ALD Applications
Room Evergreen Ballroom & Foyer - Session AA5-TuP
Emerging Applications Poster Session

AA5-TuP-1 Bottom up Stabilization of Perovskite Quantum Dots LED via Atomic Layer Deposition*, **Rong Chen**, K Cao, Q Xiang, B Zhou,* Huazhong University of Science and Technology, China

Flexible displays are becoming the most promising and attractive techiques in the future. Quantum dots(QDs) have attracted great attentions due to their excellent optical properties, such as tunable wavelength, narrow emission, long carrier diffusion length, and high photoluminescence quantum efficiency. These properties make QDs the most promising optical materials for flexibles displays. However, as the instability of QDs based light emitting diodes limits their practical applications, QDs based LEDs are still under laboratory developments.

In this talk, we will discuss ALD based protection approaches from nanoscale QDs passivation to macroscopic encapsulation to improve the stability and boost its performance of QD-LEDs. First, the low-temperature selective ALD method has been developed for defects elimination. This protection method can preserve QDs monomers without damaging surface ligands and improving the quantum efficiency. For the QD light emitting layers, voids are formed during the stacking which may induce instability from electric, heat transfer. The ALD based filling process has been developed to improve charge transport within the layer. To study the surface interaction mechanisms of ALD precursors with the QDs layer, in-situ characterizations such as quartz crystal microbalance (QCM), infrared spectrometer (IR) are utilized to monitor the ALD process and the interactions with QDs layers. The oxides filling between quantum dots could reduce the carrier transport barrier and enhance carrier injection. Finally, it is imperative to develop efficient and ultrathin encapsulation to improve the stability towards ambient environments and flexibility of displays. Ultrathin multi-stacking films are designed and fabricated based on the combination of spatial ALD, molecule layer deposition and chemical vapor deposition. Such composite films could greatly enhance the water and oxygen resistance, while retain low stress and flexibility of the devices. It has demonstrated that the ALD approaches are versatile and useful for several fabricating steps in flexible QDs displays.

AA5-TuP-2 ALD Bilayers for X-ray Windows with Long Lifetime*, **Agnieszka Kurek**, Y Shu,* Oxford Instruments Plasma Technology*; H Knoops,* Oxford Instruments Plasma Technology, UK*; A O'Mahony, O Thomas, R Gunn,* Oxford Instruments Plasma Technology*; Y Alivov, C McKenzie, B Grigsby, A Degtyaryov,* Oxford Instruments X-ray Technology

X-ray-emitting devices require a window transparent to low energy X-rays while keeping the device at vacuum. Polycrystalline Be windows are often used since they have high X-ray transparency due to the low atomic number of Be. However, Be is sensitive to environmental moisture and shows degradation over time via two routes. Firstly, ambient gas can penetrate the Be window through the crystalline grain boundaries deteriorating the vacuum. Secondly, water vapour reacts with Be material causing corrosion and forming an oxide layer which can delaminate and reduce the window thickness over time. The window can become so thin it can no longer hold a vacuum inside the X-ray device – effectively ending the lifetime of the tube. Here, we show how the application of conformal, pinhole-free ALD bilayer coatings can extend the lifetime of X-ray windows more than five times with negligible influence on X-ray transmittance.

We have developed and patented (US20180061608A1) a robust solution using a combination of Al_2O_3 and TiO_2 less than 200 nm in thickness. The ALD coatings were deposited in an Oxford Instruments Plasma Technology FlexAL™ system at 350 °C. Thermal Al_2O_3 (~40 nm) was used as an adhesion layer, followed by in-situ deposition of thermal TiO_2 (~80 nm) as a harder, protective layer, using trimethylaluminum and tetrakis(dimethylamino)titanium, respectively. The relatively low atomic numbers of Al and Ti mean that the maximum allowed film thickness to maintain clarity of the X-ray spectra is 800-1000 nm, which is much higher than the used thickness. This window coating is an effective moisture barrier and attenuates the transmitting X-rays by less than 5 % compared to the attenuation of an uncoated window. Importantly, the ALD coating does not contaminate the output X-ray spectra. No fluorescence contamination of Al and Ti could be detected. The lifetimes of ALD coated windows were compared with that of uncoated window by determining how long they could sustain ultra-high vacuum. For all sixteen coated samples, the windows survived the test at least 5 times longer and, in many cases, >15 times longer.

The ALD coating of the X-ray windows increases lifetime of X-ray emitting equipment by more than five times minimising specialist maintenance. The excellent conformality of ALD is furthermore expected to help close off grain boundaries present in the Be windows which can be up to 100 nm deep and could otherwise be pathways for gas diffusion into the vacuum of the system. Future options include making the coating conductive as a further advantage for X-ray equipment.

