

Thin Film Division

Room: 107 - Session TF-MoA

Emerging ALD Applications

Moderator: G. Scarel, James Madison University

2:00pm **TF-MoA1 Atmospheric ALD of Al₂O₃ for a High Throughput c-Si Solar Cell Passivation**, V.I. Kuznetsov, P. Vermont, E.H.A. Granneman, Levitech BV, Netherlands **INVITED**

Surface passivation of advanced solar cells becomes more important with decreasing silicon wafer thickness (increased surface to bulk ratio). The International Technology Roadmap for Photovoltaics predicts that the thickness of wafers processed in mass production will be 100 μm by 2020. By 2012 new processes with lower Cost of Ownership (CoO) and better passivation properties will be needed [1].

It is widely accepted that Al₂O₃ layer has excellent surface passivation capabilities [2]. Solar cells with Al₂O₃ layers < 10 nm demonstrate the best results: higher efficiency and more stable structures when annealed at high temperatures [3,4]. ALD is an ideal technique for the deposition of thin layers. However, conventional ALD equipment can not be used in the PV industry because of the low throughput and associated high CoO. A suitable way to reduce the tool cost per cell is to increase the throughput of the system. The ITRPV requires a minimum throughput of production tools from 3600 wph in 2012 to 7200 wph in 2020.

We developed an ALD tool which meets these throughput requirements and is capable to process at a cost of 3-4 cent per wafer. In this tool we implemented a new approach: atmospheric, spatial ALD. Silicon wafers are transported in a linear track passing areas with TMA and H₂O precursor gas curtains. N₂ purges in between these curtains separate the different precursors thereby avoiding deposition on the track walls. The wafers are transported on a gas bearing (levitate) inside a narrow track. The Levitrack system operates in-line and has a length of ~10 m for the deposition of 10 nm of Al₂O₃. At the conference Levitrack tool details and process results will be presented. Some items are:

- Passivation quality: effective lifetime of 6.1 ms in mono-silicon 10 Ω cm at injection level of 3E15 cm⁻³.

- Layer characteristics: 1 σ uniformity <3% on 156x156 mm wafers, intrinsic layer charge of -4E12 cm⁻²

- Tool options: deposition on both or one side of the wafer (N₂ flow protects the back side of the wafer against Al₂O₃ deposition)

- Tool automation (automated wafer loading/unloading, 100 wafer cassettes and use inline, control of process, safety, and other parameters)

- Tool reliability (reliable performance at marathon runs with throughput of ~4000 wph)

- Current solar cell results (efficiency obtained for p-type crystalline silicon cell is 16.6% and for n-type is 18.3%. Improvement of 1-2% is expected to be achieved by optimizing local BSF below metal contacts and contact/shunt resistances)

1. ITRPV.net, 2nd edition, 2011

2. S.Chunduri, Photon Int., p.146, 2011

3. P.Brand, 37th IEEE PV Conference, Seattle, 2011

4. I.G.Romijn, 25th. EU PVSEC, 2010

2:40pm **TF-MoA3 Atomic Layer Deposition of Al₂O₃ for Quantum Computing**, A.C. Kozen, M. Khalil, B. Sarabi, K.D. Osborn, University of Maryland, College Park, C. Musgrave, University of Colorado, Boulder, C. Lobb, G.W. Rubloff, University of Maryland, College Park

Josephson junctions (JJ) are a primary building block of superconducting quantum computers. The JJ structure is a superconductor-dielectric-superconductor stack, with the conventional dielectric layer fabricated by thermal oxidation of an aluminum metal electrode. The coherence time of these qubits is limited by high loss tangents in the dielectric layer thought to be due to defect-related quantum two level systems (TLS) inherent in the Al₂O₃. We have identified the -OH rotor TLS associated with hydroxyl species in the Al₂O₃ as a prime defect candidate based on TLS energetics. Simulations indicate that replacement of the -OH defect with the -OD defect will reduce the dielectric loss in these systems. We demonstrate the fabrication of Al₂O₃ dielectric thin films using atomic layer deposition (ALD) from trimethylaluminum and both H₂O and D₂O precursors as a function of substrate temperature and precursor dose. ALD enables precise control of film growth at the atomic scale, while comparison of H₂O vs. D₂O as the oxidation precursor enables isotopic defect loading in the Al₂O₃

and replacement of the -OH defect with the -OD defect. We have developed the D₂O based ALD process, and characterized both D₂O and H₂O based ALD Al₂O₃ thin films by SIMS, XPS and spectroscopic ellipsometry. Our resulting Al₂O₃ films are physically identical with the exception of -OH and -OD defects, making this system an ideal platform for the study of TLS defect related dielectric loss in JJ qubits. To this end we have fabricated MIM capacitor test structures and superconducting resonators using Re and Al electrodes and performed electrical measurements. Correlation between these data and low temperature superconducting microwave resonator performance will be discussed.

