Atomic Layer Rastering

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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}

The Atomic Layer 3D printer, by its nature of exploiting a physical precursor/reactant separation, is in sharp contrast to Area Selective ALD^{4,5} which exploits a chemical reaction to achieve localization. Therefore, no pre-patterning or tricks are needed for spatial Atomic Layer 3D printing to produce localized deposition. However, the cost of achieving localization via spatial separation is the difficulty in design and manufacture of micronozzles, which the Area Selective ALD does not need to struggle with. This inherent spatial separation, agnostic of the ALD chemistry used, or the substrate, allows to explore and use techniques normally associated with fused filament printing or plotting, such as sacrificial layer deposition or rastering.

Rasterization is a traditional technique from printing and engraving, where the picture is broken down into line and then "rastered". Its use so far for nanostructuring has been limited, however using Atomic Layer 3D printing allows us to explore the creation if nanostructures by rastering. Furthermore, there are unique effects created by the nozzle geometry of Atomic Layer 3D printing, that can be exploited in rastering, which for example results in the ability to controllably print gradients.

In this study, we use the Atomic Layer 3D printer to manufacture rastered structures, from simple structure of 2 lines overlapping with various overlaps, to rastered squares in of various complexity, to a set of concentric circles with a 600 nm line overlaps. To show that the technique is not materially dependent rasters were performed both in TiO₂ and Pt. We demonstrate that we can control both the pattern, to the resolution of the kinematic apparatus, and the aspect ratio with ALD resolution.

[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]

[4] Fatemeh Sadat Minaye Hashemi, Chaiya Prasittichai, and Stacey F. Bent. Self-Correcting Process for High Quality Patterning by Atomic Layer Deposition [ACS Nano 2015 9 (9), 8710-8717, DOI: 10.1021/acsnano.5b03125]

[5] Marc J. M. Merkx, Sander Vlaanderen, Tahsin Faraz, Marcel A. Verheijen, Wilhelmus M. M. Kessels, and Adriaan J. M. Mackus. Area-Selective Atomic Layer Deposition of TiN Using Aromatic Inhibitor Molecules for Metal/Dielectric Selectivity [Chemistry of Materials 2020 32 (18), 7788-7795, DOI: 10.1021/acs.chemmater.0c02370]



Fig 1. General description of Atomic Layer Rastering, via overlapping of printed ALD lines. a) demonstrates a simple approach where lines are stacked in a single direction. b) demonstrates 2 patterns from A stacked upon each other. c) shows a simplified cross section of a rastered pattern



Fig 2. Simple 1 axis overlap of TiO₂, where 400 wide ALD lines were stacked upon each other with 50 steps from line to line. Furthermore, a gradient is imposed onto the structure from top to bottom.