AA5-TuP-3 ALD for 3D Nano MEMS Applications*, **Dorothee Dietz**,* Fraunhofer Institute for Microelectronic Circuits and Systems IMS, Germany

In the area of MEMS and nano sensor structures, the ALD becomes ever more important. Because of the highly isotropic and highly conformal deposition method, ALD is the best choice for structures with large aspect ratios or structures with complex cross sections. Moreover it is possible to deposit several different materials in the same tool, so that the functionality of the material can be tuned by stacks or doping as good as possible. Because of the low deposition temperature, ALD can be applied in post-CMOS-processes.

ALD techniques enable the fabrication of free standing 3D structures as follows: In a first step, a sacrificial layer is deposited onto a (CMOS-) substrate. Small holes or trenches are etched through it as pillars and an ALD layer is deposited and structured. In the end, the sacrificial layer is removed. This technique can be used e.g. for the processing of different gas sensors or for realizing 3D multi electrode arrays (MEA).

The first type of gas sensor, which is based on conductometric semiconductor gas sensing, operates with metal oxide (MOx) nano wires, 350 nm in width and 150 µm in length. The metal oxide (e.g. ZnO or SnO_2) is used as a functional layer but also for forming the 3D structure. Because the metal oxides need to be heated for gas sensitivity, a heater is realized with the same technology as described above. In this case, Ru, TiN or TiAlCN, is used as heater material, deposited also by ALD.

The second gas sensor is acting as a nano pellistor. The heater has to be a free standing 3D structure, because the sensor has to be thermally decoupled from the substrate underneath. All materials are deposited with ALD to achieve the high aspect ratio and because of the material properties. The heater consists of Ru, the surrounding isolation layer can be Al_2O_3 and the catalytic layer is made of Ru again.

To increase the sensitivity of the sensor, the surface of the catalyst can be increased by using a porous Al_2O_3 layer instead of a solid one. A porous Al_2O_3 layer can be achieved by doping it during the ALD in a first step e.g. with ZnO and by a selective etching of the doping material in a second step.

Another application for using this technology is processing 3D MEA. They can penetrate biological cell membranes for measuring intracellular electrical signals directly. As a conductive and biocompatible material, Ru is used for these electrodes. They are 200 nm in diameter and a few microns in height. With an additional step, the diameter at the tips can be reduced so that they can penetrate membranes easier, without the risk of destroying them.

AA5-TuP-4 Tribological Properties of Plasma Enhanced Atomic Layer Deposition TiMoN*, **Mark Sowa**,* Veeco-CNT*; A Kozen,* U.S. Naval Research Laboratory*; B Krick, N Strandwitz,* Lehigh University

In our previous study, we demonstrated a tertiary plasma enhanced atomic layer deposited transition metal nitride (TiVN) with exceptional wear rates and friction coefficients. We have extended that work with an investigation of another tertiary transition metal nitride system, $Ti_xMo_yN_z$. For films deposited at 250°C and 300W on a Veeco CNT G2 Fiji PEALD system, we have demonstrated how the ratio of TiN:MoN cycles (1:0, 3:1, 1:1, 1:3, 0:1) provides linear control of the Ti:Mo in the resulting film. Through application of an 13.56MHz RF substrate bias (0-250V) during the plasma step, ion bombardment energy of the substrate can be varied, providing a means for tweaking the films physical and chemical characteristics which in turn are shown to impact the resulting film's tribological properties. As PEALD metal nitrides have broader interest than wear layers and to gain insights on the interrelationships of the mechanical properties, the processing details, and other film properties, we also report on the resulting film composition/impurities, density, crystallinity, optical properties, resistivity, and morphology.

AA5-TuP-5 Thickness Optimization of Alumina Thin Film for Microchannel Plate Detector, ***Baojun Yan**, S Liu,* Institute of High Energy Physics, Chinese Academy of Sciences, China

Conventional lead glass microchannel plate (MCP) detector has been used in a variety of applications. The MCP performance can be improved by coating high secondary electron emissive layers, such as alumina (Al_2O_3) and magnesium oxide (MgO), via atomic layer deposition (ALD). In this poster, the alumina thin films with varied thicknesses were deposited by ALD on polished Si substrates and MCPs, respectively. The secondary electron yield (SEY) of the alumina thin films on silicon substrate were measured by pulsing electron beam. The MCPs used in our experiment had a high length to diameter ratio ~80:1 and worked in photon counting mode. The optimal thickness of alumina was obtained through comparative study the MCP performance before and after coating. In addition, the DC gain variation as a function of total charge per unit area Q (C/cm^2) were investigated.

