DS 49: Atomic Layer Deposition

Time: Friday 9:30–12:30 Location: CHE 91

Invited Talk DS 49.1 Fri 9:30 CHE 91

Synthesis, Characterization, and Application of Tunable Resistance Coatings — •Jeffrey W. Elam — Argonne National Laboratory, Argonne, IL, USA

We used atomic layer deposition (ALD) to synthesize nanocomposite coatings comprised of M:Al2O3 where M= W or Mo using alternating exposures to trimethyl aluminum (TMA) and H2O for the Al2O3 ALD and alternating MF6/Si2H6 exposures for the metal ALD. By varying the ratio of metal and the Al2O3 ALD cycles, we can tune precisely the resistance of these coatings over a very broad range from 1012-105 Ohm-cm. These films exhibit Ohmic behavior and resist breakdown even at high electric fields of 107 V/m. Moreover, the self-limiting nature of ALD allows us to grow these films inside of porous substrates and on complex, 3D surfaces. To investigate the growth mechanism we employed in situ QCM and FTIR absorption spectroscopy studies. For the Mo:Al2O3 films, QCM showed that the Mo ALD inhibits the Al2O3 ALD and vice versa. Surprisingly, FTIR revealed that the reducing agent for the Mo is not the Si2H6, but rather the TMA exposure from the subsequent Al2O3 ALD cycle. Cross sectional TEM revealed the film structure to be metallic nanoparticles (˜1 nm) embedded in an amorphous matrix. We utilized these coatings to fabricate large-area microchannel plates for large-area photodetectors, and as charge drain coatings in MEMS devices for a prototype electron beam lithography tool.

DS 49.2 Fri 10:00 CHE 91

ALD on Multi-Stacked Polystyrene Opals for Thermal Barrier Coatings — •Robert Zierold[1], Martin Waleczek[1], Josep M. Montero Moreno[1], Roman Kubrin[2], Hooi Sing Lee[3], Alexander Petrov[3], Manfred Eich[3], Gerold A. Schneider[2], and Kornelius Nielsch[1] — [1]Institut für Angewandte Physik, Universität Hamburg — [2]Institut für Keramische Hochleistungswerkstoffe, Technische Universität Hamburg-Harburg — [3]Institut für Optische und Elektronische Materialien, Technische Universität Hamburg-Harburg

Thermal Barrier Coatings (TBC) are used to protect thermally highly loaded metallic components, such as turbine blades in gas engines, from excessive heat and thus prolong the life time of the component.

Herein, we present a novel synthesis route for multi- stacked, photonic crystals made of titania and zirconia revealing a multi-bandgap structure in the infrared, a prerequisite for a TBC. Sequential self-assembly of monodisperse polystyrene particles with different diameters between 315 and 756 nm results in multi-stacked direct opals. The polymer template is then conformally molded by low temperature ALD—with its capabilty to coat complex nanostructures without shadowing effects due to its self-limited nature—processes with TiO_2 and ZrO_2 from the precursors titanium isopropoxide (TTIP) or tetrakis(ethylmethylamino) zirconium (TEMAZ), respectively, and H_2O. Subsequently, calcination of the polystyrene leads to high quality photonic crystals. Optical characterization of the tailor-made samples reveals reflectance peaks in the near infrared corresponding to the different stop-gaps of the individual layers with different periodicities.

DS 49.3 Fri 10:15 CHE 91

New opportunities with Plasma enhanced atomic layer deposition (PE-ALD) of oxides — •Massimo Tallarida[1], Karsten Henkel[1], Hassan Gargouri[2], Jörg Häberle[1], Bernd Gruska[2], Matthias Arens[2], and Dieter Schmeisser[1] — [1]Brandenburg University of Technology, Konrad Wachsmann Allee, 17, 03046, Cottbus Germany — [2]Sentech Instruments GmbH, Schwarzschildstrasse 2, 12489 Berlin, Germany

Thermal Atomic layer deposition (T-ALD) of oxides is obtained by the pulsed alternation of a metal precursor and an oxygen source, typically H_2O or O_3, and the reactions leading to ALD are thermally activated. With plasma enhanced ALD (PE-ALD), instead, the oxygen source is represented by an oxygen-containing plasma. The higher reactivity of the plasma-generated species extend the capabilities of ALD: improved film quality and increased flexibility in process conditions, such as growth at low temperature, are typical advantages of PE-ALD over T-ALD. We report on results on the preparation of thin (<100 nm) aluminum oxide (Al_2O_3) films on silicon substrates using T-ALD and PE-ALD in the SENTECH SI ALD LL system. Films were deposited in the temperature range between room temperature (RT) and 200°C. We characterized the films with spectroscopic ellipsometry (thickness, refractive index, growth rate) over 4" wafers and with X-ray photoelectron spectroscopy. All films resulted in a high degree of homogeneity, independent of the deposition temperature. Investigations with capacitance-voltage and conductance-voltage measurements showed a very low interface states density for the PE-ALD films.

