A REVIEW OF
ATOMIC LAYER DEPOSITION FOR NANOSCALE DEVICES

Edy Riyanto a, b, c, *, Estiko Rijanto b, Budi Prawara b

a State Key Laboratory for Modification of Chemical Fibers and Polymer Materials,
College of Material Science and Engineering, Donghua University, Shanghai 201620, People’s Republic of China
b Research Centre for Electrical Power & Mechatronics, Indonesian Institute of Sciences,
Komp LIPI Jl Cisitu 21/54D, Gd 20, Bandung 40135, Indonesia
b Plasma Physics & Application Laboratory,
College of Science, Donghua University, Shanghai 201620, People’s Republic of China

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Abstract
Atomic layer deposition (ALD) is a thin film growth technique that utilizes alternating, self-saturation chemical reactions between gaseous precursors to achieve a deposited nanoscale layers. It has recently become a subject of great interest for ultrathin film deposition in many various applications such as microelectronics, photovoltaic, dynamic random access memory (DRAM), and microelectromechanic system (MEMS). By using ALD, the conformability and extreme uniformity of layers can be achieved in low temperature process. It facilitates to be deposited onto the surface in many variety substrates that have low melting temperature. Eventually it has advantages on the contribution to the wider nanodevices.

Key words: thin coating, atomic layer deposition, nanoscale devices.

I. INTRODUCTION
Atomic layer deposition (ALD) is a technology which can be used to fabricate a very high-quality thin films based on alternate self-limiting surface chemical reactions which have extreme uniformity on the three-dimensional structures, high density, low porosity, freedom from defect [1-4], with conformality and precise thickness control [5-7]. It has been applied in the numerous advanced technologies for the fabrication of nanoscale thin films such as microelectronics, Complementary Metal oxide Semiconductor (CMOS) transistors, DRAM memory, MEMS/NEMS, energy conversion, photovoltaics, and display devices [8-12] that require precise control of film properties in thickness, uniformity, and conformability.

Atomic layer deposition is a technique which is originally developed to produce thin films for electroluminescent displays, but was later adopted for other substrate as well [13]. This technique is a thin film growth technique that relies on two sequential, self-limiting surface reactions between gas phase precursor molecules and a solid surface as illustrated in Fig. 1 [14-17]. The films formed by sequential pulsing of two or
more reactants, using purging with inert gas between the precursor pulses to avoid gas-phase reactions [17]. Due to self-limited film growth mechanism, the film deposited by ALD has shown excellent step coverage and conformality [6], because the reactions are driven to completion during every reaction cycle [18]. The surface is exposed to reactant A, which react to initial surface sites. Then, after the product from reaction A are purged, the surface is exposed to reactant B. This reaction regenerates the initial functional groups and prepares the surface for the next exposure to reactant A.

The thickness is grown to the desired thickness by repeating this AB sequence [19, 20]. The reactor is purged with an inert gas between the precursor pulses [21]. With a proper adjustment of the experimental conditions the process proceeds via saturative steps [21]. Under such conditions the growth is stable and the thickness increase is constant in each deposition cycle [21]. As the reactions are self-limiting, ALD does not require line-of-sight for deposition and high surface area to volume structures, and complex geometries can be conformally coated [19, 20]. In the case of Al₂O₃ ALD, in the first half-reaction trimethylaluminum (Al(CH₃)₃) molecules react with hydroxyl (–OH) groups attached to the surface, until a saturation of available reaction sites is reached. In the second half-reaction the surface is oxidized by water vapor (thermal ALD) or in oxygen plasma (plasma-assisted ALD) to form aluminum oxide [22].

Precursor chemistry plays a key role in ALD, the precursor must of course be volatile and thermally stable. These are may be gases, liquids, or solids. Precursors must chemisorb on the surface or react rapidly with the surface group and react aggressively with each other. In that way, it is possible to reach the saturation stage in a short time (less than 1 s) and thereby ensure a reasonable deposition rate [21]. This paper aims to provide information on the latest developments in thin film deposition technology by atomic layer deposition method and its application.

II. DESCRIPTION OF SYSTEM

A. The Schematic of ALD System

Fig. 2 shows the ALD flow reactor designed for the substrate coating. Two separate precursor chambers are connected to the main reactor separately by valves 4, respectively. Each precursor tube is connected with inert gas that is controlled by a mass flow controller. The pressure inside the reactor is monitored by pressure measurement gauges. Valve 10 and the vacuum pump are used for controlling the pressure inside the reactor.

