Study of Effects and Applications of Atomic Layer Deposition (ALD) (A Review)

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Abstract: Atomic layer deposition (ALD) is a extensively used vapor phase technique capable of producing thin films of a variety of materials. Based on sequential, self-limiting reactions, ALD offers exceptional conformity on high aspect ratio structures, thickness control at the Angstrom level, and tunable film composition. With these advantages, ALD has emerged as a powerful tool for many industrial and research applications. This review paper presents a brief introduction to ALD principle, techniques and its effects on materials characteristics like conductivity, dielectric properties and passivation quality, etc, and current applications pertaining to microelectronics and energy and other fields including Cu(In,Ga)Se2 solar cell devices, high-k transistors, capacitors and solid oxide fuel cells etc. Various examples are taken into consideration to elucidate the variety of technologies that are impacted by ALD, the range of materials that ALD can deposit – from metal oxides such as Zn1_xSnxOy, ZrO_2, Y_2O_3, to noble metals such as Pt – and the way in which the unique features of ALD can enable new levels of performance and deeper fundamental understanding to be achieved.

Keywords: Atomic Layer Deposition, Microchemistry, Microelectronics, precursor, substrate, Al_2O_3.

1. INTRODUCTION

Atomic layer deposition (ALD) is a thin film deposition technique that is based on the sequential use of a gas phase chemical process. ALD is considered a subclass of chemical vapour deposition. ALD was introduced by Dr. Tuomo Suntola and co-workers in 1974 in Finland to improve the quality of ZnS films used in electroluminescent displays [1]. ALD has been developed in two independent discoveries under names atomic layer epitaxy (ALE, Finland) and molecular layering (ML, Soviet Union) [2],[3]. Suntola started the development of the ALE technology for new applications like photovoltaic devices and heterogeneous catalysts in Microchemistry Ltd., established for that purpose by the Finnish national oil company Neste Oy. In the 1990s, ALE development in Microchemistry was directed to semiconductor applications and ALE reactors suitable for silicon wafer processing.

The name "atomic layer deposition" was proposed in writing as an alternative to ALE in analogy with CVD by Markku Leskelä (professor at the University of Helsinki) [4].

Atomic layer deposition (ALD) is a technique capable of depositing a variety of thin film materials from the vapor phase. ALD has shown great promise in emerging semiconductor and energy conversion technologies. This review is intended to introduce the reader to the basics of ALD and highlight.

The majority of ALD reactions use two chemicals, typically called precursors. Different forms of chemical vapor deposition (CVD), physical vapor deposition (PVD), and atomic layer deposition (ALD) are based on saturated surface reactions. ALD is a self-limiting adsorption reaction process and the amount of deposited precursor molecules is determined only by the number of reactive surface sites and is independent of the precursor exposure after saturation.

A major driving force for the recent interest is the prospective seen for ALD in scaling down microelectronic devices according to Moore's law [6]. ALD is an active field of research, with hundreds of different processes published in the scientific literature, though some of them exhibit behaviors that depart from that of an ideal ALD process., have synthesized many exciting new precursors for ALD and have created a large number of atomic layer deposition materials, such as coatings with improved properties for metals, semiconductors, insulators, oxides, nitrides, dielectrics, magnetic, and refractive coatings (Table 1). Chemists [7], [8].

Table 1 - Precursors for ALD and atomic layer deposition materials

OXIDES					NITRIDES		SULFIDES	METALS /
Al_2O_3	Fe_2O_3	Li_3PO_4	$NiFe_2O_4$	V_2O_5	AlGaN	MnN	CdS	Co
Al:HfO_2	Fe_3O_4	LiPON	NiO	WO_3	AlN	NbN	CoS	Cu
Al:ZnO	$FePO_4$	$LiFePO_4$	NiO	Y_2O_3	BxGa1-xN	NbTiN	Cu_2S	Fe
AlGaN	Ga_2O_3	Li_2MnO_4	PO_4	YSZ	BxIn1-xN	SiN	Cu_2ZnSnS_4	Mn
BOx	HfO_2	Li_5TaOz	SiO_2	$ZnAl_2O_4$	CoN	TaN	In_2S_3	Ni
$BiFeO_3$	HfSiON	MgO	SnO_2	ZnO	Hf3N4	TiN	MnS	Pd
CeO_2	In_2O_3	MnO_2	SrO	ZnMgO	InAlN	WN	PbS	Pt
Co_3O_4	ITO	MoO_3	$SrTiO_3$	ZnOS	InGaN	ZrN	Sb_2S_3	Ru
$CoFe_2O_4$	La_2O_3	NaTiO	Ta_2O_5	ZrO_2	InN		SnS	Bi_2Te_3
Er_2O_3	Li_2O	Nb_2O_5	TiO_2				ZnS	Sb_2Te_3