AA5-TuP-6 Optical Coatings Deposited on Nonlinear Crystals by Atomic Layer Deposition, ***Ramutis Drazdys**, R Buzelis, M Drazdys,* Center for Physical Sciences and Technology, Lithuania

Growing requirements for optical coatings deposited on temperature and environment sensitive crystals force to look for alternatives to conventional physical vapor deposition technologies. KDP, DKDP, $LiNbO_3$ are nonlinear optical materials that have been difficult to coat due to specifics of surface adhesion and thermal properties. Atomic layer deposition (ALD) is widely used in nanotechnology and semiconductor devices [1] and recently attracted more interest in manufacturing of optical components [2,3]. The main goal of our research was to develop antireflection (AR) coatings on nonlinear crystals with high laser induced damage threshold (LIDT). HfO_2 and Al_2O_3 thin layers deposited using TDMAH and TMA precursors and H_2O as oxidant by Savannah 200 system from Ultratech at low temperature (<100°C) were investigated. Experimental deposition processes of HfO_2 and Al_2O_3 thin film 150 nm thickness single layers were made at temperatures from 40°C to 100°C with different pulse and purge time duration parameters. To prevent the HfO_2 layer crystallinity we used the nanolaminate concept [4] where each HfO_2 layer with thickness of 20 nm incorporate a certain number of Al_2O_3 monolayers. Growth rates, dependency on precursor pulse and chamber purge durations were determined by using quartz crystal monitoring and optical spectra data. Refractive index and absorption dispersions were determined. Setup with the Nd:YAG laser (from EKSPLA co.) generating pulses with repetition rate 15 Hz, pulse duration ~3 ns was used for LIDT measurements. The investigation of the optical transmission and reflection of produced thin layers allowed to determine optical loses in UV region. These results gave us the possibility to choose optimal technological parameters for AR coating formation on nonlinear crystals substrates. The following design of experimental AR coating was selected: substrate / 75nm HfO_2 / 200nm Al_2O_3. In previous investigations determined growth rates per pulse cycle were used for layers thickness control. The same coating design was used to manufacture AR coatings by IBS and e-beam evaporation. The LIDT measurements of AR coatings demonstrated comparable or higher damage levels for ALD coatings.

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AA5-TuP-7 Atomic Layer Deposition of Nickel and Nickel Oxide Thin-Films for Astronomical X-ray Optics Applications, ***Hossein Salami**, A Uy, A Vadapalli,* University of Maryland*; V Dwivedi,* NASA Goddard Space Flight Center*; R Adomaitis,* University of Maryland

Nickel and nickel oxide films have optical, electrical and magnetic properties that when combined with good chemical stability makes them attractive for many applications. Nickel oxide is a p-type semiconductor that can be used as a transparent electrode, or in manufacturing nonvolatile resistance random access memories, or for chemical sensing purposes. In its pure form, nickel film can be used as adhesion layer for copper interconnects [1]. Because of its X-ray reflecting property, another application of pure nickel film is in multi layer coatings for X-ray optics [2,3].

In this talk, we will discuss atomic layer deposition process for Ni and NiO thin-films using two different metal precursors, nickelocene and nickel acetylacetonate, in combination with ozone as the oxygen source. We will present two different routes to depositing metallic Ni: direct metal deposition or metal-oxide deposition with a subsequent reduction step. Our initial results confirm the deposition of NiO film and its reduction using molecular hydrogen predicted by thermodynamic analysis. Advantages of each route and their effect on the properties of the final product will be presented. Furthermore, specifically for astronomical applications, roughness and X-ray reflectivity of the prepared thin-films and the conformal coating of high aspect-ratio X-ray optics will be discussed in detail.

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AA5-TuP-8 Atomic Layer Deposition and Chemical Vapor Deposition of Zirconium Boride for Various Applications: New Work Function, Barrier Metal, Hard Mask and Area Selective Deposition, ***Jun-Hee Cho**, J Park, W Chae, J Park, S Lee, M Kim,* DNF Co. Ltd, Republic of Korea

Zirconium boride is an attractive material for microelectronic, hard coating, and other applications. Because, it has high melting point (3040 °C), a high mechanical hardness, excellent wear properties, and excellent corrosion resistance toward molten metals [1]. In this work, we talk about new applications of ZrB_x for new work function, barrier metal, hard mask and area selective deposition (ASD). ZrB_x film have been deposited both by sputtering and chemical vapor deposition (CVD) routes. An inherent shortcoming of sputtering is its non-conformal nature. In conventional CVD of ZrB_x films, the $ZrCl_4$ and BCl_3 precursors are reduced with H_2, but the incorporation of residual chlorine atoms has proven to be detrimental to film properties. In addition, thermal atomic layer deposition (ALD) was not studied in detail [2, 3]. In this study, ZrB_x films have been deposited by thermal ALD and CVD process using single precursor $Zr(BH_4)_4$ for new work function, barrier metal, hard mask and ASD. The work function of deposited ZrB_x film by ALD at 250 to 350 ℃ is 3.93 to 3.96 in the bulk and 3.86 to 3.64 in the surface respectively (Fig. 1). The step coverage was showed 100 % in aspect ratio 19:1 pattern at 250 ℃(Fig. 2). The resistivity of ZrB_x film was about 450 μΩ ㎝ and showed amorphous structure.

