ALD for Manufacturing
Room On Demand - Session AM2
Spatial/R2R/Fast ALD

AM2-1 Surface Modification and Stabilization of Photoluminescence Perovskite Nanocrystals via Atomic Layer Deposition*, Y. Jing,* Huazhong University of Science and Technology, China*; K. Cao,* ***Rong Chen****,* State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China

Photoluminescence perovskite nanocrystals (NCs) have shown significant potential in optoelectronic applications in view of their narrow band emission with high photoluminescence quantum yields (PLQYs) and color tunability. However, their poor stability in light, heat and water environments still hinders practical applications in optoelectronic and bioimaging fields due to their ionic character. Atomic layer deposition (ALD) has been developed as an attractive method to stabilize the crystal structure of perovskite NCs through encapsulation and surface passivation. In this presentation, several stabilization methods through ALD are introduced. First, a low-temperature Al2O3 ALD process was developed to enhance the stability of CsPbBr3 quantum dots-silica sphere in light, water and heat, which originated from the crystal structure stabilization after ALD coating. Nonetheless, a significant photoluminescence (PL) quenching of NCs was typically observed upon Al2O3 ALD. Accordingly, a specially designed ALD reactor integrated a FTIR spectrometer was exploited, which enabled in-situ characterizations to investigate ligands exchange and evolution during deposition after each precursor dosing. It was found that the surface chemical reaction between ALD precursor and capping oleic acid (OA) ligands led to reorganization of OA ligands that increased surface trap sites, leading to PL quenching. Based on the reaction mechanisms observed, a hybrid passivation strategy was developed to simultaneously enhance the photoluminescence quantum yield and the stability of perovskite NCs by two-step modification with surface halogen replenishment and ALD. Consequently, the PL quenching was avoided and the perovskite NCs/Al2O3 nanocomposites exhibited exceptional stability against water, light and heat. Our work provides a versatile method for preparing ultrastable perovskite NCs through ALD method and significantly improves their potential in LED illumination and backlight displays.

AM2-4 Influence of Reactor and Pattern Geometry on Atomic Layer 3D Printing*, **Ivan Kundrata**, M. Plakhotnyuk,* ATLANT 3D Nanosystems, Denmark*; J. Bachmann, M. Barr, S. Tymek,* Friedrich-Alexander Universität Erlangen-Nürnberg, Germany*; P. Brüner,* IONTOF GmbH, Germany

As additive manufacturing in its various forms is shifting the paradigm of traditional manufacturing, the same space opens in the field of thin film deposition. Atomic layer deposition is, due to its inherent separation of reactions, uniquely suitable for adaptation into a 3D printer. In fact, the concept of spatial atomic layer deposition, which can be considered as a precursor for 3D atomic layer printing, goes all the way back to 1974.[1] Despite the many challenges of creation and miniaturization of spatial ALD reactors, atomic layer 3D printing was successfully proved as a concept recently.[2,3]

However, for the best performance of atomic layer 3D printing, the influence of geometry of both the reactor and the pattern being printed has to be examined. Generally, due to the necessary spatial separation of precursor and reactant, edge effects are necessarily present. Moreover, deviations from the perfect printing geometry cause additional line edge effects and selectivity defects.

In this study, we created a general theoretical model of effects caused by spatial separation on the printed pattern. The theoretical model was then confronted with experiments performed on the atomic layer 3D printer developed by ATLANT 3D Nanosystems.

The theoretical effects and samples analyzed include edges of lines, overlaps of lines including rastering and gradients, multiple paths overlaps during pattern printing and step pattern printing. To prove that these effects are independent of the specific material, the effects are explored for TiO_2, ZnO, and Pt.

[1] Tuomo Suntola, Jorma Antson.Method for producing compound thin films. US4058430A,United States Patent and Trademark Office, 29 November 1974.

[2] Ivan Kundrata, Maksym Plakhotnyuk, Maïssa K. S. Barr, Sarah Tymek, Karol Fröhlich, Julien Bachmann (2020, June 30) An Atomic-Layer 3D Printer [Conference presentation] ALD/ALE 2020

[3] Cesar Arturo Masse de la Huerta, Viet H. Nguyen, Abderrahime Sekkat, Chiara Crivello, Fidel Toldra-Reig, Pedro Veiga, Carmen Jimenez, Serge Quessada, David Muñoz-Rojas.Facile patterning of functional materials via gas-phase 3D printing [2020, Cornell University Condensed Matter, Materials Science]

AM2-7 Realization and Dual Angle In-situ OES Characterization of Saturated 10-100 ms Precursor Pulses in a 300 mm CCP Chamber Employing de Laval Nozzle Ring Injector for Fast ALD*, **Abhishekkumar Thakur**, S. Wege, S. Bürzele, E. Ricken,* Plasway Technologies GmbH, Germany*; M. Krug,* Fraunhofer IKTS, Germany*; J. Sundqvist,* BALD Engineering AB, Sweden

ALD-based spacer-defined multiple patterning schemes have been the key processes to continued chip scaling, and they require PEALD or catalytic ALD for low temperature and conformal deposition of spacers (typically SiO_2) on photoresist features for the subsequent etch-based pitch splitting. Other SiO_2 applications in the logic and the memory segments include gap fill, hard masks, mold oxides, low-k oxides, hermetic encapsulation, gate dielectric, inter-poly dielectric ONO stack, sacrificial oxide, optical films, and many more. ALD is limited by low throughput that can be improved by raising the growth per cycle (GPC), using new ALD precursors, performing batch ALD or fast Spatial ALD, shrinking the ALD cycle length, or omitting purge steps to attain the shortest possible ALD cycle. Today's latest and highly productive platforms facilitate very fast wafer transport in and out of the ALD chambers. Current 300 mm ALD chambers for high volume manufacturing are mainly top-down or cross-flow single wafer chambers, vertical batch furnaces, or spatial ALD chambers. We have developed a Fast PEALD technology [1], realizing individual precursor pulses saturating in the sub-100 ms range. The key feature of the technology is the highly uniform, radial injection of the precursors into the process chamber through several de Laval nozzles [2]. To in-situ study (concomitantly from the top and the side of the wafer surface) individual ALD pulses in the 10-100 ms range, we use two fast scanning (≤10 ms acquisition time per spectrum ranging from 200 nm to 800 nm) Optical Emission Spectrometers with a resolution in the range of 0.7 nm. We present the results for PEALD of SiO_2 exhibiting substrate surface saturation for 30 ms of BDEAS pulse (Fig. 1) and 50 ms of O_2 plasma pulse (Fig. 2). All the processes were carried out in a 300 mm, dual-frequency (2 MHz and 60 MHz) CCP reactor in the temperature range of 20 °C to 120 °C and at ~1 Torr max. pulse pressure. The in-situ, time-resolved OES study of O_2 plasma pulse, indicating saturation ofO^* ($3p^5Pà3s^5S$) emission peak already at 50 ms pulse duration (Fig. 3, 4) and associated extinction of reactive O* within 161 ms (Fig. 5), suggest room for yet faster process. The mean GPC diminishes with the electrostatic chuck temp (Fig. 6). We will present a more optimized PEALD SiO_2 process and stacking of Fast PEALD SiO_2 on top of Fast PEALD Al_2O_3 in the same chamber without breaking the vacuum. The results will comprise XPS, TEM, film growth uniformity across 300 mm wafer, and residual stress investigation for the film stack.

Ref.

[1] AVSALD2020, Abstract# 2415, Oral Presentation AM-TuA14

[2] Patent US20200185198A1

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