Atomic layer deposition holds tremendous promise across a wide array of industries, including energy, optical, electronics, nanostructures, biomedical, and more.

2. PRINCIPLE AND TECHNIQUE of ALD

The principle of atomic layer deposition is similar to chemical vapor deposition (CVD) except the ALD reaction breaks the CVD reaction into two half-reactions, keeping the precursor materials separate during the reaction [9].

ALD film growth is self-limited and based on surface reactions, which makes achieving atomic scale deposition control possible. By keeping the precursors separate throughout the coating process, atomic layer thickness control of film grown can be obtained as fine as atomic/molecular scale per monolayer.

Atomic layer deposition accomplished through sequential pulsing of special precursor vapors, each of which forms about one atomic layer during each pulse (reaction cycle). Reaction cycles are then repeated until the desired film thickness is achieved, versus chemical vapor deposition that introduces multiple precursor materials simultaneously. ALD is perfect and effective in case if it is uniform in thickness, even deep inside pores, trenches and cavities. A wide variety of thin films can be deposited using gas, liquid, or solid precursors.

Starting with a conditioned surface, the ALD cycle is composed of four steps (pictured in Figure 1 for ALD of Al_2O_3 using trimethyl aluminum (TMA) precursor and water) [10].

A first precursor gas is introduced into the process chamber and produces a monolayer of gas on the wafer surface. Then a second precursor of gas is introduced into the chamber reacting with the first precursor to produce a monolayer of film on the wafer surface. Two fundamental mechanisms: Chemisorptions saturation process and Sequential surface chemical reaction process

Step 1: During the precursor dosing, adsorption of precursor molecules occurs on reactive surface sites and reaction products are formed. The excess precursor and reaction products are purged out of the deposition chamber and a (sub) monolayer of precursor remains adsorbed on the substrate surface.

Step 2: The co-reactant (in this case water) is introduced into the chamber and reacts with the adsorbed TMA molecules to form a (sub) monolayer of the desired material (Al_2O_3).

Step 3: Un-reacted co-reactant molecules and by-products are purged out and after consecutive cycles a uniform layer of desired material (Al_2O_3) if deposited.

Deposition of Al_2O_3 layer is shown in Figures (1-7) [11]..

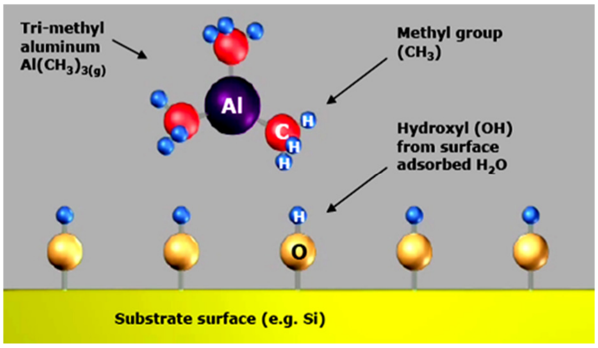


Figure 1 (a). ALD cycle for Al_2O_3 deposition- Formation of Si-O-H (Step 1a)

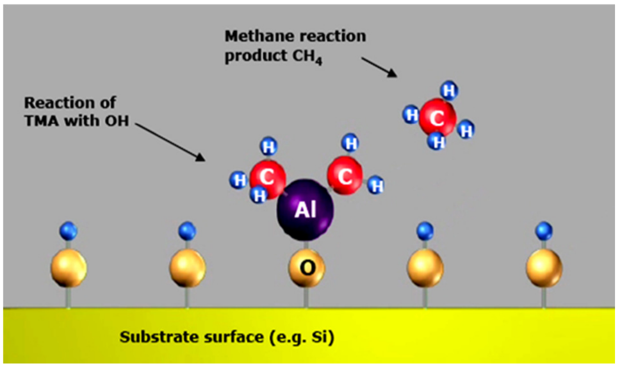


Figure 1 (b) ALD cycle for Al_2O_3 deposition- Formation of Si-O-Al$(CH_3)_3$ (Step 1b)

