Impact of Film Thickness and Thermal Treatment on the Excellent Surface Passivation of c-Si by ALD Al2O3 for Solar Cell Applications

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migation of cations or anions across the film's thickness. In this respect, oxygen vacancies seem to play an important role. In this work, HfO2 MIM RRAM cells are elaborated and tested in two electrical modes: voltage sweep mode and constant voltage stress (CVS) mode. The HfO2 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, HfO2 would be an interesting candidate for the RRAM technology. HfO2 films (10 nm) were grown at 350°C by atomic layer deposition (ALD) using alternate cycles of H2O and HfCl4 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 HfO2/Pt interface (absence of PtO oxides). Top gold electrodes (100 nm thick, 2 nm in diameter) were deposited on the HfO2 films by dc sputtering.

The voltage sweep mode shows that HfO2 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/HfO2 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. 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. Foygner, 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 target plasma 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.

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 voltages and fill factors. Alternatively, ALD can be used for photodecide 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 electronic transport and shuttle transport behavior. Advanced designs allow for highly efficient radial charge collection, even from inherently transporting materials. The use of ALD to structure 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 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 recharging 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 Al2O3 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. Griner, 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. LiCoO2 has been the dominant cathode material in LIBs. The instability of LiCoO2 particles comprising the cathode leads to the deterioration of the LIB. Efforts to stabilize LiCoO2 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 Al2O3 ALD grown on LiCoO2 particles dramatically enhances their specific discharge capacity.

After coating the LiCoO2 particles with Al2O3 ALD in a rotary reactor, battery cathodes were prepared and cycled against a Li/Li+ anode near the threshold for 50% Li extraction at 1 C-rate after the first two charge-discharge cycles. A control electrode prepared by a sputtered Al2O3 film was tested for comparison. With respect to the third charge-discharge cycle, the LiCoO2 particles coated with 2 ALD cycles showed a 89% capacity retention after 120 charge-discharge cycles. In comparison, the bare LiCoO2 particles displayed only a 45% capacity retention after 120 charge-discharge cycles.

LiCoO2 particles coated with 6 and 10 Al2O3 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+ diffusion and restricted electron mobility within the insulating Al2O3 ALD layer. We propose two mechanisms by which the Al2O3 ALD may enhance the cycle performance of the LIBs. The Al2O3 film may prevent the LiCoO2 particles from decomposing electrolyte and forming a solid-electrolyte interphase. Alternatively, the Al2O3 film may protect the LiCoO2 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 Al2O3 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) Al2O3 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 Al2O3 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 Al2O3 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 strain-induced reduction of doping concentration and freedom in the design of optimal front passivation/antireflection schemes. To activate the Al2O3 surface passivation a post-deposition anneal is required, but also the thermal budget during the plasma enhanced chemical vapor deposition of an a-SiN_x:H capping layer was found sufficient to activate the passivation. Although an anneal effect can be observed in a large temperature range.
passivation/antireflection stacks against an industrial "firing" process paper demonstrate the suitability of thin ALD-synthesised Al2O3 passivation
demonstrate the relative stability of Al 2O3 and Al 2O3/
screen printed solar cells, thermal stab ility is required. In this paper we
(350 - 600 °C) the optimal post-deposition anneal temperature window
films for large scale photovoltaic applications.
To date much of the usefulness of ALD has been demonstrated in enclosed
patterning, attributes that make it an ideal tool for upcoming needs in
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 reagents 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 prepatternning substrates with growth inhibitors.
These inhibitors can be applied to flexible substrates with conventional
printing techniques. By leveraging selective area deposition, we combine the
two advantages of ALD: high-quality films with printing-like patterning, all at
atmospheric pressure. This combination is likely a key step in enabling
high-quality printed electronics on 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.

4:20pm TF3-MoA8 Spatial ALD: Fabrication of Films and Devices at
Atmospheric Pressure, D.H. Levy, S.F. Nelson, M.S. Barbery, L.W. Tutt,
R.S. Kerr, G. Zwaldio, 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 reagents 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
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high-quality printed electronics on 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
depth 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 m2 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 TiO2 deposition in a large
batch consisting of 36 shelves (240x300 mm2) double side coating using
Beneq P400 A. Batch uniformity over 8 m2 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 CaF2.03 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
~5×10−10 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 most Pirani sensors for venting applications and the trend is to
cycle faster 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. Ibbara,
B&K 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 × 10−10 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.)