Fig. 3 shows the schematic illustration of the constructed ALD. The ALD consist of the reaction chamber part and the supply part for reactants, carrier gases and purge gases. The illustration of the Fig. 2 are as follow, (1) Reaction chamber, (2) Shower head, (3) Substrate holder, (4) Reactant canister, (5) Carrier & purge gas, (6) Diaphragm valve, (7) Vacuum gauge, (8) Mass flow controller, (9) Control system.

The typically gas flow mechanism of the existing ALD systems are generally classified...
into two categories, these are the laminar gas flow type which have advantages on the high material utilization efficiency and minimization of the reaction volume with inherently disadvantages on the thickness non-uniformity due to source depletion at inlet area makes it unsuitable for large area deposition, on the other hand the shower-head type has uniform source flux, but a long purge time due to the large reaction volume and the low conductance of the shower-head hole makes it difficult to realize a pure ALD process [24].

B. Reaction Mechanism

The mechanisms that have been identified for bonding gaseous reactants on solid supports in a saturating manner are illustrated with molecule MLn used as an example. In MLn, M is a central metal atom, L is a ligand attached to it and n is the number of ligands. MLn can be represented Al(CH3)3 [25].

The most common example of saturating gas-solid reactions is ligand exchange reaction, where the reactant molecule (MLn) is split and one of its ligands (L) combines with a surface group (a) to form a volatile compound that is released as a gaseous reaction product (aL) [25]. Symbol Il denotes the surface.

\[ \text{II} - a + \text{MLn} (g) \rightleftharpoons \text{II} - \text{MLn-1} + \text{aL} (g) \]  (1)

Water and trimethylaluminum are commonly used as precursors in the deposition of Al2O3 by using atomic layer deposition [26, 27]. Al2O3 is one of the most attractive and extensively studied materials by ALD [4, 18, 26], because of its chemical and thermal stability, and good adhesion to the various materials [28]. On the alumina coating, it was previously shown that when H2O is used as a source for oxygen, Al2O3 is formed by the chemical exchange between Al(CH3)3 and H2O [4,29], it can be used to illustrate the basic principles of ALD. Al2O3 is a binary material. The binary reaction for Al2O3 is [4,16]:

\[ 2 \text{Al(CH3)3} + 3 \text{H2O} \rightarrow \text{Al2O3} + 6 \text{CH4} \]  (2)

This binary reaction can be divided into two reactions to define Al2O3 ALD [15, 20,30,31,32]:

\[ \text{AlOH}^{*} + \text{Al(CH3)3} \rightarrow \text{AlOAl(CH3)2}^{*} + \text{CH4} \]

\[ \text{AlCH3}^{*} + \text{H2O} \rightarrow \text{AlOH}^{*} + \text{CH4} \]  (3)

where asterisks indicate the surface species. Al2O3 ALD can be deposited at the low temperatures required for coating polymers. The Al2O3 ALD films are amorphous and extremely conformal to the underlying substrate [31].

III. GROWTH THEORY

The requirements of the amorphous materials growth are the surface mobility of the adsorbed precursor fragment should be so low that the precursor fragment is localized at the point where it first adheres to the surface, as well as the network of reactive sites should provide more location possibilities than the atomic arrangement for the film material. This can be achieved if the adsorbed precursor fraction is capable of forming bonds to both bridging and terminating atoms. An experimental example for film formation under such condition could be growth of Al2O3 by Al(CH3)3 and H2O. This system has a flexibility in the network of reactive sites in the way that Al(CH3)x may form relatively strong bonds to both terminating and bridging oxygen atoms, and thus disturb a repetitive construction pattern needed in order to form a crystalline material [17].

Al2O3 ALD is a particularly robust and well-defined ALD system [14], and can be considered a rather typical and “ideal” ALD process [26]. Al2O3 ALD films can be pinhole-free as demonstrated by electrical instruments and can be deposited on polymer substrates [14]. One basic condition for a successful ALD process is that the binding energy of a monolayer chemisorbed on a surface is higher than the binding energy of subsequent layers on top of the formed layer, that it can be controlled by the reaction temperature. The temperature must be kept low enough to keep the monolayer on the surface until the reaction with the second reactant occurs, but high enough to re-evaporate or break the chemisorption bond. The greater the difference between the bond energy of a monolayer and the bond energies of the subsequent layers, the better the self-controlling characteristics of the process [33].