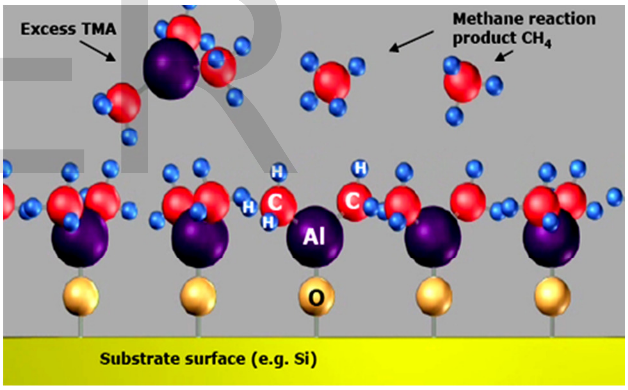


Figure 1(c). ALD cycle for Al_2O_3 deposition- Formation of uniform layer of Al_2O_3 (Step 1c)

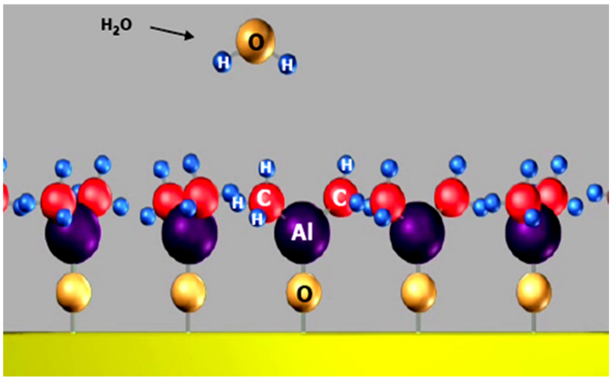


Figure 2(a). Cycle 2, Repeat of step 1a (Step 2a)

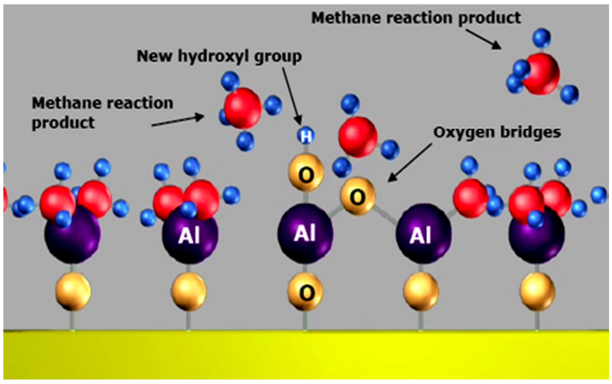


Figure 2(b). Cycle 2, Repeat of step 1b (Step 2 b)

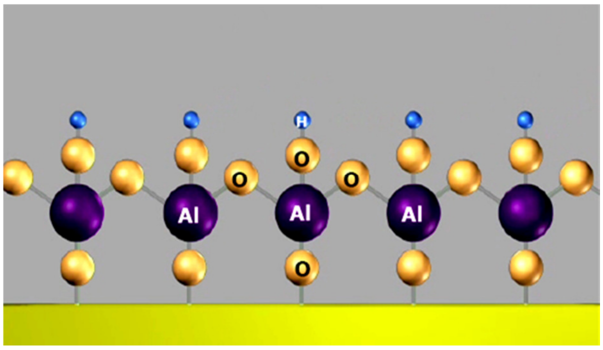


Figure 2 (c) Cycle 2, Repeat of step 1c (Step 2c)