3:00pm **TF-MoA4 Supported Core-Shell Pt-Pd Nanoparticles Synthesized by Atomic Layer Deposition**, M.J. Weber, A.J.M. Mackus, Eindhoven University of Technology, Netherlands, M.A. Verheijen, C. van der Marel, Philips Innovation Services, Netherlands, W.M.M. Kessels, Eindhoven University of Technology, Netherlands

Recently, atomic layer deposition (ALD) has become the subject of great interest as a new way to synthesize supported metallic nanocatalysts (1, 2). In comparison to their single-metal counterparts, bimetallic nanoparticles (NPs) can present a higher selectivity and an enhanced catalytic activity. In this contribution, we present an innovative ALD process enabling the synthesis of supported bimetallic core-shell NPs. Although ALD was primarily developed to deposit conformal thin films, metals have the tendency to form nanoclusters on the substrate during the initial cycles of the process. In this work, Platinum-Palladium core-shell NPs were successfully deposited on Al₂O₃ using ALD of Pt and Pd. The selective growth property of noble metal ALD (3) has been exploited to cover Pt nanoclusters with a Pd shell. An ALD process using MeCpPtMe₃ and O₂ has been used to deposit Pt nanoclusters, and ALD with Pd(hfac)₂ and H₂ enabled to selectively cover them with a Pd shell. High Angle Annular Dark Field (HAADF) TEM images confirm the fact that bimetallic core-shell NPs of 3-4 nm were synthesized (on Al₂O₃ covered TEM windows). Information on the chemical state of the Pd and Pt was obtained from XPS analysis. Average values of the Pd shell thickness as obtained by a model analysis of the XPS data were found to be in agreement with the TEM data. This new process is expected to be also applicable to other Platinum group metals. The tailoring of such NPs by changing the ALD process parameters in order to obtain different particles sizes and compositions is also addressed. It is expected that the fuel cells industry, but also advanced sensors technologies, can benefit considerably from an enhancement of catalytic activity and selectivity of nanocatalysts prepared by ALD.

- 1: Stair, *J. Chem. Phys.* **2008**, 128, 182570

- 2: Christensen et al., *Small* **2009**, 5, No. 6, 750-757

- 3: Mackus et al., *J. Appl. Phys.* **2010**, 107 (11), 116102-1/3

3:40pm **TF-MoA6 Photoluminescence Characteristics of TiO₂ Film Deposited on Vertically Oriented Si Nanowire by Remote Plasma Atomic Layer Deposition**, J.S. Lee, T.Y. Park, Y.B. Ko, H.Y. Jeon, J.G. Park, J.H. Ryu, H.T. Jeon, Hanyang University, Republic of Korea

Titanium dioxide (TiO₂) has been regarded as one of the most promising photocatalysts for environmental protection because of its high photocatalytic activity, high chemical stability, low toxicity, and low cost. Anatase and rutile structures of TiO₂ are two main phases with band gap energies of 3.3 and 3.1 eV, respectively. The structures of both anatase and rutile consist of chains of TiO₆ octahedra. However, two crystal structures are obviously different. It is well-known that the difference in crystal structures causes different mass density (3.894 g/cm³ for anatase and 4.250 g/cm³ for rutile) and electronic band gap. The anatase phase has a more negative conduction band edge than that of the rutile phase. It results in superior photocatalytic activity of anatase phase than that of the rutile phase. Therefore, the structure of TiO₂ films and high surface area are heavily important factors in photocatalytic efficiency.