It is correlated to the basic technique of ALD that it depends on the difference between chemisorption and physisorption. The physisorption involves the weak van der Waal's forces, whereas chemisorption involves the formation of relatively strong chemical bonds and requires some activation energy, therefore it may be slow and not always reversible. The chemisorptions will dominate at the certain temperatures, which correspond to the best condition of ALD operating. On the other hand the chemisorption is the reason that the process is self-controlling and insensitive to the pressure and substrate changes. It is due to the only one of atomic or molecular layer can be adsorbed at the same time [33].
IV. CHARACTERISTIC OF ALD GROWTH

Temperature is one of the three parameters, together with the reactant and the surface, that determine the amount and the type of species adsorbed in irreversible, saturating chemisorptions [26]. Fig. 4 shows the growth rate of ALD as a function of growth temperature, illustrating general growth characteristics. When the ALD process is performed at temperatures which provide sufficient thermal energy for the chemical reactions, the growth rate usually remains constant with self-terminating reactions [8, 26, 34]. This temperature range is often called the “ALD process window”. This nearly constant growth rate for a range of growth temperature during ALD provides better reproducibility in film thickness than those of other deposition methods [8, 18]. If the growth temperatures are greater than the ALD window temperature, the growth rate usually increases. It is due to the thermal decomposition of the precursor which leads to disturb the self limitation mechanism [8].

The distinctive feature of ALD is that the reactions are saturative, which makes the films growth self-limiting. Experimentally it can be verified by observing that the deposition rate per cycle stabilizes to a constant level with increasing precursor pulse time or dose.

The self-limiting growth ensures that each cycle deposits the same amount of material on all surfaces independent of the precursor dose received as long as the dose is high enough to saturate the reactions [35]. As a consequence, the ALD methods offer excellent large area uniformity, conformality and film thicknesses are accurately controlled simply by the number of deposition cycles applied [35, 36]. Two factors have been identified to cause the saturation of the surface with adsorbed species in a self-terminating gas-solid reaction, these are steric hindrance of the ligands and the number of reactive sites. Steric hindrance of the ligands can cause the ligands of the chemisorbed species to shield part of the surface from being accessible to the reactant [26].

One of the most important characteristic of ALD is the ability to deposit relatively high quality films at low growth temperatures. However, thermal activation for precursor molecule adsorption and surface reaction with reactant is necessary for ALD, thus substrate heating is required. For a certain material systems such as Al₂O₃ ALD which using TMA and water, it is possible to deposit relatively pure films at growth temperature lower than 100°C [37, 38]. Although the film density was lower and the hydrogen content in the film was higher compared to film deposited at elevated growth temperatures, the film properties were relatively good with smooth surfaces and low leakages currents [37, 38]. Increased ALD cycle time is necessary at lower temperatures because of the slower reaction rates and longer required purge times for H₂O reactant [38].

The studies have shown that ALD process temperature for polymers application should be limited to lower than 150°C [37]. Most of polymers do not have reactive nucleation sites for ALD [37, 39]. It makes complicate for the ALD surface reactions. Many polymers, such as polyethylene and polypropylene are saturated hydrocarbons that lack typical chemical functional groups such as hydroxyl (-OH) species [36, 39]. Al₂O₃ ALD is remarkably robust and has demonstrated an ability to deposit Al₂O₃ films on nearly every substrate. The ability of Al₂O₃ to deposit with low temperature on a variety substrates led to the judgment that Al₂O₃ ALD was a good candidate for the deposition of inorganic films on polymers [39].

Although, the polymer substrates that do not have reactive nucleation sites can be coated by the penetration of TMA molecules [18], the existence of reactive sites is very important. It has an effect on the quality of the films that will be achieved. ALD on polymer surfaces containing surface groups receptive to ALD nucleation, such as –OH and other polar groups is expected to produce more uniform and conformal film coverage, without substantial subsurface

![Fig. 4. General growth characteristics of ALD as a function of growth temperature.](image)

![Fig. 5. Growth mechanism of Al₂O₃ ALD on the inorganic polymer.](image)
growth [40]. Reactant penetration and subsurface inorganic nucleation in a polymer film can negatively effects material properties. Subsurface oxide growth can also impede the performance of ALD barrier layers formed on polymers films [41].