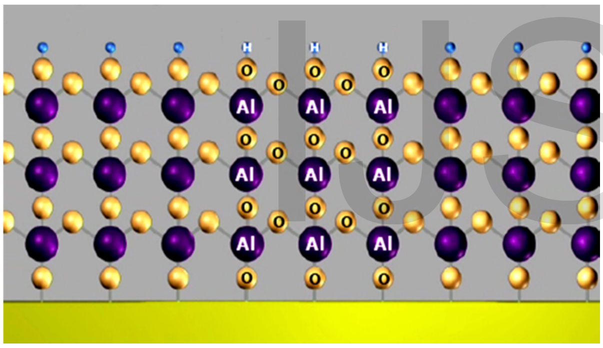


Figure 3. Deposition of Al_2O_3 uniform layer After 3 cycles

The cycle is repeated to deposit additional monolayers to achieve the targeted film thickness. Since each pair of gas pulses (one cycle) produces exactly one monolayer of film, the thickness of the resulting film may be precisely controlled by the number of deposition cycles. Four main types of ALD reactors (i) Closed system chambers (ii) Open system chambers (iii) Semi-closed system chambers and (iv) Semi-open system chambers. Closed system chambers are most commonly used reactors.

3. EFFECTS of ALD

Atomic Layer Deposition (ALD) offers precise control down to the atomic scale. ALD holds tremendous promise across a wide array of industries, including energy, optical, electronics, nanostructures, biomedical, and more. The ALD results [11] in the enhanced optical activity, thermal & photo-sensitivity, electrical conductivity, passivation quality [12] dielectric property, storage capacity, Barrier protection of materials have been investigated for their unique material properties, including band gap semi conducting properties, photoluminescence, and absorbance have been observed in two dimension dichalcogenides as the film thickness is reduced to one monolayer thickness [13].

ALD is exceptionally effective at coating surfaces that exhibit ultra high aspect ratio topographies, as well as surfaces requiring multilayer films with good quality interfaces technology.

4. APPLICATIONS of ALD

A wide variety of ALD based materials have extensive applications in various industries, including energy, optical, electronics, nanostructures, biomedical, and more. The present research reveals the ALD applications in various fields like - anti-tarnishing coatings on silver, thin films for photovoltaic applications in energy sector, passivations and hermetic barrier coatings on plastics and metals, tribological coatings for high precision parts, premiering applications on plastics and metals for other surface finishes, Storage capacitor dielectrics, High-k gate oxides, thin films for LEDs, barrier layers on glass, gate oxide, barrier layers, primer layers, gate electrode, optical coatings, flat panel displays, solar panels, magnetic heads, memory devices, fuel cells e.g. single metal coating for catalyst layers, sensors, Bio MEMS, Pinhole-free passivation layers for OLEDs and polymers, Passivation of crystal silicon solar cells, gas permeability reduction of plastics, wear resistance, primer for other coatings, smoothening of rough surface, construction *f* 3D structures, nozzles pipes, porous structures, adhesion layers, organic semiconductors, highly conformal coatings for microfluidic and MEMS applications, other nanotechnology and nano-electronic applications, coating of nonporous structures. Some most important ALD materials and their applications are illustrated below-

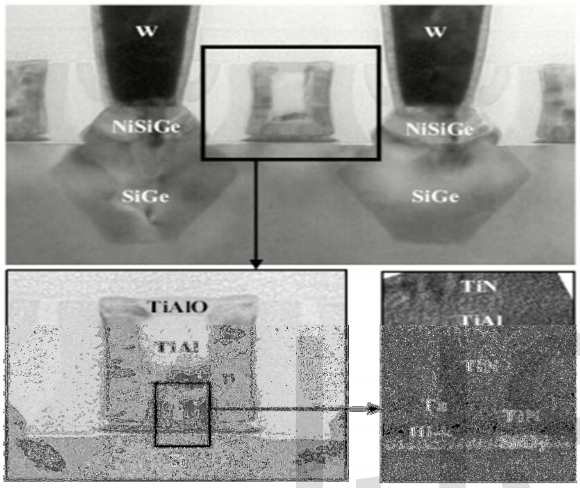
4.1 Microelectronics applications

In microelectronics, ALD is studied as a potential technique to deposit High-k (high permittivity) [14]. Gate oxides, high-k memory capacitor dielectrics, ferroelectrics, and metals and nitrides for electrodes and interconnects. In high-k gate oxides, where the control of ultra thin films is essential, ALD is only likely to come into wider use at the 45 nm technology. In metallizations, conformal films are required; currently it is expected that ALD will be used in mainstream production at the 65 nm node. In dynamic random access memories (DRAMs) [15], the conformality requirements are even higher and ALD is the only method that can be used when feature sizes become smaller than 100 nm.[16]. Several products that use ALD include magnetic recording heads, MOSFET Gate stacks, DRAM capacitors, nonvolatile ferroelectric memories, and many others.

