations in hardness that results from polycrystallinity of the material. We report on how the hardness is impacted by film thickness (50-1000 Å) and the underlying material. We also show how crystallinity produced by deposition or anneal temperature influences hardness of ALD films.

AA4-TuP-3 High Acid Corrosion Resistance of Nb_2O_5 Thin Film Deposited by Room Temperature ALD*, **Kazuki Yoshida,** K Saito, M Miura, K Kanomata, B Ahmmad, S Kubota, F Hirose,* Yamagata University, Japan

Metal oxide thin films like aluminum oxide (Al_2O_3), silicon oxide (SiO_2), and titanium oxide (TiO_2) have been well known as gas barrier materials for moisture. For acid corrosion, Al_2O_3 exhibits a slight deliquescence against hydrochloric acid. On the other hand, niobium pentoxide (Nb_2O_5) has been studied as a cathode protective layer of a fuel cell and a corrosive barrier film for metal. By laminating Nb_2O_5 on Al_2O_3 using thermal ALD, the corrosion resistance was enhanced to a certain degree. However, the deposition temperature was over 200℃ although the high-temperature process is not acceptable for not heat-tolerant flexible electronics. In this study, a laminated film of Al_2O_3 and Nb_2O_5 was deposited by room temperature atomic layer deposition (RT-ALD) and we report the improved acid corrosion resistance.

We used plasma excited humidified Ar as an oxidizing gas, trimethylaluminum (TMA) and tert -butylimidotris-(ethylmethylamido)niobium (TBTEMN) as precursors of Al_2O_3 and Nb_2O_5, respectively. The RT-ALD system is shown in Figure 1. We prepared SUS 304 plates with a size of 20 × 50 mm^2 as samples. The SUS plates were cleaned by ultrasonic cleaning with using acetone, isopropyl alcohol, and deionized water to remove organic impurities. The surface was slightly etched with dilute hydrochloric acid to remove the surface scratches, For the corrosion resistance test, we immersed substrates into the concentrated hydrochloric (36 wt%).

Figure 2 shows the anti-corrosion film coated substrate immersed in concentrated hydrochloric acid for 30 minutes. Al_2O_3 thin films were deposited 30 nm both (a) and (c). The Nb_2O_5 was deposited with a thickness of 5nm both the substrate(b) and (c). The substrate (c) is laminated Nb_2O_5 on Al_2O_3. As we can see from Fig.2, the corrosion resistance for hydrochloric acid is clearly improved by laminating Nb_2O_5. We consider the RT deposited Nb_2O_5 is applicable for not heat tolerant flexible and MEMS application.

AA4-TuP-4 Effects of Composition Ratios on Mechanical and Electrical Properties of AZO – Zincone Composite Thin Film Deposited on Transparent Polyimide Film Using Atomic and Molecular Layer Depositions.*, **Seung Hak Song,** B Choi,* Korea University, Republic of Korea

The combination of ALD and MLD techniques enables the fabrication of various functional organic – inorganic composite thin film structures. It is possible to fabricate thin films with various mechanical and electrical properties by adjusting the ratio of organic / inorganic components. In this study, a composite thin film composed of Al-doped zinc oxide (AZO) and the zincone organic film were deposited on a transparent polyimide substrate using diethylzinc (DEZ) with H_2O and hydroquinone (HQ) precursors. The characteristics of the hybrid thin film are varied significantly with the change of composition ratios, so the change of mechanical and electrical properties of the thin films according to the ratio of zincone organic film were measured. Various nano-structures of hybrid thin film were fabricated by controlling the composition ratio and process conditions, and their morphology and characteristics were analyzed. To investigate the ratio of thin films with high durability and electrical conductivity, the variation of electrical resistivity of thin films according to bending was measured.

AA4-TuP-5 Room-temperature Atomic Layer Deposition of Aluminosilicate Thin Film on Flexible Films*, **Yoshiharu Mori,** K Yoshida, K Kanomata, M Miura, B Ahmmad Arima, S Kubota, F Hirose,* Yamagata University, Japan

In recent years, aluminosilicate thin films are applied in various fields such as ion absorbers. Aluminosilicate is generally prepared by hydrothermal synthesis. However, it is based on high temperature and pressure processes. It is also not suited for the fabrication on electronic devices. To solve these problems, we newly developed room temperature ALD of aluminosilicate using tris [dimethylamino] silane (TDMAS), trimethylaluminum (TMA) and plasma excited humidified argon. We realized deposition of aluminosilicate on flexible films at room temperature as shown in Fig.1. Fig.2 shows a wide scan XPS spectrum measured from the RT grown aluminosilicate on a PEN film. We confirmed significant peaks of Si, Al and O. The aluminosilicate film thickness was measured by spectroscopic ellipsometry that exhibited the growth per cycle of 0.16 nm/cycle at room temperature. This suggest the possibility of the film thickness control with a precision of nanometer. We confirmed the ion absorption ability of the film. It was confirmed that Na and K cations were effectively absorbed on the film. The ion exchange properties from Na to K was also confirmed. The present RT-ALD offers the ion exchange function on flexible films. This research is expected to be applied as heavy metal ion filters and ion sensitive field effect transistors.

