

# Impact of Film Thickness and Thermal Treatment on the Excellent Surface Passivation of c-Si by ALD Al<sub>2</sub>O<sub>3</sub> for Solar Cell Applications

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migration of cations or anions across the film's thickness. In this respect, oxygen vacancies seem to play an important role.

In this work, HfO<sub>2</sub> MIM RRAM cells are elaborated and tested in two electrical modes: voltage sweep mode and constant voltage stress (CVS) mode. The HfO<sub>2</sub> choice is based on the fact that hafnia-based dielectrics are the most promising materials for the manufacturing of CMOS gates below the 45 nm technology node. Therefore, as far as integration and process compatibility are concerned, HfO<sub>2</sub> would be an interesting candidate for the RRAM technology. HfO<sub>2</sub> films (10 nm) were grown at 350°C by atomic layer deposition (ALD) using alternate cycles of H<sub>2</sub>O and HfCl<sub>4</sub> precursors (1 Torr) on Pt (100 nm) / Ti (10 nm) / Si wafers. The films are crystallized in the monoclinic phase and their gap is around 5.5 eV. Angle-resolved X-ray photoelectron spectroscopy (ARXPS) performed on thinner films (2 nm) reveals a homogeneous composition across the films thickness with a sharp HfO<sub>2</sub>/Pt interface (absence of PtO oxides). Top gold electrodes (100 nm thick, 2 mm in diameter) were deposited on the HfO<sub>2</sub> films by dc sputtering.

The voltage sweep mode shows that HfO<sub>2</sub> RRAM is bipolar and that the switching mechanism is probably due to the oxygen vacancies migration and accumulation through the electrical field to the Pt/HfO<sub>2</sub> interface. These positively charged vacancies may act as dopant and form a locally conductive channel in the dielectric. In the CVS mode the device's resistance was observed to be unstable, displaying fluctuations between the high resistance state and the low resistance state which are typical of random telegraph signals. The role played by oxygen vacancies on these fluctuations will be discussed and a mechanism based on a competition between the oxygen vacancies alignment by the electric field and their thermal redistribution by Joule heating will be proposed.

5:00pm **TF2-MoA10 Plasma Beam Deposition of Silver Mirrors**, *J.D. Barrie, C.T. Chu, P.D. Chaffee, C.J. Panetta, K.A. Folgner, P. Fuqua*, The Aerospace Corporation

The high reflectivity of silver coatings in the visible and infrared makes them the mirror of choice for many demanding applications. Unfortunately, these mirrors tend to be affected by exposure to atmospheric contaminants, resulting in corrosion that reduces reflectivity and increases scatter, limiting the mirrors' useful service life. Factors that can affect the stability of silver mirrors include interface adhesion, impurities and pinholes in the dielectric protection layers, and the microstructure and stress levels in the films. This paper examines the preparation of silver mirrors by plasma beam deposition, a relatively new technique for thin film fabrication developed and patented by Plasma Quest, Ltd., and licensed by The Aerospace Corporation. In this method, a high-density inductively-coupled RF-plasma is created external to the deposition chamber, is electromagnetically steered towards a source target, and finally is accelerated towards the target by application of a bias on the target. The separation of plasma generation and transport offers significant advantages in process control. We will present data on how varied deposition conditions, such as plasma beam density and target bias, affect stress and durability of high reflectivity silver mirrors.

## Thin Film

**Room: B4 - Session TF3-MoA**

## Energy Applications and Scaling

**Moderator:** S.M. George, University of Colorado at Boulder

2:00pm **TF3-MoA1 Dye-Sensitized Solar Cells: Fabricating Photoelectrodes via Atomic Layer Deposition**, *J.T. Hupp*, Northwestern University **INVITED**

Dye-sensitized solar cells (DSSCs) utilize high-area semiconducting metal-oxides as photo-electrodes. The electrodes typically take the form of aggregated nanoparticulate films, supported by planar transparent conducting oxides (TCOs). Depending on the precise composition of the rest of the DSSC, unwanted back electron transfer from the dye-coated electrode to solution-phase (or solid state) redox shuttle can be a major performance-limiting process. We find that atomic layer deposition of insulating alumina or zirconia effectively passivates surface states that mediate the back transfer. Indeed, in some instances a single ALD cycle can slow back electron transfer by as much as four orders of magnitude, with concomitant spectacular improvement in cell photovoltages and fill factors. Alternatively, ALD can be used for photoelectrode fabrication. Especially intriguing is the fabrication of quasi-one-dimensional photoelectrodes on high-area anodic alumina oxide or silica aerogel templates. In comparison to conventional 3D nanoparticulate architectures, the 1D electrode architectures offer superior electron transport and shuttle transport behavior.