4.2 Gate oxides

Deposition of the high-k oxides Al_2O_3, ZrO_2, and HfO_2 has been one of the most widely examined areas of ALD. The motivation for high-k oxides comes from the problem of high tunneling current through the commonly used SiO_2 gate dielectric in metal-oxide-semiconductor field-effect transistors (MOSFETs) [17] when it is downscaled to a thickness of 1.0 nm and below. With the high-k oxide, a thicker gate dielectric can be made for the required capacitance density, thus the tunneling current can be reduced through the structure.

Intel Corporation has reported using ALD to deposit high-k gate dielectric for its 45 nm CMOS technology [18].



4.3 Transition-metal nitrides

Transition-metal nitrides, such as TiN and TaN find potential use both as metal barriers and as gate metals. Metal barriers are used in modern Cu-based chips to avoid diffusion of Cu into the surrounding materials, such as insulators and the silicon substrate, and also, to prevent Cu contamination by elements diffusing from the insulators by surrounding every Cu interconnection with a layer of metal barriers. The metal barriers have strict demands: they should be pure; dense; conductive; conformal; thin; have good adhesion towards metals and insulators. The requirements concerning process technique can be fulfilled by ALD. The most studied ALD nitride is TiN which is deposited from $TiCl_4$ and NH_3. [19].

Metal films

Motivations of an interest in metal ALD are:

1. Cu interconnects and W plugs, or at least Cu seed layers [20] for Cu Electro-deposition and W seeds for W CVD,
2. Transition-metal nitrides (e.g. TiN, TaN, WN) for Cu interconnect barriers
3. Noble metals for ferroelectric random access memory (FRAM) and DRAM capacitor electrodes
4. High- and low-work function metals for dual-gate MOSFETs.

4.4 Magnetic recording heads

Magnetic recording heads utilize electric fields to polarize particles and leave a magnetized pattern on a hard disk. Al_2O_3 ALD is used to create uniform, thin layers of insulation [21]. By using ALD, it is possible to control the insulation thickness to a high level of accuracy. This allows for more accurate patterns of magnetized particles and thus higher quality recordings [22].

4.5 DRAM capacitors

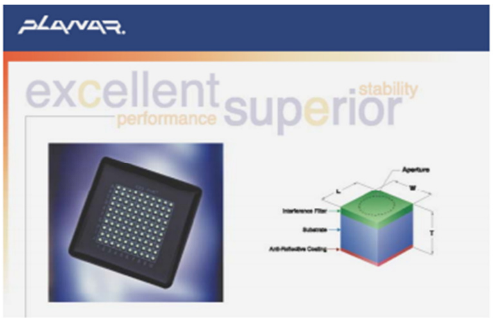
Dynamic random-access memory (DRAM) capacitors are yet another application of ALD. An individual DRAM cell can store a single bit of data and consists of a single MOS transistor and a capacitor. Major efforts are being put into reducing the size of the capacitor which will effectively allow for greater memory density. In order to change the capacitor size without affecting the capacitance, different cell orientations are being used. Some of these include stacked or trench capacitors [23]. With the emergence of trench capacitors, the problem of fabricating these capacitors comes into play, especially as the size of semiconductors decreases. ALD allows trench features to be scaled to beyond 100 nm. The ability to deposit single layers of material allows for a great deal of control over the material. Except for some issues of incomplete film growth (largely due to insufficient amount or low temperature substrates), ALD provides an effective means of depositing thin films like dielectrics or barriers [24].