In this study, TiO₂ film was deposited by remote plasma atomic layer deposition (RPALD) and its phase formation temperature, impurity concentration, and chemical states of the were characterized by various analyses such as Auger electron spectroscopy (AES), X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). The TiO₂ film was deposited on the flat Si substrate and vertically oriented Si nanowire by using remote plasma atomic layer deposition (RPALD) method. RPALD method has advantage to deposit thin film with uniform thickness on the 3-dimensional structure like vertically oriented Si nanowire. In addition, the RPALD method is possible to reduce damage by high energetic ion and to enhance the chemical reactivity between metal-organic precursor and reactant gas for deposition of high quality film. The vertically oriented Si nanowire was fabricated by Ar-annealing of Si substrate with Au nanocrystal at 1000 °C. And we have

compared the photoluminescence (PL) features of these TiO₂ films with these two different specific surface areas. We have found that TiO₂ film deposited vertically aligned Si nanowire has higher PL intensity than that of TiO₂ deposited flat Si substrate due to large area density of vertically oriented Si nanowire.

4:00pm TF-MoA7 Fast Atomic Layer Deposition for High Throughput and Low Temperature Applications, P. Poodt, A. Illiberi, M. Smets, R. Knaepen, TNO, Netherlands, F. Roozeboom, TNO & Eindhoven University of Technology, Netherlands, A. van Asten, TNO, Netherlands

Atomic Layer Deposition is a deposition technique capable of producing ultrathin conformal films with control of the thickness and composition of the films at the atomic level. The major drawback of ALD is its low deposition rate (~ 1 nm/min). Recently, fast ALD concepts were developed based on the *spatial* separation of the half-reactions, instead of temporal, combined with gas-bearing technology¹. With this technique, deposition rates for Al₂O₃ of more than 1 nm/s have been reported². This has led to the development of the high-throughput, industrial scale ALD tools for surface passivation of crystalline silicon solar cells^{2,3}.

A new field of applications for fast ALD are flexible electronics⁴, including system-in-foil, flexible displays, OLEDs and solar cells. Flexible electronics are slowly but surely evolving from lab-scale to industrial production. This opens up new possibilities for fast ALD as high-throughput production tool for functional layers such as transparent oxide (semi)conductors (e.g. ZnO) and moisture barriers (e.g. Al₂O₃). One important prerequisite is that these applications require low temperature processes (below 100°C), as they are often temperature sensitive. We present two approaches for low temperature Fast ALD; low temperature *thermal* fast ALD and atmospheric plasma enhanced fast ALD.

A *low temperature thermal fast ALD* process for alumina from tri-methyl aluminum and water has been developed. It was observed that the kinetics of the water half-reaction is significantly different than at high temperatures (>200°C). Multilayer adsorption of water molecules at low temperatures seems to hinder the self-limiting nature of the ALD process at temperatures below 75°C. Nevertheless, if very low temperatures are not required, low temperature thermal fast ALD is a very suitable technique. Potentially low deposition temperatures could be achieved by *atmospheric plasma enhanced fast ALD*. We have integrated an atmospheric plasma source in our reactor in which an He/O₂ plasma is created to act as the oxidant half reaction. However, the chemistry of atmospheric plasmas is different than that of conventionally used low pressure plasmas and has a lower reactivity that can limit the throughput.

Another important aspect of fast ALD for flexible electronics is the processing of flexible substrates, either sheet-to-sheet or roll-to-roll. Approaches for roll-to-roll fast ALD, their challenges and possible solutions will be briefly discussed.

¹ P. Poodt *et al.*, *Adv. Mater.* 22 (2010) 3564.

² www.solaytec.com .

³ I. Cesar, *et al.*, *Proc. 35th IEEE PVSC*, Honolulu, Hawaii (2010), in press

⁴ J. van den Brand *et al.*, *Microelect. Rel.* 48 (2008) 1123

4:20pm TF-MoA8 Industrial ALD Equipment for PV and OLED Applications, M. Putkonen, Beneq Oy, Finland

Atomic Layer Deposition (ALD) has been successfully applied to antireflection, buffer and passivation layers for PV as well as moisture barriers for OLED packaging. In these applications ALD offers superior performance compared to the corresponding layers deposited with other methods. Outside IC manufacturing ALD has largely been confined to laboratories so far due to non-availability of larger scale, high throughput ALD systems. For example, ALD is widely seen as the desired manufacturing technology for producing high quality functional layers into solar cells: e.g. buffer layers into CIGS and surface passivation into both p-type and n-type c-Si solar cells, but ALD commonly considered too slow for high throughput manufacturing.

