Atomic layer deposition in catalysis: crossing roads with semiconductor technology

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Highlights

- Atomic layer deposition (ALD) is an advanced catalyst preparation method, which roots back to early atomic layer epitaxy (ALE) and molecular layering (ML) works
- By ALD one can in principle e.g. change the surface termination of a material, prepare particles of a controlled size down to single-atoms, and prepare protective overcoats
- The development of ALD for catalysis benefits immensely from parallel developments related to use of ALD for semiconductor technology
- ALD growth on porous materials is limited by diffusion and all ALD coatings on catalysts start from an egg-shell distribution

Atomic layer deposition (ALD), which is based on the repeated sequences (i.e. cycles) of separated self-terminating gas-solid reactions of at least two compatible compounds, has become of global interest for catalyst preparation [1]. ALD's roots date back to Atomic Layer Epitaxy (ALE) [2] and Molecular Layering (ML) [3], developed in Espoo Finland since 1974 [2] and St. Petersburg USSR since 1960s [2,3], respectively. ALD is best known today as an enabler of Moore's law (shrinking transistor size), but as a multitool of nanotechnology, it is applicable in multiple other areas, too. As recently reviewed (and as not generally known), ALD has been applied for catalyst preparation already since 1970s (ML) and 1980s (ALE); recent overview of (thermo)catalysis ALD publications is shown in Figure 1 [4]. ALD can be used in catalyst preparation in multiple ways, some of which are illustrated in Figure 2 [4].

This keynote will introduce the principles of ALD; briefly overview the historical eras of ALD for catalysis; place ALD for catalyst preparation into context of ALD for particulate material processing and semiconductor wafer processing in general; and discuss case examples of ALD-made catalysts. Two aspects of ALD for catalyst preparation will be highlighted that are surprisingly little discussed in scientific literature. (i) The propagation of an ALD coating is limited by diffusion and the extent of metal added inevitably starts as an egg-shell distribution, before a uniform distribution can be achieved [5]. (ii) The exothermic nature of the reactions inevitably causes temperature excursions when "thin-wall" substrates, such as catalyst supports (or complex 3D semiconductor architectures), are used [6].

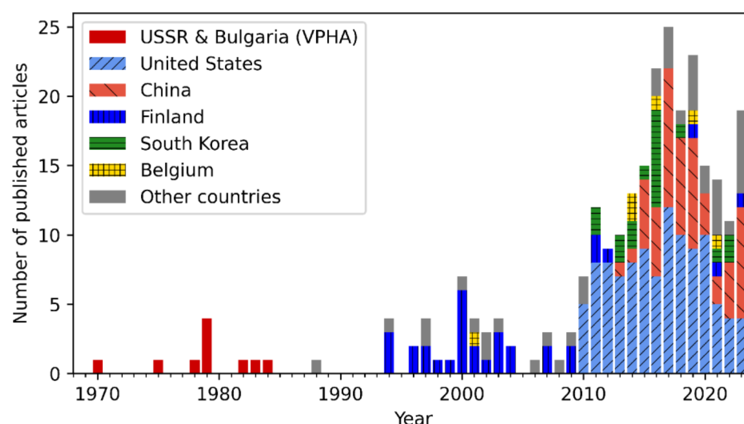

Figure 1. Number of (thermo)catalysis ALD publications per year and per country (five highest numbers of publications), as reported by Piechulla et al. [4] on the basis of a systematically collected dataset. Copyright by the authors, published with CC-BY-NC-ND 4.0.

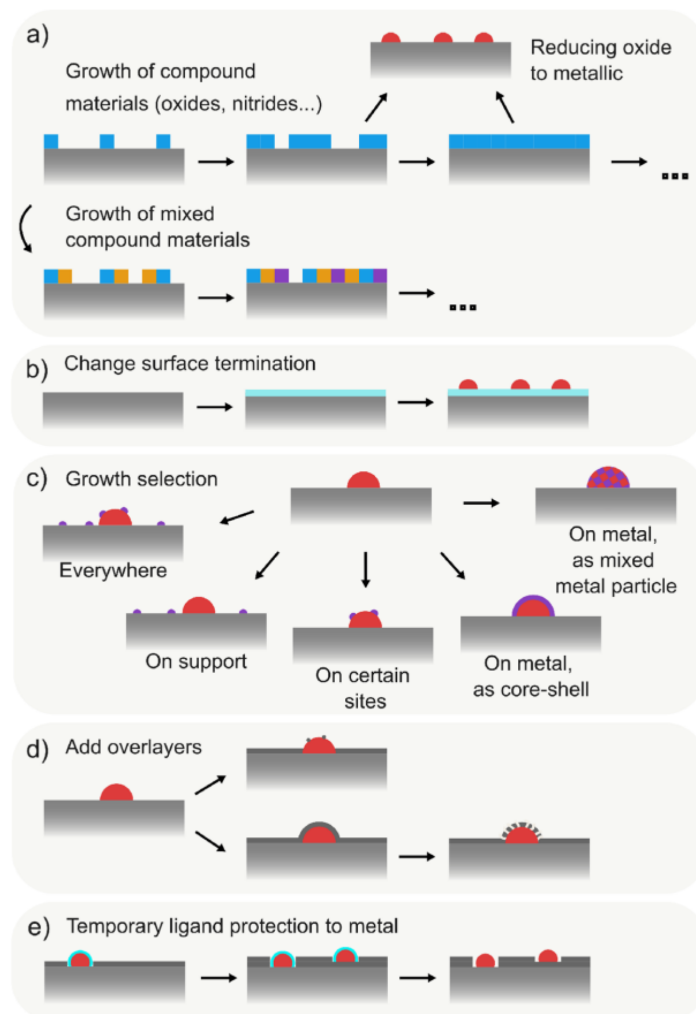

Figure 2. Various schemes of catalyst preparation by ALD, as reported in the literature and as reviewed in Ref. 4. (a) Growth of a compound layer in ALD cycles, either of the same material or mixed material. Optional reduction afterward to make a metallic film. (b) Change of the surface of a high-surface-area material to another, to be used as a support, with addition of active component on it afterward. (c) Variations of selective growth, with growth everywhere, or only on the support (typically oxide on oxide), growth on specific sites of a metal nanoparticle (typically an oxide on undercoordinated sites such as edges and corners), and growth of metal on metal to create either a core–shell nanoparticle or a mixed alloy. (d) Use of an overcoat (also called overlayer) to prevent catalyst deactivation, covering the support and the active component partly or fully. Heat treatment may be needed to expose the active component for catalysis through creation of porosity in the overcoat. (e) ABC-type of sequence, where after the reaction of the metal compound of interest (A), ligand removal step is not made, but another compound layer is grown (BC). The sequence ABC can be repeated. Ligand removal step is performed as final step. Image from Ref. 4; in Wikimedia Commons with CC BY 4.0.

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Keywords

Atomic layer deposition; history, egg-shell distribution, diffusion-reaction