Optics

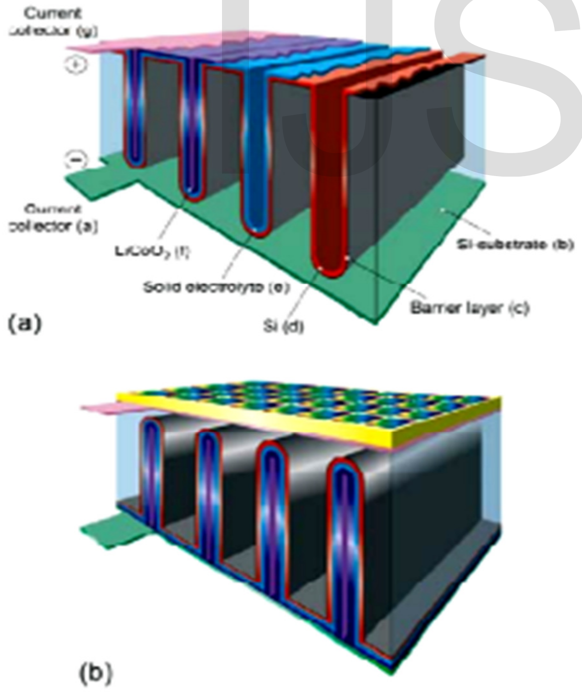
High uniformity and accurate thickness control make ALD attractive for optics. Planar developed a multiple-cavity Fabry-Perot filter for WDM (wavelength division multiplexing) applications. The device consists of about 200 layers and has thickness of device consists of about 200 layers and has thickness of 45 µm

High-Efficiency Silicon Solar Cells

Recently, it was shown that thin films of aluminum oxide (Al_2O_3) grown by atomic layer deposition (ALD) provide an excellent level of surface passivation on low-resistivity p- and n-type silicon wafers. The PERC-type solar cell structure demonstrate the applicability of Al_2O_3 rear surface passivation to high-efficiency silicon solar cells [25].



Li ion batteries: all solid state, 3D structure (all films: el t d t ll t l t l t d b ALD) Electrodes, current collectors, electrolyte made by ALD) - supercapacitors - thermoelectric materials (Bi_2Te_3 Zn_4Sb_3 thermoelectric materials $(Bi)_2Te_3$, Zn_4Sb_3) Schematic picture of a 3D integrated all-solid-state Li-ion battery for which surface enlargement can be ion battery for which surface enlargement can be accomplished by electrochemical etching or Reactive Ion Etching (RIE) of a silicon substrate (a). Autonomous energy Autonomous energy-generating and storage device generating and storage device, combining a Si-solar cell with an integrated all-solid state battery(b). [26], [27]. [28].



Energy Storage

ALD deposited films have been investigated in energy storage and battery applications with demonstrated levels of improved performance.

Cu2S / carbon nano-tubes (CNT) cathodes @260 mA h g-1 and Li2S @ 800 mA h g-1 (Figure 4)

[29], [30].

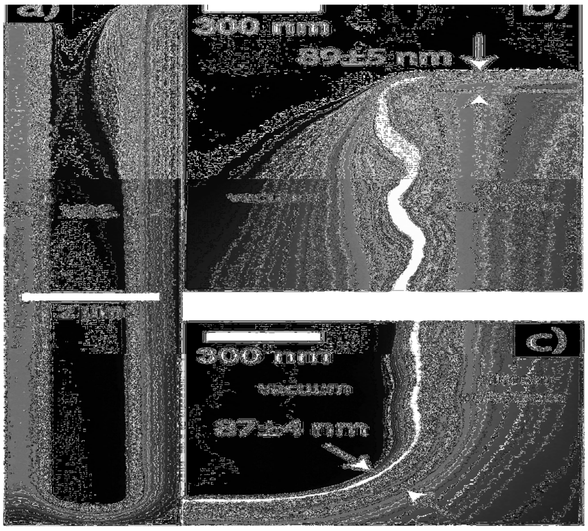


Figure 4. Cu2S / SnS2 / ZnS trilayer deposited on a silicon trench wafer

Biomedical applications

Understanding and being able to specify the surface properties on biomedical devices is critical in the biomedical industry, especially regarding devices that are implanted in the body. A material interacts with the environment at its surface, so the surface properties largely direct the interactions of the material with its environment. [Surface chemistry and surface topography affect protein adsorption, cellular interactions, and the immune response [31].

Some current uses in biomedical applications include creating flexible sensors, modifying nanoporous membranes, polymer ALD, and creating thin biocompatible coatings. ALD has been used to deposit TiO_2 films to create optical waveguide sensors as diagnostic tools [32].