AA4-TuP-6 ALD Layers for Reduced Wear on Micro Cutting Tools*, T Junghans, **Hans-Dieter Schnabel,*** Westsächsische Hochschule Zwickau, Germany

In modern life, the usage of electronics is increasing day by day. Therefore, many circuit boards need to be machined. One of the major problems in circuit board manufacturing is the wear of micro cutting tools used for it.

Hard and corrosion resistant coatings might be a good opportunity to reduce the wear of these tools [1,2]. Due to the small size of the tools, with diameters of 300 µm and 3 mm, most traditionally used coating techniques are unable to produce conformal coatings on them [3]. This is why the works presented in a poster aimed for thin wear reducing films generated with atomic layer deposition.

The materials used were Al_2O_3 and TiN in various thicknesses from 20 nanometer to 150 nanometer. Those were used because of their properties, like hardness and corrosion resistance [1,4] and the well-established ALD-processes. In order to achieve dense films and low deposition temperatures the processes were plasma enhanced. Al_2O_3 was deposited with TMA as precursor in combination with an oxygen-argon plasma. The TiN films were generated by reacting TDMAT with an ammonia-argon plasma.

The poster shows that Al_2O_3 and TiN do not differ in wear behavior. Therefore, the focus is on Al_2O_3, due to the more stable and less time-consuming process. As the film thickness becomes bigger than 50 nm the Al_2O_3-layers are spalling off of the tools. Therefore, a lower or none reduction of wear was achievable with films as thick as or thicker than 50 nm. The work also shows that especially thin films of about 20 nm thickness achieved high reduction in tool wear. This shows that ALD-layers have promising properties in the field of wear reducing coatings for micro cutting tools.

[1] Y.L. Su and W.H. Kao; Journal of Materials and Performance: 7 (5), 1998

[2] Bull, S.J. et al.; Surface and Coatings Technology: 36, 1988

[3] Mayer, T.M. et al.; Applied Physics Letters, Vol. 82, No. 17, 2003

[4] Arslan E. et al.; Surface and Coatings Technology: 204, 2009

AA4-TuP-7 Fabrication of Atomic Layer Deposited Alumina as Protective Coating of Silver*, **Gwon Deok Han**, J Park, J Koo, J Shim,* Korea University, Republic of Korea

Silver is one of the precious metals widely used in human life. Silver has the disadvantage of being easily corroded or discolored when exposed to moisture and oxygen. Protective coatings of thin oxide films are effective in preventing corrosion and discoloration of silver products such as cookware, coins and jewelry. It is especially important to make a thin, uniform protective coating to protect the silver products from external environments. In this respect, atomic layer deposition (ALD) is considered the best technique for forming a protective oxide layer. ALD has an excellent function to form a uniform film without pinholes even in a complex three-dimensional (3D) structure with a high aspect ratio.

In this study, we evaluated the anti-corrosion performance of ALD alumina coatings for silver products [1]. The protection stability of the alumina coating layer was tested using an artificial sweat solution. The stability of the protective layer was evaluated by depositing alumina layers of changing thicknesses of 20-80 nm on silver samples and immersing the coated samples in artificial sweat solutions. We have demonstrated that a relatively thick alumina layer is effective in protecting the original properties of silver samples. In this meeting, we will discuss the protection performance of ALD alumina including its microstructure, optical properties and corrosion resistance.

[1] Park, S. W., Han, G. D., Choi, H. J., Prinz, F. B., & Shim, J. H. Evaluation of atomic layer deposited alumina as a protective layer for domestic silver articles: Anti-corrosion test in artificial sweat. *Applied Surface Science*, *441*, 718-723 (2018).