DS 49.4 Fri 10:30 CHE 91

X-ray linear dichroism in atomic layer deposited Titanium dioxide layers — •Chittaranjan Das, Massimo Tallarida, and Dieter Schmeisser — Applied physics and sensors,BTU Cottbus, Germany

Among the various metal oxides TiO2 has been investigated because of its wide range of applications in various fields such as self-cleaning, photocatalysis, solar cell, water splitting, bio-implants. In order to increase its efficiency in water splitting and solar cell energy conversion, it is necessary to understand the crystal structure and electronic properties of thin films. Generally the process of synthesis may modify the electronic properties of TiO2. In the present work we show X-ray linear dichroism (XLD) measurements of TiO2 thin films of different polymorphs. Titania thin films were produced by atomic layer deposition (ALD) and were characterized in-situ with X-ray photoelectron and absorption spectroscopy at synchrotron radiation center BESSY-II. We found that that all titania phases show XLD at Ti-L and O-K edges, but the intensity of XLD is different for different phases. We discuss our data in terms of the partial density of states.

DS 49.5 Fri 10:45 CHE 91

Control of thickness of SiO2 interfacial layer for photocatalytic water splitting on Si photocathodes — •Chittaranjan Das, Massimo Tallarida, and Dieter Schmeisser — Applied physics and sensors,BTU Cottbus, Germany

Silicon with a band gap of 1.1eV is an excellent candidate for visible photocatalytic water splitting. But p-type Si has a low quantum yield and are less efficient for water splitting [1]. It has been shown that preventing oxidation of Si surface can shift the onset potential for water reduction by about 300mV towards more positive [2]. We investigated in detail the influence of the SiO2 layer thickness on the onset potential for water splitting on Si photocathodes: we used p-type Si substrates covered with SiO2 layers of varying thickness. Then, we deposited a thin TiO2 film on using atomic layer deposition (ALD) to inhibit Si oxidation during the electrochemical experiment. In this way we could shift the onset potential up to 200mV, depending on the SiO2 thickness.

[1]E. L. Warren, S. W. Boettcher, M. G. Walter, H. A. Atwater, and N. S. Lewis: J. Phys. Chem. C 115 (2011) 594. [2]B. Seger, Anders B. Laursen, P. C. K. Vesborg, T. Pedersen, O. Hansen, S. Dahl, I. Chorkendorff, Angew. Chem. Int. Ed. 2012, 51, 9128 *9131

Coffee break (15 min)

DS 49.6 Fri 11:15 CHE 91

Atomic layer deposition of $Sr_xTi_{1-x}O_y$: Stoichiometry variation and layer characterization — •Solveig Rentrop[1], Barbara Abendroth[1], Hartmut Stöcker[1], Ralph Strohmeyer[1], Jura Rensberg[2], Juliane Walter[1], and Dirk C. Meyer[1] — [1]Institut für Experimentelle Physik, TU Bergakademie Freiberg — [2]Institut für Festkörperphysik, Universität Jena

Resistance switching of metal-insulator-metal (MIM) capacitor structures is one of the possible routes for future non-volatile random access memories. A promising ternary dielectric for MIM devices is $Sr_xTi_{1-x}O_y$. In this material, the layer composition is found to determine dielectric and optical properties as well as the band gap.

Here, we present studies on the atomic layer deposition of amorphous $SrTiO_3$ from $Sr(iPr_3Cp)_2$, $Ti[N(CH_3)_2]_4$ and H_2O at substrate temperatures of 300 °C and 320 °C, resp. By changing the Sr/Ti pulse ratio, we are able to tailor the stoichiometry from stoichiometric to Sr or Ti excess. The layer composition is obtained from X-ray fluorescence spectroscopy and Rutherford backscattering. The tuned band gap value is determined by using a Tauc plot of the ellipsometric absorption coefficient. Moreover, we investigated the dependencies of optical constants, layer density and surface morphology on the layer

composition.

Carbon incorporated during deposition increases the leakage current. By X-ray photoelectron spectroscopy the carbon content was measured after Ar ion cluster sputtering. The results show that we are able to deposit carbon free $Sr_xTi_{1-x}O_y$ layers for different Sr/Ti ratios.

DS 49.7 Fri 11:30 CHE 91

Ta_2O_5 by thermal-activated ALD — •Marcel Junige[1], Ralf Tanner[1], Christian Wenger[2], Grzegorz Lupina[2], Matthias Albert[1], and Johann W. Bartha[1] — [1]Technische Universität Dresden — [2]IHP GmbH, Frankfurt (Oder), Germany

Ta_2O_5 is a dielectric material with a comparably high permittivity as well as refractive index and thus gains interest for several electronic or optical applications. Atomic Layer Deposition (ALD) is a vacuum technique, which enables the coating of complex-shaped surfaces by alternatively applying self-terminating physicochemical reactions.

We investigated the thermal-activated ALD using the halogen-free metal-organic precursor TBTEMT and ozone gas (O_3) as co-reactant at an actual deposition temperature of 215 °C. We pre-heated a Silicon sample for 30 min at the respective process conditions and pre-cleaned the initial surface for 180 s in O_3 in order to remove ambient carbon contaminations prior to the ALD.