Quality and quality control

The quality of an ALD process can be monitored using several different imaging techniques to make sure that the ALD process is occurring smoothly and producing a conformal layer over a surface. One option is cross-sectional SEM images or transmission electron microscopy (TEM) images, which allow for inspection at the micro and nano scale. Another optical quality evaluation tool is spectroscopic ellipsometry (SE). Using SE in between the depositions of each layer added on by ALD provides information on the growth rate and material characteristics of the film can be assessed. [33].

Applying this analysis tool during the ALD process, sometimes referred to as in situ spectroscopic ellipsometry, allows for greater control over the growth rate of the films during the ALD process. This type of quality control occurs during the ALD process rather than assessing the films afterwards as in TEM imaging, or XRR.

5. ADVANTAGES AND LIMITATIONS of ALD

5.1 Advantages

ALD provides a very controlled method to produce a film to an atomically specified thickness. Also, the growth of different multilayer structures is straightforward. Due to the sensitivity and precision of the equipment, it is very beneficial to those in the field of microelectronics and nanotechnology in producing small, but efficient semiconductors. ALD is typically run at lower temperatures along with a catalyst which is thermo-chemically favored. The lower temperature is beneficial when working with fragile substrates, such as biological samples. Some precursors that are thermally unstable still may be used so long as their decomposition rate is relatively slow [34].

5.2 Disadvantages

High purity of the substrates is very important, and as such, high costs will ensue (Stanford). Although this cost may not be much relative to the cost of the equipment needed, one may need to run several trials before finding conditions that favor their desired product. Once the layer has been made and the process is complete, there may be a requirement of needing to remove excess precursors from the final product. In some final products there are less than one percent of impurities present [35].

6. ECONOMIC VIABILITY & LIMITATIONS of ALD

Atomic layer deposition instruments can range anywhere from Rs. 130,00000 to Rs.520,00000 based on the quality and efficiency of the instrument. There is no set cost for running a cycle of these instruments; the cost varies depending on the quality and purity of the substrates used, as well as the temperature and time of machine operation. Some substrates are less available than others and require special conditions, as some are very sensitive to oxygen and may then increase the rate of decomposition. Multi-component oxides and certain metals traditionally needed in the microelectronics industry are generally not cost efficient [36]. The process of ALD is very slow and the precursors so used must be volatile and these problems are known to be its major limitation.

7. FUTURE PERSPECTIVE of ALD

With devices becoming ever smaller and increasingly structured into complex three dimensional shapes, the need for controllable and conformal thin films has never been greater. ALD, with its sequential self-limiting reactions, is able to meet these demands in one of the most effective methods possible. Comparable techniques, such as CVD and PVD, cannot always provide the same level of uniformity, conformality and thickness control at the Angstrom level. Because of the advantages of ALD, ALD processes have been developed for a wide variety of materials, ranging from metals to metal oxides to complex ternary materials, allowing ALD to become incorporated into industrial procedures.

On the basis of effectiveness and applicability of ALD based materials, this technology will surery be result into the more precise smart devices. The applications of ALD and nanotechnology shall be helpful in developing high data storage devices, supercomputers, power and energy storage devices, rocket and satellite technology. Power transmission, media communication and wireless technology shall be even more precise and faster. It can be expected that in the next decade the technology shall help in exploring the universe.