The growth mechanism of ALD onto the polymer substrate that does not have surface functional group is depicted as Fig.5. It have shown that the precursor of Al(CH3)3 diffuses into the near surface region of the polymer (a), cluster of the ALD material form in the near surface region as a result of bimolecular reaction between the two ALD precursors (b), the clusters grow and eventually begin to coalesce (c), a continuous film is formed that prevents the diffusion of additional precursor into the polymer (d), and it will be continued that the ALD materials grows linearly on the continuous ALD film [18].

Because of the covalent bonding, the adhesion of ALD-grown Al2O3 layer with the substrate is commonly excellent. Biopolymers which typically have functional surface groups contribute to improve the bonding between the substrate and the Al2O3 layer. It is the possibility that has made the biopolymeric materials more interesting substrates to create efficient gas and moisture barrier materials than regular oil-based polymers, such as polyethylene, polypropylene, or polyethylene terephthalate, for instance [42]. The ability to deposit films at low growth temperature is very attractive for polymer-based devices and for coating heat-sensitive materials such as polymers and biomaterials. The growth temperature for metal ALD is generally higher than that for oxide ALD, partially due lower reactivity of reducers than oxidizers [37].

V. ALD FOR NANOTECHNOLOGY APPLICATION

A. MEMS Devices

Micro Electro Mechanical Systems (MEMS) comprise a variety of functional mechanical devices fabricated on length scales from fractions of a micrometer to millimeters [43,44] that offers considerable potential due to small size, small weight, and low power of fabricated devices which can enable compelling advantages in certain product specifications [45,46]. Some of the applications of MEMS are motion sensing, optical switching, mechanical actuators [43, 47, 48], chemical sensors [43,48], and photonic applications [43,49]. Adhesion, friction and wear at the nanometer scale become critical and can be detrimental to the efficiency, power output and reliability of MEMS devices [50,51]. Al2O3 atomic layer deposition with 10 nm thickness in MEMS devices application has been applied on the wear resistant films of the surface-micromachined (SMM) devices [20,43,52]. In order to achieved 10 nm of Al2O3 was deposited using 100 cycles of trimethylaluminum (Al(CH3)3) and water (H2O) as precursors.

Fig. 6(b) shows the cross section image of the structure of the hub [43]. The aluminum oxide (Al2O3) deposited film as examined in three locations of the structure. Locations 1-3 are points of examination of the ALD film by TEM.

Location 1 is on the top of the gear surface, which is possible to be exposed by direct line-of-sight to the gas source. Location 2 is on the underside of the gear, shadowed from the gas source, and location 3 is at the end of a long channel inside the hub structure with the film thickness ranges of all of those are from 10 nm at location 1 to 10.5 nm at location 3 [43].

B. Dynamic Random Access Memory (DRAM)

The data storage in DRAMs is based on introducing a charge into the memory capacitor. The charge must be repeatedly refreshed (“dynamic”), the time interval between the
refreshments depending on the leakage current through the capacitor. The charge storage capacity of the capacitor is determined by its capacitance, which can be increased by decreasing the thickness of the dielectric layer, by using a dielectric material with a higher dielectric constant [49, 53], or by increasing the active capacitor area [53].

In the stacked DRAM memory cells, the capacitors are fabricated above the silicon substrate. Fig.8. shows the examples of stacked capacitor structures. In trenched DRAM memory cells, the memory capacitors are buried into the silicon substrate. The capacitors are fabricated into high aspect ratio trenches, and thus have high effective surface areas [53], which can be contributed by ALD process [49].

VI. SUMMARY

ALD has shown the reliability on the application of microelectronics, MEMS, DRAM, and many other nanoscale devices with accurately controlled thickness of thin films by the number of deposition cycles applied. One of the most important factors that have effect on the deposited thickness and uniformity is the temperature which can be indicated by using the range of ALD window process. At the certain temperatures, the chemisorptions will dominate to achieve the best condition of ALD operating with the process is self-controlling and insensitive to the pressure and substrate changes. In the coating application by TMA molecules as precursor, the ALD can be used to be deposited onto the substrates that have or without reactive nucleation sites, especially on the polymer substrates. Subsurface growth mechanism occurred as initial growth onto the hydrophobic polymers. Although it can be grown, the existence of reactive sites is very important to obtain the quality of the films with outstanding properties.

REFERENCES