AA4-TuP-8 Characterization of Laminated Thin Films for Encapsulation using Single Si Precursor by PEALD*, **Joong Jin Park**, S Lee, H Lim, S Jang, S Kim, G Park, S Lee, M Kim,* DNF Co. Ltd, Republic of Korea

OLEDs(Organic Light-Emitting Diodes) are used in display devices such as mobile and TV, and next-generation OLED displays should be flexible and foldable. Flexible and foldable OLED displays require curvature radius less than 2.5R. In addition, a good encapsulation property is required in a thin thickness. Therefore, it is essential for OLED to realize these characteristics through laminated thin film rather than single thin film. The laminated thin film can reduce the diffuse reflection by generating the antireflection film effect due to the difference of the refractive index of each single layer film. It is also effective in reducing stress in the film and blocking ultraviolet rays. [1, 2]

Recently, the ALD process has been applied as a method of depositing thin films with excellent film quality. These ALD methods are used to develop thin film encapsulation technology because of the self-limiting surface reaction and the advantages of the reaction fraction.

In this paper, structure of the SiO2 / SiNx stack films were fabricated by using PEALD(Plasma Enhanced Atomic Layer Deposition) method at low temperature (90 ℃) using a single precursor, NSi-01. The thickness and refractive index of the thin film were measured using a Woollam M2000D spectroscopic ellipsometer. In addition, WVTR (Water Vapor Transmission Rate) was measured by using MOCON Aquatran 2 for thin films deposited on polyethylene naphthalate (PEN). In the structure of the SiO2 / SiNx stack film, the refractive index was measured to be 1.47 / 1.85, confirming the possibility of antireflection effect through the multilayer. The WVTR characteristics were measured over 100 hours according to the thickness of the thin film. At a thickness of less than 150 Å, the SiO_2 thin film or SiNx thin film had poor WVTR characteristics. In order to overcome this problem, SiO2 / SiNx structure was deposited. It is also expected that 2 to 3% of carbon in the deposited SiNx film will lower the film stress and maintain the flexibility of the entire film (Figure 1). The SiO2/SiNx/SiO2 laminated thin films exhibited excellent WVTR characteristics with the prevention of destruction of the encapsulation characteristics at a thin thickness(Figure 2). From this work, we confirmed the possibility of a laminated thin film consisting of a silicon oxide film and a nitride film by PEALD in one chamber using one precursor. In particular, the production of a laminated thin film can prevent both reflection and moisture absorption, and it is expected that the next generation OLED encapsulation will be applicable.

AA4-TuP-9 Low-cost Fabrication of Flexible Transparent Electrodes based on Sprayed Nanocomposites Silver Nanowires and Al Doped ZnO Deposited by Spatial ALD*, V Nguyen, J Resende, D Papanastasiou, C Jimenez, D Bellet,* LMGP Grenoble INP/CNRS, France*; S Aghazadehchors,* LMGP, France*; N Nguyen,* Université de Liège*; **David Muñoz-Rojas**,* LMGP Grenoble INP/CNRS, France

We report the study of nanocomposite transparent electrodes based on Aluminium doped Zinc Oxide (ZnO:Al) thin films and silver nanowire (AgNW) networks. The electrodes are fully fabricated by low-cost, open-air techniques, namely, atmospheric pressure spatial atomic layer deposition and spray coating. We show that the transparency and the conductivity of the ZnO:Al/AgNW nanocomposites can be tuned by controlling the AgNW network density. We also demonstrate that the thermal, electrical and mechanical stabilities of the composites are superior to those of AgNW networks or ZnO:Al thin films separately. We have also developed a theoretical model to explain the relationship between the conductivity of the composites and the AgNW network density. Our results provide a means to predicting the physical properties of such nanocomposites for applications in solar cells and other optoelectronic devices. Finally, the deposition methods used open the way towards stable, low-cost flexible and transparent electrodes for industrial application.

AA4-TuP-10 Nanomechanical Properties of Crystalline Anatase Titanium Oxide Films Synthesized using Atomic Layer Deposition*, **Yousuf Mohammed**, P Lin, K Zhang, H Baumgart, A Elmustafa,* Old Dominion University

Titanium dioxides (TiO_2) thin films have received significantly attentions due to their remarkable biocompatibility, stability, nontoxicity, and excellent photocatalytic properties. TiO_2 films are used in artificial heart valves, photocatalyst in solar cells. The photocatalytic activity of titanium dioxide is exhibited in both the anatase and the rutile phases. Likewise, the photocatalytic properties of TiO_2 thin film coatings are noticeable in medical applications in bactericidal coatings of wound care gauze or in coatings of surgical instruments to be sterilized and for antimicrobial surfaces in hospitals. Fabrication of TiO_2 films has intensified in the last two decades due to their notable optical and electronic properties and their excellent potential applications for gas sensing. Another application for anatase TiO_2 in photovoltaics, when their team realized impressive photovoltaic performance advances with perovskite/ TiO_2 heterojunction solar cells, which were fabricated with pure phase anatase TiO_2 nanosheets with dominant (001) facets serving as the electron collector.