REFERENCES

1. "History of Atomic Layer Deposition (ALD)," Finnish MicroNanoTechnology Network (FMNT), 24 April 2006. <http://www.fmnt.fi/index.pl?id=2913&isa=Category&op=show>.
2. Ahvenniemi, Esko; Akbashev, Andrew R.; Ali, Saima; Bechelany, Mikhael; Berdova, Maria; Boyadjiev, Stefan; Cameron, David C.; Chen, Rong; Chubarov, Mikhail (2016-12-16).
3. "Review Article: Recommended reading list of early publications on atomic layer deposition—Outcome of the "Virtual Project on the History of ALD"". Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films. 35 (1): 010801. doi:10.1116/1.4971389. ISSN 0734-2101.
4. Markku Leskelä (professor at the University of Helsinki) at the ALE-1 conference, Espoo, Finland.
5. Moore, Gordon E. (1965-04-19). "Cramming more components onto integrated circuits". Electronics. Retrieved 2016-07-0.
6. Mikhail Ladanov et al. Effects of the physical properties of atomic layer deposition grown seeding layers on the preparation of ZnO nanowires Journal of Physics and Chemistry of Solids, Volume 74, Issue 11, November 2013, Pages 1578–1588.
7. Puurunen, Riikka L. (2014-12-01). "A Short History of Atomic Layer Deposition: Tuomo Suntola's Atomic Layer Epitaxy". Chemical Vapor Deposition. 20 (10-11-12):332–344. doi:10.1002/cvde.201402012.
8. http://beneq.com/en/thin-films/technology/atomic-layer-deposition.
9. A. Knop–Gericke, "Preparation of Model Systems by Physical Methods," a lecture given at Modern Methods in Heterogeneous Catalysis Research Lecture Series, Fritz Haber Institute of the Max Planck Society. 24 April 06, <http://w3.rz-berlin.mpg.de/%7Ejentoft/lehre/ catalysis0405.html.
10. "Atomic Layer Deposition," Cambridge NanoTech Inc., 24 April 06. <http://www. cambridgenanotech.com.
11. "How Atomic Layer Deposition Works" Applied Materials.https://www.youtube.com/ watch?v=KOEsgZU1sts.
12. R. Kotipalli et al, Passivation effects of atomic-layer-deposited aluminum oxide, EPJ Photovoltaics 4, 45107 (2013) www.epj-pv.org.
13. http://www.cambridgenanotechald.com/applications/chalcogenides.shtml].
14. Nanotechnology. 2015 Feb 13;26(6):064001. doi: 10.1088/0957-4484/26/6/064001. Epub 2015 Jan 21.
15. https://en.wikipedia.org/wiki/Dynamic_random-access_memory.
16. https://en.wikipedia.org/wiki/Atomic_layer_deposition#cite_note.
17. https://en.wikipedia.org/wiki/MOSFET.
18. https://en.wikipedia.org/wiki/45_nanometer.
19. K.E. Elers et al.,Chem. Vap. Deposition 4,149, 2002.
20. Waechtler, T.; et al. (2011). "ALD-grown seed layers for electrochemical copper deposition integrated with different diffusion barrier systems". Microelectron. Eng. 88: 684–689. doi:10.1016/j.mee.2010.07.004.

21. http://www.miics.net/archive/getfile.php?file=162 .
22. A.Paranjpe et al. J. Electrochem. Soc. 148 (2001) G465.
23. http://smithsonianchips.si.edu/ice/cd/MEMORY97/SEC07.PDF .
24. Archived September 8, 2005, at the Wayback Machine .
25. G. Agostinelli, A. Delabie, P. Vitanov, Z. Alexieva, H.F.W. Dekkers, S. De Wolf, G. Beaucarne, Sol. En. Mat. Sol. Cells 90, 3438 (2006).
26. Notten et al. Adv. Mater. 19 (2007) 4564.
27. B. Hoex, S.B.S. Heil, E. Langereis, M.C.M. van de Sanden, W.M.M. Kessels, Appl. Phys. Lett. 89, 042112 (2006).
28. S. Dauwe, Low-temperature rear surface passivation of crystalline silicon solar cells, Ph.D. thesis, ISFH, University of Hanover, Germany, 2003.]
29. Riha, S. C. et al. Stabilizing Cu 2S for Photovoltaics One Atomic Layer at a Time. Acs Appl Mater Inter 131010083550003 (2013). doi:10.1021/am403225e .
30. Thimsen et al. , Chemistry of Materials, 24(16), 3188–3196 (2012).
31. Surface chemistry and surface topography affect protein adsorption, cellular interactions, and the immune response https://en.wikipedia.org/ wiki/Atomic_layer_deposition#cite_note-32.
32. https://en.wikipedia.org/wiki/Atomic_layer_deposition#cite_note-33.
33. https://en.wikipedia.org/wiki/Atomic_layer_deposition#cite_note-insitu-37.
34. George, S.M. (2010). "Atomic Layer Deposition: An Overview". Chem. Rev. 110: 111–131. doi:10.1021/cr900056b.
35. http://files.instrument.com.cn/FilesCenter/20060216/18273.pdf.
36. Molecular Beam Epitaxy & Atomic Layer Deposition Systems - SVT Associates.