ARRADIANCE *Sneak Preview*

Small-Molecule Inhibitors for Area Selective ALD on Arradiance Gemstar

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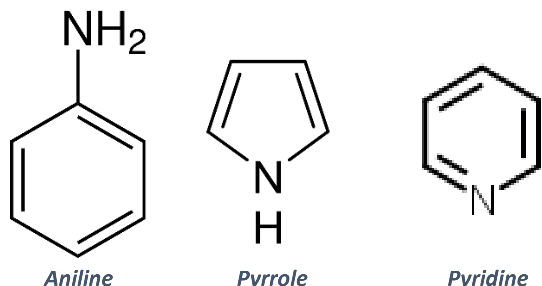
Area-selective atomic layer deposition (ASALD) deposits a film on one surface but not on another, taking advantage of chemical differences between the surfaces. In modern semiconductor technology, this enables further scaling and avoids repeated lithography steps that cause edge placement errors. ASALD uses an ALD precursor which reacts preferentially with the desired surface. One emerging strategy to enhance the selectivity is to cover the non-growth area with inhibitor molecules prior to dosing the ALD precursor. The inhibitor molecule must cover the non-growth surface and prevent the ALD precursor from reacting there. The first inhibitor molecules to be used were self-assembled monolayers (SAMs), consisting of large molecules which prevent precursors from reaching the surface. SAMs are effective in large areas but allow some growth near edges. SAMs also require many hours to form, an attribute not well suited to high-volume manufacturing. Small molecule inhibitors (SMIs) have been proposed to overcome these challenges. They can be applied quickly, and even redosed in every ALD cycle.

Stacey Bent's group at Stanford University, in collaboration with Ralf Tonner-Zech's group at the University of Leipzig, investigated the adsorption chemistry of three small-molecule inhibitors used to deposit Al_2O_3 using the dimethyl aluminum isopropoxide (DMAI) precursor on SiO_2 with selectivity over copper and copper oxides. Prior to deposition, the authors exposed the substrates to the inhibitors in a purpose-built chamber allowing high doses. The authors then redosed the SMI prior to the DMAI precursor in ALD processes using each of three different SMIs: aniline, pyridine, and pyrrole, all in an Arradiance GEMStar™ ALD system. They achieved 99.9% selectivity after 125 cycles when using pyrrole and aniline, while pyridine proved to not provide satisfactory selectivity.



The pyridine finding is surprising, given that the water contact angle and XPS measurements showed that pyridine clearly adsorbs on copper and copper oxide surfaces…, so why did it fail as an inhibitor? Fortunately, the investigators identified a likely cause by performing density functional theory (DFT) calculations. They found that while aniline and pyrrole assume a planar position, pyridine remains in an upright position on the surface, allowing precursor molecules to filter past the pyridine inhibitor and reach the substrate surface. The possibility of considering SMIs based on their adsorption orientation will significantly benefit future AS-ALD process designs, benefiting industry by increasing yields and reducing manufacturing steps for the devices that drive our world.

Arradiance GEMStar™ systems enable AS-ALD work, particularly by permitting up to six precursors to be used in one process. For more information on GEMStar™ Technology, ALD systems or Foundry services, please contact Arradiance.

1. Alexander Shearer, Fabian Pieck, Josiah Yarbrough, Andreas Werbrouck, Ralf Tonner-Zech, and Stacey F. Bent, "Role of Molecular Orientation: Comparison of Nitrogenous Aromatic Small Molecule Inhibitors for Area-Selective Atomic Layer Deposition *Chemistry of Materials* **2025** *37* (1), 139-152 DOI: 10.1021/acs.chemmater.4c02231