In this presentation we introduce commercial high capacity ALD tools for PV and OLED diffusion barrier applications as well as discuss more about the requirements for high throughput industrial ALD tools. Conventional ALD deposition parameters and characteristics, such as stability of precursor temperatures even with extremely high precursor doses and optimising the flow path are needed before strict coating requirements can be fulfilled.

The TFS 1200 deposition system is designed to improve efficiency of CuInGaSe₂ (CIGS) type thin film PV cells using Zn(O,S) buffer layer. It has throughput in inline and off-line configurations of 12 and 24 modules/hour, respectively. (substrate size 120 x 120 cm², 20 nm Zn(O,S)) We have obtained thin film thickness uniformity of ± 3 % with the cycle time of 2.0 s. With 60 x 120 cm² substrate size these numbers will be

doubled to 24-48 modules/hour. These values fulfill the throughput requirements of CIGS production lines (20-60 modules/h). Even higher throughputs can be obtained using batch type tools for CIGS buffer layers.

TFS NX 300 is a fully automated cassette to cassette ALD manufacturing system for Al₂O₃ surface passivation. It consists of 4 processing tubes each with the capacity for a 500 wafer batch. For this application we have modified thermal ALD-process for Al₂O₃ which has a higher growth rate than the conventional thermal (TMA/H₂O) ALD process and the film quality is equal to plasma assisted ALD film quality giving throughput of >3000 wafers/h.

The Beneq TFS 600 is a vacuum-line integrated ALD system for OLED moisture barrier coating. Reaction chamber is designed for batch processing up to 35 substrates measuring 500 mm x 400 mm. For this application we have been developing low-cost multilayer barrier structure giving WVTR <10⁻⁶ g/m²/d.

4:40pm TF-MoA9 Conductive Coatings on Nonwoven Fiber Mats by Atomic Layer Deposition, W. Sweet, J.S. Jur, G.N. Parsons, North Carolina State University

Conductive fiber mats offer unique possibilities in the development of many sensing and protective electronic systems. In this work, atomic layer deposition (ALD) is applied to produce conformal coatings of conductive ZnO on complex fiber systems such as nonwoven polypropylene and nylon. The conductivity of these materials were evaluated using a modified 4-probe method specific for fabric structures and correlated with the overall mass gain of the fabric samples after ALD processing. This analysis provided a detailed evolution of the conductive films on the fabric mats. For example, nonwoven polypropylene coated with ZnO showed a significant initial mass increase, eventually becoming linear with increasing ALD cycles. The corresponding conductivity of these films remained low (< 3 S cm⁻¹), even after 500 ALD ZnO cycles. Inserting a thin insulating ALD Al₂O₃ layer prior to the ZnO growth, linear ZnO mass gain was achieved after low ALD cycles. Transmission electron microscopy shows that the Al₂O₃ barrier reduces the penetration of the ZnO vapor phase reactants into the polypropylene. As a result, a higher effective conductivity (> 25 S cm⁻¹) was achieved after 200 ALD ZnO cycles that corresponded well with measurements from simultaneous ZnO growth on a planar silicon oxide surface. For comparison, ZnO deposition on nonwoven nylon-6 exhibits uniform growth without Al₂O₃ pretreatment and the conductivity again changes significantly with the Al₂O₃ pretreatment. Implications of the deposition temperature, film thickness, and the use of aluminum doping, on the chemical, mechanical, and electrical properties of ZnO films deposited on polypropylene and nylon nonwovens will be discussed.

5:00pm TF-MoA10 ALD IrOx Thin Film to Improve Microelectrode Array Performance in Stem Cell Applications, T. Ryyänen, J. Lekkala, Tampere University of Technology, Finland, L. Ylä-Outinen, S. Narkilahti, University of Tampere, Finland, J. Hämäläinen, M. Leskelä, University of Helsinki, Finland

We promote atomic layer deposition (ALD) and especially ALD deposited iridium oxide (IrOx) thin film [1] as a novel alternative to improve electrical characteristics of microelectrode arrays (MEAs) used in stem cell and other tissue engineering applications. The additional microelectrode coating on microelectrode base material is traditionally used to decrease impedance and noise levels, and to increase charge transfer capacity of microelectrodes in MEAs. However, most of the common microelectrode coatings suffer from certain drawbacks. For example 1) electrochemical activation used to decrease the impedance of sputtered IrOx by one decade is not applicable for long term cell measurements due to rather fast deactivation, 2) widely used electrodeposited platinum (Pt black) suffers often from poor adhesion on underlying microelectrode base material, and 3) lately actively studied carbon nanotube (CNT) coatings still have unsolved issues related to difficult fabrication processes and concerns about biocompatibility and long term adhesion. Thus there is obvious demand for another stable solution in addition to sputtered titanium nitride (TiN) thin film favored by one of the leading commercial MEA manufacturers.