Advanced designs allow for highly efficient radial charge collection, even from inherently transporting materials. The use of ALD to construct these electrodes will be described. If time permits, additional DSSC applications will be described, including ALD-based corrosion inhibition and ALD-based fabrication of cells that employ plasmonic amplification.

2:40pm **TF3-MoA3 Energy Conversion at Nano Scale**, *F.B. Prinz*, Stanford University **INVITED**

Selective mass and charge transfer drive energy conversion in any living system. Not unlike nature, man-made energy conversion systems such as fuel cells depend on membranes with selective ionic conduction.

Our experiments have shown that we can fabricate freestanding oxide membranes with a thickness of tens of nanometers using Atomic Layer Deposition (ALD). In particular, we used Yttria stabilized Zirconia and Gadolinia doped Ceria as electrolyte membranes for the creation of a new class Solid Oxide Fuel Cells (SOFCs) which are capable of operating several hundred degrees centigrade below the temperature of traditional SOFCs. First principles calculations help in understanding oxide ion incorporation and ion conductivity as a function of dopant concentration.

ALD promises improved thin films for photovoltaics. Precise depth control of photon absorbing layers allows engineering of bandgaps over a wide range of energy levels. However, high grain boundary density in ALD films may increase exciton recombination rates, thereby reducing conversion efficiency.

3:40pm **TF3-MoA6 Al<sub>2</sub>O<sub>3</sub> ALD for Improved Performance of Li Ion Batteries**, *A.S. Cavanagh, Y.S. Jung*, University of Colorado at Boulder, *A.C. Dillon*, National Renewable Energy Laboratory, *M.D. Groner*, ALD NanoSolutions Inc., *S.H. Lee, S.M. George*, University of Colorado at Boulder

Lithium ion batteries (LIBs) are emerging as the dominant power source for portable electronics. Improvement in their capacity lifetime during charge-discharge cycles must be achieved before LIBs can be used for plug-in-hybrid and electric vehicles. LiCoO<sub>2</sub> has been the dominant cathode material in LIBs. The instability of LiCoO<sub>2</sub> particles comprising the cathodes leads to the deterioration of the LIB. Efforts to stabilize LiCoO<sub>2</sub> particles have concentrated on nanometer thick coatings of metal oxides, metal fluorides and metal phosphates deposited using sol-gel techniques. In this study, we demonstrate that Al<sub>2</sub>O<sub>3</sub> ALD grown on LiCoO<sub>2</sub> particles dramatically enhances their specific discharge capacity.

After coating the LiCoO<sub>2</sub> particles with Al<sub>2</sub>O<sub>3</sub> ALD in a rotary reactor, battery cathodes were prepared and cycled against a Li/Li<sup>+</sup> anode near the threshold for 50% Li extraction at 1 C-rate after the first two charge-discharge cycles. A control cathode prepared using uncoated LiCoO<sub>2</sub> particles was tested for comparison. With respect to the third charge-discharge cycle, the LiCoO<sub>2</sub> particles coated with 2 Al<sub>2</sub>O<sub>3</sub> ALD cycles showed a 89% capacity retention after 120 charge-discharge cycles. In comparison, the bare LiCoO<sub>2</sub> particles displayed only a 45% capacity retention after 120 charge-discharge cycles.

LiCoO<sub>2</sub> particles coated with 6 and 10 Al<sub>2</sub>O<sub>3</sub> ALD cycles showed lower specific capacities when run at a 1 C-rate after the first two charge-discharge cycles. This lower capacity is attributed to the slower Li<sup>+</sup> diffusion and restricted electron mobility through the insulating Al<sub>2</sub>O<sub>3</sub> ALD layer. We propose two mechanisms by which the Al<sub>2</sub>O<sub>3</sub> ALD may enhance the cycle performance of the LIBs. The Al<sub>2</sub>O<sub>3</sub> film may prevent the LiCoO<sub>2</sub> particles from decomposing electrolyte and forming a solid-electrolyte interphase. Alternatively, the Al<sub>2</sub>O<sub>3</sub> film may protect the LiCoO<sub>2</sub> particles from corrosion by HF.

