Sundew Technologies LLC

Atomic Layer Deposition

Atomic Layer Deposition (ALD, originally named Atomic Layer Epitaxy, ALE) was first introduced as a conceptual new deposition technique using physical vapor deposition (PVD). In this version atomic elements were evaporated from two separated sources to grow compound films. The vapors of each particular element were pulsed in time by means of physical vapor blocking (shutters) and the substrate temperature was adjusted to be higher than the sublimation temperatures of both single atomic elements. Compound materials could be deposited if the sublimation temperature of the compound was higher than the substrate temperature. For example, in the first published process Zinc (Zn) and Sulfur (S) were evaporated on a substrate that was too hot to grow Zinc or Sulfur. The substrate was exposed to the vapors one element at a time. The conditions could only allow a single layer of Zn to grow on S and a single layer of S to grow on Zn. Therefore, the growth proceeded in one layer per Zn; S cycle intervals to grow Zinc-Sulfide.

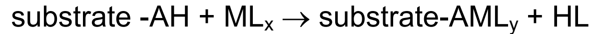
Conceptually, ALD processes should follow the basic idea that was implemented as discussed above. Films are deposited by a repetitive sequence of single layer deposition cycles. Each cycle is composed of several gas-surface interactions that are all ***self-limiting***. The self-limiting property of the cycles is the foundation of ALD.

PVD based ALD (PV-ALD) is limited to very few systems. Therefore, it found very limited practical use. In addition, it requires line of sight and Ultra-High-Vacuum conditions. Chemical vapor deposition based ALD (CV-ALD) has become the dominant ALD implementation. Generally, CV-ALD is a process wherein conventional chemical vapor deposition (CVD) processes are divided into single-layer deposition cycles, wherein each separate deposition cycle goes to saturation at a single molecular or atomic layer thickness, and self-terminates.

The deposition is the outcome of chemical reactions between reactive molecular precursors and the substrate. In similarity to CVD, elements composing the film are delivered as molecular precursors. The net reaction must deposit the *pure* desired film and eliminate the "extra" atoms that compose the molecular precursors (ligands). In the case of CVD the molecular precursors are fed simultaneously into the CVD reactor. A substrate is kept at temperature that is optimized to promote chemical reaction between the molecular precursors concurrent with efficient desorption of byproducts (so that the byproducts do not incorporate into the film). Accordingly, the reaction proceeds to deposit the desired pure film.

For ALD applications, the molecular precursors are introduced into the ALD reactor separately. This is practically done by flowing one precursor at a time, i.e. a metal precursor – ML_x (M = Al, W, Ta, Si etc., L = CH_3, Cl, F, C_4H_{11}, etc.) that contains a metal element – M which is bonded to atomic or molecular ligands – L to make a volatile molecule. The metal precursor reaction is typically followed by inert gas purging to eliminate this precursor from the chamber prior to the separate introduction of the other precursor. An ALD reaction will take place *only* if the surface is *prepared* to react directly with the molecular precursor. Accordingly the surface is typically prepared to include hydrogen-containing ligands - AH that are reactive with the metal

precursor. Surface – molecule reactions can proceed to react with all the ligands on the surface and deposit a layer of the metal with its passivating ligand.

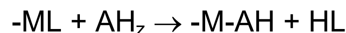


$$\text{substrate -AH} + ML_x \rightarrow \text{substrate-AML}_y + HL$$

where HL is the exchange reaction by-product. During the reaction the initial surface ligands – AH are consumed and the surface becomes covered with L ligands, that cannot further react with the metal precursor – ML_x. Therefore, the reaction self-saturates when all the initial ligands are replaced with $–ML_y$ species.

After completing the metal precursor reaction the excess precursor is typically removed from the reactor prior to the introduction of another precursor. The second type of precursor is used to restore the surface reactivity towards the metal precursor, i.e. eliminating the L ligands and redepositing AH ligands.

Most ALD processes have been applied to deposit compound films. In this case the second precursor is composed of a desired (usually nonmetallic) element – A (i.e. O, N, S), and hydrogen using, for example H_2O, NH_3, or H_2S. The reaction:

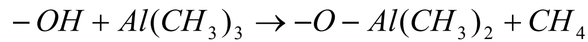


$$-ML + AH_z \rightarrow -M\text{-}AH + HL$$

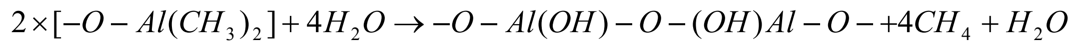
(for the sake of simplicity the chemical reactions are not balanced) converts the surface back to be AH-covered. The desired additional element, A, is deposited and the ligands L are eliminated as volatile byproduct molecules. Again, the reaction consumes the reactive sites (this time the L terminated sites) and self-saturates when the reactive sites are entirely depleted.

The sequence of surface reactions that restores the surface to the initial point is called the ALD *deposition cycle*. Restoration to the initial surface is the ***keystone*** of ALD. It implies that films can be layered down in equal metered sequences that are all identical in chemical kinetics, deposition per cycle, composition and thickness. Self-saturating surface reactions make CV-ALD insensitive to transport nonuniformity originating either from hardware limitations or surface topography (i.e. deposition into high aspect ratio structures). Non uniform flux can only result in different completion time at different areas. However, if each of the reactions is allowed to complete on the entire area, the different completion kinetics bears no penalty.

