

Review of Atomic Layer Deposition of Nanostructured Solar Cells

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Abstract-

This study reviews atomic layer deposition technique with a special interest on solar cells applications. Atomic layer deposition is a vapour phase deposition technique used for producing thin films for several applications. This review focuses on the chemistry of Atomic Layer Deposition of solar cells, merits and demerits of ALD on thin film solar cells. Solar cells have attracted a lot of interest due to their potential for affordable, clean and sustainable energy. Solar cells can be deposited using different deposition techniques but Atomic layer deposition currently attracts attention owing to the merits. ALD has functional merit to bulk materials, great processing flexibility and affordability. The review examined the merits of ALD and solar cells and areas for future study. It offers affordability, ease of control of film growth, conformal and improvement on the deposition of solar cells. Despite few demerits, ALD is poised to be the deposition technique of choice for modifying interfaces of the film for improved performance.

Key words: Atomic Layer Deposition, Solar cells, Review, Thin films

1. Introduction

Clean, inexpensive and sustainable energy has been a keystone of increasing wealth and economic development of emerging economies. There is currently more investment in such technologies as alternate materials to meet global power needs of about 17 TW [1]. The emphasis is on the reduction of the cost and complexity of production of such technologies. About 120,000 TW of solar energy gets to the earth and only 600 TW is useful for consumption [2]. This makes solar energy the most abundant renewable and clean energy source. However, solar energy currently contributes just 1.1% of the total energy supply [3]. This low penetration may be attributed to several factors related to cultural, technology and economy. Sunlight is not evenly distributed globally and so is the level of acceptance/penetration of solar energy. Although, there is currently an increase in thin films solar cells research with emphasis on cost reduction for global consumption. Despite the decrease in solar cost in several developed countries, the same cannot be said of most developing countries. Domestication of solar energy technologies in all country will drastically reduce the cost and increase the acceptance globally. Module cost has been reduced but other factors still inhibit widespread of solar technology. The cost of solar is still unaffordable in several countries due to some factors. These factors include shipping, permits, labour and inspection cost incurred from importing solar in such countries [4-6]. A reduction in area per module and increased efficiency can crash the overall solar costs. This implies solar with theoretical efficiencies above the Shockley-Queisser limit with a cost less than \$0.20 per watts [7, 8]. Thin film technology especially nanostructured metal oxide and scalable deposition like ALD can break the Shockley-Queisser limit [9, 10].

Thin films Materials can be deposited using various techniques [11]. There has been an attempt to review atomic layer deposition and its applications by some studies in the past [12-16]. Puurunen [17] did a review of the surface chemistry of ALD. Although, Parsons, Elam [18] gave a review of the history and origin of Atomic layer deposition science from the 1960s until 2013. Marin, Lanzutti [19] reviewed the ALD techniques, drawback and the instruments used for ALD analysis/characterization. Miikkulainen, Leskelä [12] reviewed the basics of ALD, the process of ALD reactant and ALD processing of ternary compounds. Kim [13] did a review of ALD processing of metals and nitride films and their areas of applications in semiconductor fabrication. Guo, Ye [14] reviewed the surface chemistry of ALD and its reaction mechanism for surface modification of polymeric materials. Tynell and Karppinen [20] did a comprehensive review of atomic layer deposition of ZnO and the applications. Kessels, Hoex [21] understudied the prospects of ALD for solar cells manufacturing. The study focused on the ALD deposition for first, second and third generation solar cells.

This study will explore the fundamentals, applications of ALD and examples of ALD deposited solar cells. This will open frontiers for more research on ALD deposition of thin film solar cells.

1.1 Deposition of Thin film

Thin film deposition is classified into three groups by means of its nature of deposition as illustrated in Figure 1 [22]. This classification is broadly grouped based on the chemical or physical process of the thin films [23]. Deposition of the thin film is done above the substrate surface. The material to be deposited is added to the substrate in layers. This layer can be structural or as a spacer that can be removed thereafter [24]. Chemical deposition occurs when the hot substrate and inert gases react chemically in a low atmospheric pressure chamber. Chemical deposition is divided into gas-phase and solution-processed. The gas-phase are atomic layer epitaxy, chemical vapour deposition and atomic layer deposition [25]. The solution-processed are spray pyrolysis, chemical bath deposition, screen printing, sol-gel, dip-coating and spin-coating [26-30]. Chemical deposition can also be sub-classified, based on precursor phase, into the spin coating, plating, atomic layer deposition, and chemical vapour deposition. The chemical vapour deposition (CVD) include plasma-enhanced CVD, low-pressure CVD and very low-pressure CVD [31].

However, physical deposition involves the physical movement of the material toward the substrate surface. This material can be liquid, solid or vapour. Physical deposition process includes sputtering (DC and RF), thermal evaporation, ion plating, pulsed laser deposition and Molecular Beam Epitaxy (MBE) [32-35].