In our initial studies the about 120 nm thick ALD IrOx layer decreased the impedance of 30 µm diameter titanium microelectrodes down to 450 kΩ at 1 kHz, which is several times less than without the coating and consistent with the impedance reported for unactivated sputtered IrOx coated microelectrodes [2]. Stem cell growth experiments performed with human embryonic stem cell derived neuronal cells (hESC-N) [3, 4] showed that in field potential measurements ALD IrOx thin film decreases the noise level significantly compared to non-coated microelectrodes. Also, no biocompatibility or adhesion problems were detected. Even if already as such the ALD IrOx thin film clearly improves the MEA performance, we expect that by optimizing the thin film thickness and ALD process parameters from the default 3000 cycles of Ir(acac)₃ and ozone, the impedance level of the ALD IrOx coated microelectrodes can be decreased

even further. Thus impedance levels of 100 k Ω and below could be reached, which would make ALD IrOx thin film a strong competitor for the other commonly used microelectrode coatings. In addition to offering an economical, easily controllable, and highly reproducible fabrication process for a thin film improving the electrical characteristics of MEAs, ALD technology may in the future offer also other interesting coating solutions for cell culturing platforms, for example controlling cell growth via functionalized coatings.

[1] J. Hämäläinen *et al.*, Chem. Mater. 20 (2008) 2903.

[2] S. Gawad *et al.*, Front. Neuroeng. 2 (2009) 1.

[3] R. Lappalainen *et al.*, Regen. Med. 5 (2010) 749.

[4] T. Heikkilä *et al.*, Exp. Neurol. 218 (2009) 109.

Authors Index

Bold page numbers indicate the presenter

— G —

Granneman, E.H.A.: TF-MoA1, 1

— H —

Hämäläinen, J.: TF-MoA10, 2

— I —

Illiberi, A.: TF-MoA7, 2

— J —

Jeon, H.T.: TF-MoA6, 1

Jeon, H.Y.: TF-MoA6, 1

Jur, J.S.: TF-MoA9, 2

— K —

Kessels, W.M.M.: TF-MoA4, 1

Khalil, M.: TF-MoA3, 1

Knaapen, R.: TF-MoA7, 2

Ko, Y.B.: TF-MoA6, 1

Kozen, A.C.: TF-MoA3, **1**

Kuznetsov, V.I.: TF-MoA1, **1**

— L —

Lee, J.S.: TF-MoA6, **1**

Lekkala, J.: TF-MoA10, 2

Leskelä, M.: TF-MoA10, 2

Lobb, C.: TF-MoA3, 1

— M —

Mackus, A.J.M.: TF-MoA4, 1

Musgrave, C.: TF-MoA3, 1

— N —

Narkilahti, S.: TF-MoA10, 2

— O —

Osborn, K.D.: TF-MoA3, 1

— P —

Park, J.G.: TF-MoA6, 1

Park, T.Y.: TF-MoA6, 1

Parsons, G.N.: TF-MoA9, 2

Poodt, P.: TF-MoA7, **2**

Putkonen, M.: TF-MoA8, **2**

— R —

Roozeboom, F.: TF-MoA7, 2

Rubloff, G.W.: TF-MoA3, 1

Ryu, J.H.: TF-MoA6, 1

Ryynänen, T.: TF-MoA10, **2**

— S —

Sarabi, B.: TF-MoA3, 1

Smets, M.: TF-MoA7, 2

Sweet, W.: TF-MoA9, **2**

— V —

van Asten, A.: TF-MoA7, 2

van der Marel, C.: TF-MoA4, 1

Verheijen, M.A.: TF-MoA4, 1

Vermont, P.: TF-MoA1, 1

— W —

Weber, M.J.: TF-MoA4, **1**

— Y —

Ylä-Outinen, L.: TF-MoA10, 2