In-situ real-time Spectroscopic Ellipsometry with a highest possible sampling rate of ca. 1 data point/s confirmed a timewise saturation of the TBTEMT adsorption and of the subsequent ligand removal. An ellipsometric multi-time analysis of a deposition run with 100 ALD cycles determined the homogeneous growth per cycle around 0.64 Å/cycle, the refractive index at 500 nm wavelength around 2.1 and the Tauc optical band gap around 4.3 eV, indicating an amorphous phase. In-vacuo X-ray Photoelectron Spectroscopy revealed a Ta_2O_5 film of high purity with a tantalum-to-oxygen ratio of (29:71) at.% as well as carbon and nitrogen contaminants below the detection limit.

DS 49.8 Fri 11:45 CHE 91

Simulation of the deposition and growth of nano-crystalline MgF2 films via the low-temperature atom beam deposition method — Sridhar Neelamraju, •Johann Christian Schön, and Martin Jansen — MPI for Solid State Research, D-70569 Stuttgart

We model the deposition of magnesium difluoride (MgF2) clusters on a sapphire substrate and the subsequent growth of ordered MgF2-phases via the low-temperature atom beam deposition method. For the modeling procedure we use empirical potentials to describe the interactions within the substrate and the MgF2 deposit, and between the deposited atoms and the substrate. First, we established that primarily MgF2- and Mg2F4-clusters form in the gas phase, and thus the deposition could be described by the adsorption of such molecules on the substrate at low temperatures [1]. Next, the deposited MgF2-layers are annealed, and the structure of the resulting amorphous and nano-crystalline compounds is analyzed and compared with the results (pair distribution functions) of the experimental deposition [2]. We show that the appearance of an (at standard conditions) kinetically unstable CaCl2-type phase in the experiment [3] is due to the concurrent existence of a nano-crystalline CdI2-type modification of MgF2 predicted in earlier theoretical studies [4].

[1] S. Neelamraju et al., J. Chem. Phys. 137:194319 (2012); S. Neelamraju et al., Phys. Chem. Chem. Phys. 14:1223 (2012) [2] X. Mu et al., J. Appl. Cryst. 46:1105 (2013) [3] A. Bach et al., Inorg. Chem. 50:1563 (2011) [4] M.A.C. Wevers et al., J. Solid State Chem. 136:223 (1998)

DS 49.9 Fri 12:00 CHE 91

Structural changes in HfO_2 thin films: thickness and doping dependence — •Simone Brizzi[1], Massimo Tallarida[1], Christoph Adelmann[2], Lars-Ake Ragnasson[2], Sven Van Elshocht[2], and Dieter Schmeisser[1] — [1]Brandenburg University of Technology, Konrad-Wachsmann Allee 17, 03046 Cottbus, Germany — [2]Imec, Kapeldreef 75, B-3001 Leuven, Belgium

In this work we show results regarding MOCVD and ALD HfO_2 as well as Al-doped HfO_2. We use Synchrotron Radiation Photoemission Spectroscopy (SRPES) to determine Hf/O atomic ratios and X-ray Absorption Spectroscopy (XAS) to investigate the electronic properties related to their crystallization. MOCVD films are synthesized at temperatures ranging from ambient to 400°C and show structures from completely amorphous to monoclinic. ALD films are amorphous as deposited, and can crystallize after post-deposition anneal depending on the percentage of Al-doping. We discuss PES results in order to determine how close to stoichiometry the Hf/O atomic ratios of the films are, as well as the doping level. From XAS data, instead, we can point out how orbital hybridizations are related to structural and physical properties.

DS 49.10 Fri 12:15 CHE 91

Charging effect in HfO2 films deposited on SiO2/Si by atomic layer deposition — •Silma Alberton Correa, Simone Brizzi, Massimo Tallarida, and Dieter Schmeisser — Department of Applied Physics and Sensors, Brandenburg University of Technology, 03046 Cottbus, Germany

Thin films of hafnium oxide (HfO2) deposited by atomic layer deposition (ALD) have been studied extensively as a high-k replacement for the SiO2 gate in field effect transistors. The use of ALD process allows one to grow homogeneous thin films at low temperatures with a precise control of thickness [1]. Some important electrical considerations for the application of a high-k dielectric include the presence of fixed charge (Qf) and charge trapping in the dielectric. For instance, in the case of Al2O3 thin films deposited on Si, the thickness of the interfacial SiO2 layer was identified as a key fundamental parameter determining Qf [2]. A similar trend can be also expected in HfO2/Si structures. Therefore, in this work, we proposed an in situ evaluation of photon induced charge trapping in HfO2 films deposited on SiO2/Si structures. For that, tetrakis-di-methyl-amino-hafnium (TDMAHf) and H2O were employed as precursors to deposit HfO2 films on SiO2/Si samples with variable thickness of the SiO2 interlayer. Measurements were performed by Synchrotron Radiation Photoemission Spectroscopy (SRPES). Results indicated that the charging process is dependent on the thickness of the SiO2 interlayer and on the quality of the HfO2 film. [1] M. Leskelä and M. Ritala, Thin Solid Films 409, 138 (2002). [2] G. Dingemans et al., J. Appl. Phys. 110, 093715 (2011).