Several deposition techniques have been used in the past to deposit TiO_2 films on silicon substrates, including reactive DC sputtering, RF magnetron sputtering, ion beam induced chemical vapor deposition, metal-organic chemical vapor deposition, chemical vapor deposition, mist CVD and the atomic layer deposition (ALD). The ALD has emerged as a modern chemical reaction based technique to deposit monolayers of inorganic compounds. ALD possesses unique film deposition uniformity and exact composition control with atomic precision and absolute conformality.

Crystalline TiO_2 films of 500 nm thickness were synthesized using ALD on p-type Si (100) substrates. The crystal structures of the TiO_2 thin films were characterized by the X-ray diffraction (XRD). The film thickness and surface morphology were inspected using field emission scanning electron microscopy (FE-SEM) and AFM. The nanomechanical properties were measured using a nanoindenter equipped with a three-sided Berkovich diamond tip to evaluate the hardness and modulus of the TiO_2 thin films. Due to low temperature ALD deposition, the X-ray diffraction revealed a single-phase TiO_2 anatase growth and the FE-SEM images indicate columnar grain structure growth with primarily vertical directions of the polycrystalline TiO_2 films. The measured hardness of the anatase ALD TiO_2 films at 20% film thickness has been measured as 5 Gpa, which is considerably softer compared to the reported benchmark values of the better known rutile phase of ~ 12 Gpa. The elastic modulus of the TiO_2 thin films was estimated as 138 and 145 Gpa.

AA4-TuP-11 Encapsulation of Magnetic Nanostructures by ALD for Improved Stability and Performance*, **Devika Choudhury**, Y Zhang, K Gao, A Mane, J Elam,* Argonne National Laboratory

Morphology of magnetic nanoparticles is an important aspect responsible for controlling the optical, electrical and magnetic properties. Their interesting shapes and sizes result in novel properties significantly different from their bulk counterparts. For example, 1D magnetic nanostructures often exhibit significantly modified properties and enhanced coercivity as compared to the their bulk magnets thus making them attractive for wide range of applications. These materials are not only extensively used in high-density magnetic data-storage mediums, magnetic sensors and spintronic devices, but also suitable for valuable biomedical applications as well.

Metal alloys such as PtCo, SmCo, FeNi and FeCo are well known for their desirable magnetic properties and use. However, due to their nanosize scale, these materials readily oxidize under ambient conditions. Poor chemical stability results in diminished magnetic properties thus limiting their practical usage.

Atomic Layer Deposition (ALD) has emerged as one of the most widely accepted techniques to provide conformal coating of controlled thickness on high curvature structures and a popular method for encapsulation of various type of microstructures. In this work, we report the coating of magnetic metallic alloys using ALD method to improve stability and performance of the nanostructures. Different chemistries are used for the deposition of a variety of protecting layers. Comparison on the effectiveness of the coatings are drawn from the stability and their magnetic properties such magnetic saturation values obtained from SQUID measurements.

AA4-TuP-12 Diffusion Barrier Properties of ALD TiSiN Films*, **Jerry Mack**, J Heo, S Chugh, H Kim, S Rathi, N Mukherjee,* Eugenus, Inc.

The decreasing feature sizes and increasing aspect ratios in semiconductor process flows have imposed stringent requirements on the physical and electrical properties of metal-to-semiconductor interfaces. This has resulted in fundamental material challenges for low-resistance contacts and ultra-thin diffusion-barrier films. Physical vapor deposition (PVD) based TiN film is a widely used diffusion barrier layer. However, deposition of ultra-thin TiN exhibits pronounced islanding which leads to rough film with polycrystalline grain structure. Furthermore, inhomogeneities due to grain boundaries offer diffusion pathways and lead to device degradation. In the current study, we present our findings on the diffusion barrier properties of amorphous ternary alloy films composed of Ti, Si and N (TiSiN), an excellent alternative to TiN films. These films were grown using Atomic Layer Deposition (ALD) technique on the Eugenus 300mm QXP commercial mini-batch reactor. In one set of experiments, TiSiN films were deposited on highly-doped polycrystalline Si:B films followed by diffusion studies of boron. In another set of experiments, fluorine precursor based CVD Wsi_x film was deposited on TiSiN, followed by diffusion studies of fluorine. Secondary Ion Mass Spectrometry (SIMS) and High-resolution electron energy loss spectroscopy (HREELS) were utilized to detect the effectiveness of the barrier film to prevent boron and fluorine diffusion.

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