4:00pm **TF3-MoA7 Impact of Film Thickness and Thermal Treatment on the Excellent Surface Passivation of c-Si by ALD Al<sub>2</sub>O<sub>3</sub> for Solar Cell Applications**, *G. Dingemans, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, the Netherlands

The surface passivation of c-Si by atomic layer deposited (ALD) Al<sub>2</sub>O<sub>3</sub> has recently gained considerable interest after extremely low surface recombination velocities (< 10 cm/s) have been reported for low resistivity n- and p-type c-Si wafers [1]. The incorporation of an Al<sub>2</sub>O<sub>3</sub> film for boron doped emitter passivation led to enhanced efficiencies of 23.2% for n-type c-Si solar cells [2]. From the cumulative research, various questions related to the thermal stability and other processing aspects of the Al<sub>2</sub>O<sub>3</sub> films appeared. In this contribution we will show that a decrease of film thickness down to ~5 nm does not compromise the passivation quality, enabling a straightforward reduction of deposition time and providing freedom in the design of optimal front passivation/antireflection schemes. To activate the Al<sub>2</sub>O<sub>3</sub> surface passivation a post-deposition anneal is required, but also the thermal budget during the plasma enhanced chemical vapor deposition of an α-SiN<sub>x</sub>:H capping layer was found sufficient to activate the passivation. Although an anneal effect can be observed in a large temperature range

(~350 - ~600°C) the optimal post-deposition anneal temperature window was found to be much smaller. Within the optimum temperature range, the largest anneal effect was observed to take place during the first minutes of the process. For the successful implementation of Al<sub>2</sub>O<sub>3</sub> in conventional screen printed solar cells, thermal stability is required. In this paper we demonstrate the relative stability of Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>/a-SiN<sub>x</sub>:H passivation/antireflection stacks against an industrial "firing" process reaching temperatures > 800°C. Although the minority carrier lifetime was found to decrease during the firing process, values in excess of 1 ms were obtained on 2 Ω cm *n*-Si wafers after firing. These lifetimes suggest that surface recombination will not likely be the efficiency limiting step for solar cells that combine Al<sub>2</sub>O<sub>3</sub> passivation and screen printed metallization as recombination in the metallized area will be dominant. The findings in this paper demonstrate the suitability of thin ALD-synthesised Al<sub>2</sub>O<sub>3</sub> passivation films for large scale photovoltaic applications.

[1] B. Hoex, J. Schmidt, P. Pohl, M. C. M. van de Sanden, and W. M. M. Kessels, *J. Appl. Phys.* 104, 044903 (2008)

[2] J. Bennick, B. Hoex, M.C.M. van de Sanden, W.M.M. Kessels, O. Schultz, S. Glunz, *Appl. Phys. Lett.* 92, 253504 (2008)

**4:20pm TF3-MoA8 Spatial ALD: Fabrication of Films and Devices at Atmospheric Pressure, D.H. Levy, S.F. Nelson, M.S. Burberry, L.W. Tutt, R.S. Kerr, G. Zwadlo, Eastman Kodak Company INVITED**

Atomic Layer Deposition (ALD) has proven itself in the fabrication of high-quality films with good uniformity and thickness control. ALD films serve as barriers, surface treatments, dielectrics, and semiconductors. The process has numerous benefits including superior conformality and ease of selective patterning, attributes that make it an ideal tool for upcoming needs in nanofabrication.

To date much of the usefulness of ALD has been demonstrated in enclosed systems where the gases used to effect the deposition are delivered and removed from a chamber in a timed sequence. An alternative to this approach is to keep gas flows of the various reactants at steady state but confined to specific regions of a coating head. Movement of the substrate relative to the coating head yields the required alternating exposure sequence. This method, termed spatial ALD (S-ALD), relies upon methods to isolate closely spaced gas streams. The design approaches to eliminate reactant mixing and to produce good uniformity will be described. Successful gas manipulation has the benefit that not only can reaction gases be isolated from each other, but also these gases can be isolated from the surrounding environment to allow for open-air operation. Because there is no containment chamber and operation occurs at atmospheric pressure, S-ALD is well suited to large and ultimately continuous substrates, such as a moving web.

The use of S-ALD to deposit films onto a range of substrates, both rigid and flexible, as well as webs, will be discussed. The ALD process also allows selective film growth by pre patterning substrates with growth inhibitors. These inhibitors can be applied to flexible substrates with conventional printing techniques. By leveraging selective area deposition, we combine the high quality of ALD films with printing-like patterning, all at atmospheric pressure. This combination is likely a key step in enabling high-quality printed electronics onto flexible substrates.

The performance of films deposited by the S-ALD approach will also be presented, functioning as barriers and components in patterned semiconductor devices. In general, performance of S-ALD films in terms of electrical and physical properties are consistent with the published performance of conventional ALD materials.