CV-ALD sequences usually deposit less than a full layer per cycle. The deposition per cycle is controlled by the stable coverage of ligands, (i.e. -AH or –L) on the intermediate surfaces that are generated by saturated ALD reactions. Ligands exist on surfaces as thermodynamic stabilizers. Surfaces also self-stabilize by rearrangement. The stable ligands coverage is the outcome of competition between the two forms of surface stabilizations and generally decreases with temperature. Usually, ALD films grow smoothly without micro-roughness, despite a typical 0.25-0.3 of a monolayer growth per cycle. An illustration of an ALD process is given below. In this example the process utilizes $Al(CH_3)_3$ and H_2O to grow Al_2O_3 films with typical growth per cycle of 0.25 molecular layer per cycle (at 300 °C process temperature). The ALD cycle applies the reactions:

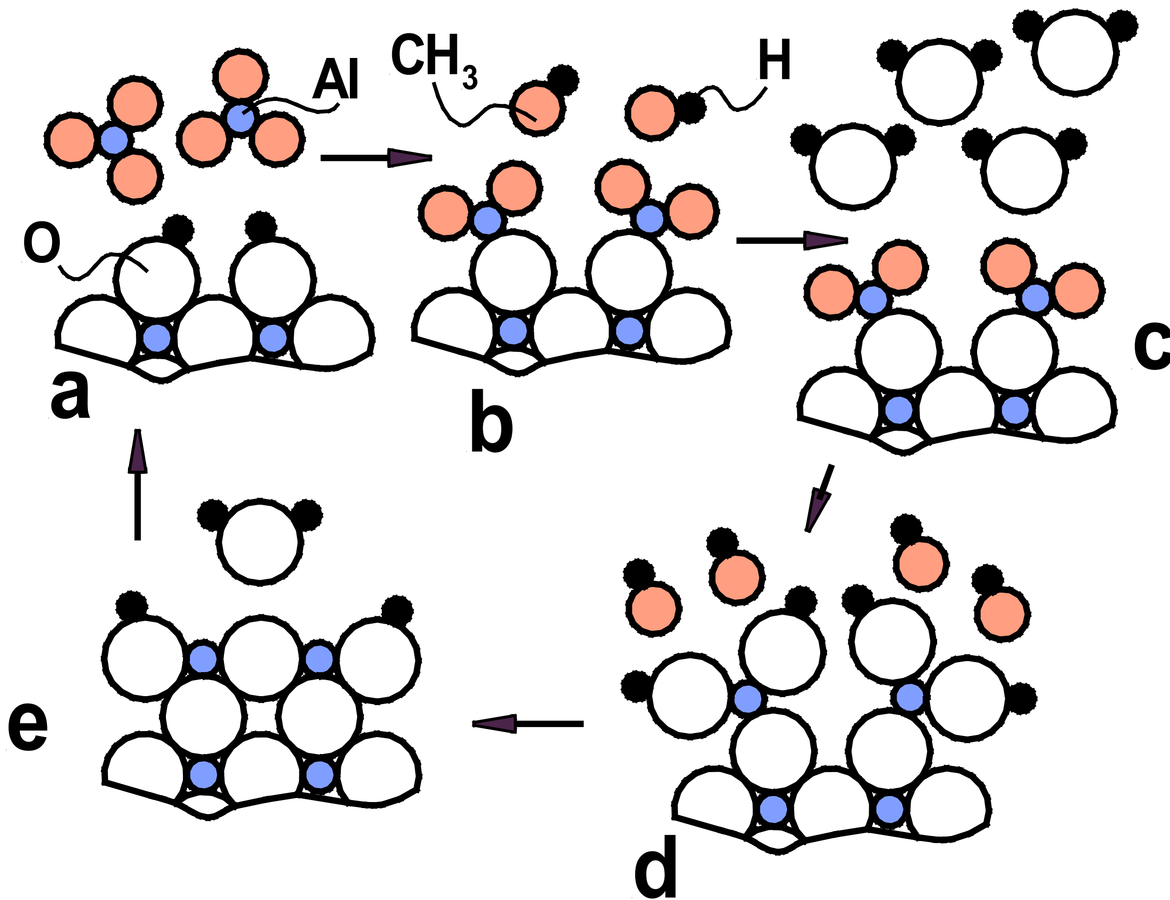


$$-OH + Al(CH_3)_3 \rightarrow -O - Al(CH_3)_2 + CH_4$$



$$2 \times [-O - Al(CH_3)_2] + 4H_2O \rightarrow -O - Al(OH) - O - (OH)Al - O - +4CH_4 + H_2O$$

Where during the cycles, a laterally cross-linked unit of Al_2O_3 is formed over each 2 initial –OH sites. The example is further illustrated in the cartoon below.



a. An –OH terminated surface is exposed to a flux of $Al(CH_3)_3$ precursor.
b. In this first reaction step the $Al(CH_3)_3$ molecules react with the surface –OH sites. The reaction produces a volatile CH_4 molecule and attaches $-Al(CH_3)_2$ per each initial –OH site. The reaction self-saturates when all the –OH sites are reacted.
c. The surface is now exposed to a flux of H_2O precursor.

d. In this second reaction step the H_2O molecules react with the $–CH_3$ sites. The reaction produces a volatile CH_4 molecule and attaches –OH per each initial $–CH_3$ site. The reaction self-saturates when all the $–CH_3$ sites are reacted.
e. Concurrent with d. Driven by the thermodynamic stability of the 2:3 Al:O atomic stoichiometry and the thermodynamics of the surface, adjacent $–Al(OH)_2$ species cross-link by each reacting one of the –OH species to produce a volatile H_2O molecule and a linked $-Al-O-Al-$ network. The cycle is complete and the starting point number density of –OH sites is restored.

Additional Information

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2. S. M. George, A. W. Ott, J. W. Klaus, *J. Phys. Chem.* 100 (1996) 13121.
3. O. Sneh, R. B. Clark-Phelps, A. R. Londergan, J. L. Winkler and T. E. Seidel, *Thin Solid Films* 402 (2002) 248.