Inherently Selective Atomic Layer Process based on spatial micronozzles:

microreactor Selective Area Direct Atomic Processing (µSADALP^{TM})

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In parallel to additive manufacturing leading the revolution in traditional manufacturing, by supplementing the weaknesses of substractive machining, so can additive manufacturing supplement the weaknesses of traditional thin film deposition techniques. Where lithography struggles, for example with rapid iterations for prototyping or incompatibility with the used chemistry, additive manufacturing can shine. Indeed, several approaches are in development for 3D nanopriting[1,2,3].

Atomic Layer Deposition, and in more general Atomic Layer Processing, offers a unique opportunity for 3D printing due to its two-step chemical reaction. While simple in theory, due to well-developed examples of Spatial Atomic Layer Deposition (SALD), in practice minimization of SALD requires substantial effort into the creation of suitable micro-nozzles. Uniquely, ATLANT 3D Nanosystem has developed proprietary Spatial ALD micronozzles, naming the process microreactor Selective Area Direct Atomic Processing - µSADALP^{TM}.

The µSADALP^{TM} process generates inherently localized deposition through the in-house developed microreactor. The microreactor or micronozzle confines the flows of gases used for ALD within a µm-scale area on the substrate, wherein the reactive species adsorb on the surface to deposit one monolayer of the desired material. Similarly, to spatial ALD, the creation of this monolayer then hinges on the movement of the substrate.

Since the process is based on a physical separation, it is theoretically compatible with any ALD process. While some issues with high vapour pressure precursors have been identified, novel technical solutions are in the process of being funded, further driving the technology development.

Furthermore, the compatibility with Atomic Layer Etching, and selective Atomic Layer Deposition[4], the µSADALP^{TM} opens unique opportunities in the creation of novel thin-film devices, such as localized deposition on substrates difficult to process with traditional lithography based, such as UV sensitive materials, or solvent sensitive materials [Fig.1]. Secondly, sacrificial layer printing can be performed with matched material combinations, such as ZnO and TiO_2, leading to a simple creation of extremely thin free-standing structures, and extremely small gaps [Fig.2]. Thirdly, a great benefit has been identified where large variations in film thicknesses are desired, such as in pre-programmed resistive switching elements. A print of 100 patterns with different thicknesses is trivial for the printer, while not so for lithography.

In general fields such as advanced materials innovation, MEMS & sensors, RF devices (transparent antennas), Optics & Photonics (Optical coatings, surface modifications) and many other can benefit from µSADALP^{TM}.

As for now, µSADALP^{TM} is in its development stage, with several standard ALD processes explored, but further research is being done in using it for Atomic Layer Etching and Molecular Layer Deposition, or even Atomic Layer Surface Doping (ALSD) which further opens the door for more processes and thus more applicability for this technology in advanced materials, functional surfaces and electronics design, development and manufacturing.

[1] 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

[2] 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]

[3] Winkler, R., Fowlkes, J. D., Rack, P., & Plank, H. (2019). 3D nanoprinting via focused electron beams. [*Journal of Applied Physics*, *125*, 210901. https://doi.org/10.1063/1.5092372]

[4] 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]

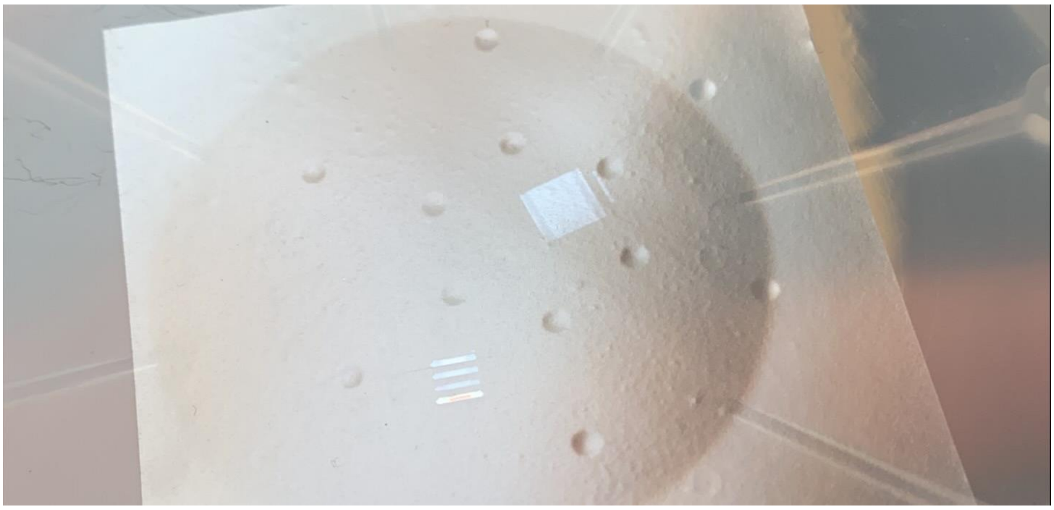

Figure 1: Localized TiO2 prints on thin flexible polystyrene foils, optical image

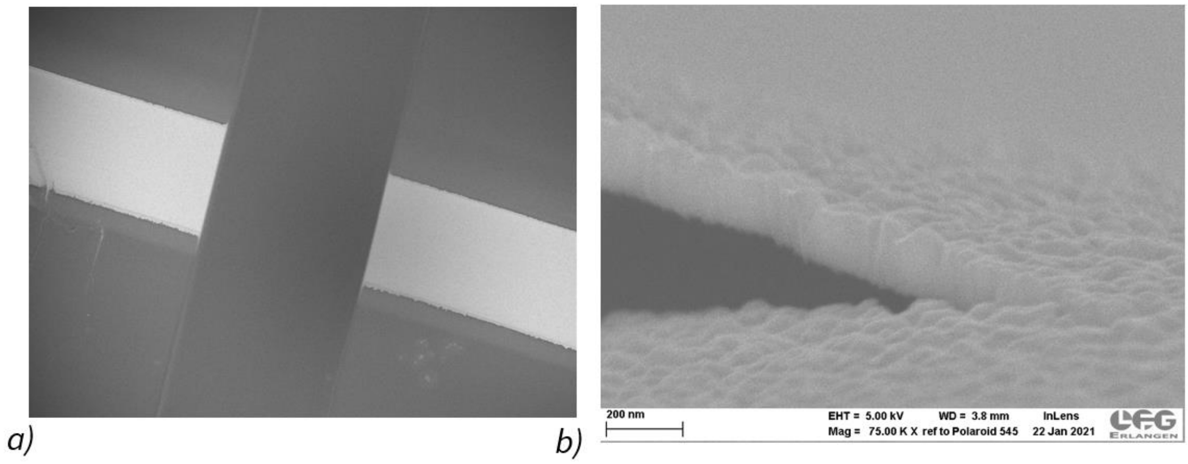

Figure 2: a) SEM of crossing printed ZnO (white line, bottom) and TiO2 (black line, top)
b) SEM of bridge edge after ZnO removal