**5:00pm TF3-MoA10 Metal Oxide and Fluoride ALD Process Development and Optimisation for Large Area Depositions, M.I. Putkonen, Beneq Oy, Finland INVITED**

ALD is a mature technology and globally most of the industrial ALD coating activities are at the moment close to the semiconductors where films are relatively thin. However, there are many industrial areas where substrate sizes can be several square meters and film thicknesses can reach over many micrometers. As a technology ALD does not have issues with thick films. However, the industrial coating system needs to be designed and built for reliable and repeatable processing of thick film stacks. The relative slowness (in nm/h) of ALD can be compensated by optimizing the batch sizes as well as ensure good flow dynamics to obtain fast cycle times. New applications outside semiconductor industry where ALD can possibly be utilized include photovoltaics, diffusion barriers, wear resistant materials and optical coatings aiming to improve competitiveness of existing products and enabling new applications.

Quite often ALD processes are not ideal although films can appear to be uniform at the R&D size substrates. When batch sizes are scaled up to several square meters even small variations in the growth rate or slight

thermal decomposition of the precursors can be detrimental. Therefore process tuning is often needed to fix the small deviations of the processes.

In this presentation different approaches to obtain uniform oxide films are discussed in detail. For example, optical thin film stack structures made by ALD there are several possibilities for high index materials but for low index materials the selection is still more limited. Scaling of the processes for batches up to 5-10 m<sup>2</sup> of total area is required to obtain reasonable throughput. At the same time the deposition cycle should still be kept a well below 3-5 seconds. For example we have made TiO<sub>2</sub> deposition in a large batch consisting of 36 shelves (240x500 mm<sup>2</sup>) double side coating using Beneq P400 A. Batch uniformity over 8 m<sup>2</sup> area was ±2%.

In addition to process optimization to large batches we show preliminary data concerning the deposition of metal fluorides by using novel precursor chemistry based on the traditional metal oxide ALD chemistry using either fluorinated metal β-diketonates or fluorinated hydrocarbons as a fluorine source. According to the RBS film stoichiometry was CaF<sub>2</sub>.03 with oxygen contamination below the detection limit, i.e. below 5 at.%. The refractive index of films deposited at 300°C was 1.43.

## Vacuum Technology

### Room: C1 - Session VT-MoA

#### Pressure, Partial Pressure, and Flow Measurement

Moderator: J. Setina, IMT

**2:00pm VT-MoA1 Investigations on the Dynamic Response of Pirani Gauges, M. Wüest, B. Andreaus, R. Stocker, INFICON, Liechtenstein**

For over 100 years the Pirani sensors measure vacuum pressure from ~5x10<sup>-5</sup> mbar to atmosphere. Pirani sensors are based on heat conduction through gas. Due to this measurement principle the accuracy of Pirani sensors is reduced near atmospheric pressure. Yet many industrial processes use the low cost Pirani sensors for venting applications and the trend is to faster cycle times. Depending on the construction Pirani sensors can display various inaccuracies during rapid pressure changes. This is because the wall temperature measurement used for temperature compensation lags the pressure change. Here we present an investigation to optimize Pirani sensor design for rapid pressure venting applications.

**2:20pm VT-MoA2 Portable Gas Sampling Instrument Capable of Measuring Leak Rates, Volumes, and Pressures without A/C Power, S. Thornberg, J. Brown, Sandia National Laboratories, L. Miller, J. Ithaca, B&W Pantex**

Certain operations (e.g., volume measurement, gas sampling, and leak rate determination) commonly employed in the field of vacuum technology typically require A/C-powered equipment (vacuum pumps, electrometers, computers, etc.) to perform the measurement or operation. However, some hazardous applications require the cessation of A/C-powered operations when certain conditions exist like the presence of a thunderstorm that can generate dangerous voltage spikes from nearby lightning strikes. To alleviate this problem, a new instrument designed and prototyped at Sandia National Laboratories is capable of performing leak tests (greater than 5 x 10<sup>-4</sup> atm cc/s air), measuring the internal volumes of complex manifolds (up to liters in volume), making absolute pressure measurements, and performing gas sampling, all without the use of A/C power. The system is designed to be very easy to use with many pneumatic valves behind the instrument panel that are controlled by simple control valves specifically designed/invented for this application. Other functions this instrument can perform are the generation of a modest vacuum (approximately 10 Torr) and backfilling the system with a user-supplied gas. The system has been prototyped, and production models have been fabricated and are in use on production lines. This presentation will highlight the design and features that enable these operations to be performed without A/C power in an operator-friendly package that is not much larger than a thick briefcase. Extensive qualification testing has been performed using these instruments, and the results will be presented to show the performance and NIST traceability. (Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.)