The deposited ZrB_x film on Si(100) by CVD is sufficient to prevent copper diffusion into silicon during a 600 °C anneal for 30 min (Fig. 3, 4). The ZrB_x film on SiO_2 by CVD has a very slow etch rate for CF_x, while a very fast etch rate for BCl_3 (Fig. 5). The wet etch was not showed in 0.5% HF solution (Fig. 5). The ZrB_x film has resistance to oxygen. ASD of $Zr(BH_4)_4$ was showed selectivity of W metal and SiO_2 substrate for ZrB_x film (Fig. 6). The deposited ZrB_x films were showed amorphous phase. The possibility of applying a new work function, barrier metal, hard mask and ASD is expected.

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AA5-TuP-9 Comparative Study of $Mo_{1-x}W_xS_2$ Alloy Gas Sensor by Atomic Layer Deposition, ***Minjoo Lee**, Y Kim, J Park, H Kim,* Yonsei University, Republic of Korea

Two-dimensional (2D) Transition metal dichalcogenides (TMDCs) are a layered structure, which stacked via weak van der Waals interaction. 2D TMDCs have attracted great attention because of their remarkable electronic and optoelectronic properties such as indirect-to-direct bandgap transition with reducing layers, superior electrical properties and strong spin-orbit coupling. Furthermore, recently the 2D TMDCs have shown the potential as a gas sensing material due to their very large surface-to-volume ratio, semiconducting property, and low power consumption. Thus, the WS_2 or MoS_2 that is the one of the most popular TMDCs has been studied for its gas sensing properties and demonstrated an excellent response to various gas molecules, such as nitrogen dioxide (NO_2), ammonia (NH_3), acetone, etc. However, due to the difficulty of uniform synthesis of 2D TMDCs and the highly sensitive characteristic of these TMDCs gas sensors, there are few researches about direct comparative study of each materials. Although only a theoretically calculated studies were reported, the result is often different according to adapted model.

In this study, layer controlled 2D MoS_2 and WS_2 synthesized with $Mo(CO)_6$ and $W(CO)_6$ and H_2S gas as precursors and a reactant using ALD in same equipment under similar conditions. Furthermore, we synthesized $Mo_{1-x}W_xS_2$ alloys using ALD super-cycle and confirmed that W composition in alloys can be controlled by changing super-cycle configuration. Synthesized 2D TMDCs were fabricated for gas sensors for comparison of gas sensing property and It showed different response and response time according to composition in alloy.

AA5-TuP-10 Fabrication of High-Aspect-Ratio Nanometric Gold Gratings*,*
O Makarova, Creatv MicroTech Inc*; **Ralu Divan**, L Stan,* Argonne National Laboratory*; C Tang,* Creatv MicroTech Inc

High-aspect-ratio gold gratings have broad applications in x-ray optics, and their quality and aspect ratio strongly affect the quality of the generated images. To fabricate the gratings, two key technological challenges must be addressed: (i) creating a high-aspect-ratio trenches with smooth vertical walls, and (ii) filling the trenches uniformly with gold.

We report fabrication of 450 nm half-pitch gold gratings with an aspect ratio of 26 using laser interference lithography (LIL), reactive etching (RIE), atomic layer deposition (ALD), and gold electroplating techniques. In the first step, gratings are patterned on the resist/chromium coated silicon wafer *via* LIL. Then, the chromium, which served as a hard mask for silicon etching is etched using RIE. This step is followed by cryogenic RIE to create deep trenches in silicon. Then, a platinum seed layer is deposited by ALD, and finally the mold is electroplated with gold.

RIE of high-aspect-ratio dense and narrow trench/wall structures of gratings imposes significantly more difficulties than the etching of isolated narrow lines or trenches, since the undercut and the negative taper can damage the thin walls. High-aspect-ratio nanoscale silicon gratings were obtained by carefully tuning all etching parameters (Figure 1a).

A continuous, conductive and conformal seed layer is essential for uniform electroplating. We performed ALD of platinum as a seed layer. To improve platinum adherence, a 10 nm alumina adhesion layer was deposited by ALD as well. The high-exposure platinum ALD was optimized to assure conformal coating of the high-aspect-ratio trenches. The nanometric trenches were filled with gold *via* conformal electroplating, when plating occurred from all surfaces. The method has an advantage of much shorter electroplating time, compare to bottom-up plating technique. However, it is challenging to avoid voids formation due to prematurely trench sealing. and achieve uniform plating over the entire trench depth because of the gold ions depletion inside the narrow and deep trenches (Figure 1b).

Use of the Center for Nanoscale Materials, an Office of Science user facility, was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

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