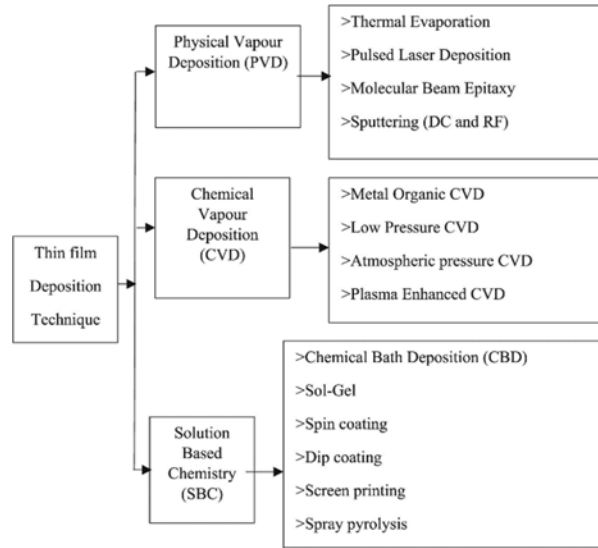


Figure 1: Classification of thin film deposition methods

2. Introduction to Atomic Layer Deposition basics

The emerging and future directions of ALD is geared towards energy applications. This includes energy conversion, energy conservation and energy storage. The main focus of energy conversion ALD studies is on fuel cells, solar cells and photo-electrochemical cells. However, energy conservation researches are towards improved catalysts. ALD study for energy storage tends to gravitate towards lithium and ultra-capacitors. The focus of ALD studies on energy applications stem from the interest in nanostructured materials. Nanostructured material is believed to be a global solution for low-cost and eco-friendly energy [36-39]. ALD is a viable tool for growing nanomaterials and deposition of nanostructured materials. This is in addition to the vast merit of the technique.

ALD is a vapour phase deposition technique used for the deposition of different categories of thin films materials [40]. It is based cyclic use of self-limited chemical reactions for adjusting of the layer thickness. ALD has shown tremendous potential for deposition of novel semiconductors and other energy conversion processes [41-43]. The quest for efficient and affordable thin-film solar cells have shifted research focus to the atomic level control of thin film thickness, uniformity and maintains quality. ALD appears to be deposition technique of choice due to the simplicity, reproducibility, conformal, and uniform nature of the as-deposited thin films [44, 45]. Also, films deposited with ALD are continuous and pin-hole free [46]. The ALD was originally known as atomic layer epitaxy (ALE) by Suntola and Antson in 1977 [47]. ALD evolved from a couple of ALE processes of incorporating metals and metal oxides deposited non-epitaxial.

2.1 Chemistry of ALD

ALD is similar to chemical vapour deposition. However, ALD comprises of chemical reactions in which the precursors react with the surface successively but the reactants are kept apart at lower temperature [48]. During this reaction, the precursor is pulsed into a vacuum chamber of about <1 Torr for a specified amount of time to enable the precursor to react with the surface. The surface reaction is disconnected using nitrogen or argon purging. This purging ensures that

unreacted precursor and by-product are removed. The purging and self-limited reactions create the ALD cycle which is shown in Figure 2i. A detailed schematic of the ALD cycle is depicted in Figure 2ii [49]. The amount of film thickness deposited in one complete cycle is known as growth per cycle (GPC). The final thickness is not dependent on the duration of the reaction but a number of the cycle. Individual layer thickness can be optimized with great accuracy.

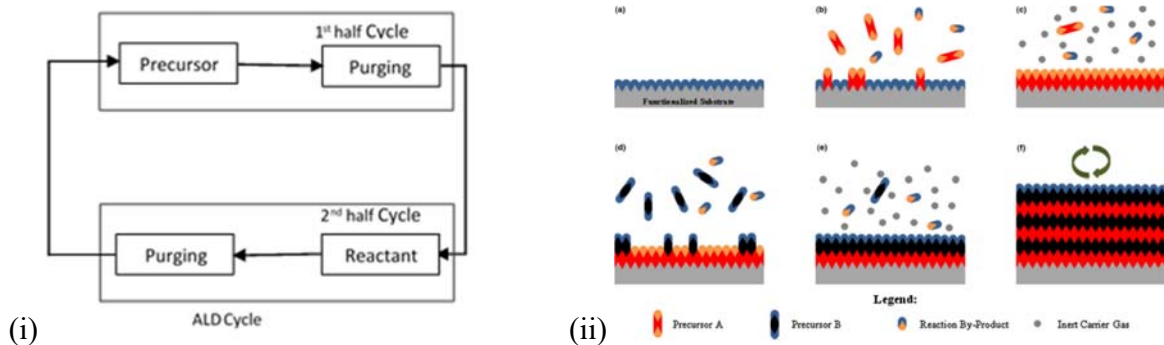


Figure 2: ALD cycle (i) summarized the ALD cycle (ii) Schematic of the ALD process. (a) Substrate surface has natural functionalization or is treated to functionalize the surface. (b) Precursor A is pulsed and reacts with the surface. (c) Excess precursor and reaction by-products are purged with an inert carrier gas. (d) Precursor B is pulsed and reacts with the surface. (e) Excess precursor and reaction by-products are purged with an inert carrier gas. (f) Steps 2–5 are repeated until the desired material thickness is achieved.

As seen in figure 2, a typical ALD cycle comprises four steps. The first step is the introduction of the reactants. This is followed by purging using inert gas to eliminate surplus reactants. The third step involves the addition of counter-reactants. The last step is purging of the unused reactants and by-product of the reaction. The anticipated thickness determines the amount of the cycle is repeated.

ALD operates at a lower temperature of $<350^{\circ}\text{C}$ compared to CVD. Atomic layer deposition temperature window is the temperature where the growth is saturated and is dependent on the specific ALD process. A poor growth rate is obtained when the deposition is done outside of the ALD window.

3. Atomic Layer deposition for thin film solar cells

Material Solar energy has been identified as an emerging energy source due to the clean and sustainable nature [50]. Electricity is generated using a photovoltaic effect when solar cells convert sunlight into electricity [51]. A lot of solar cells have been developed over the last decades. However, efficiency and affordability still hinder the uniform domestication of solar energy across the globe [52]. The uniform and affordable deposition of metal oxides (TiO, ZnO, SnO₂, HfO₂, Al₂O₃), nitrides (TaN, TiN, WN, NbN), metals (Ru, Ir, Pt) and sulphides (ZnS) can be achieved using Atomic layer deposition. A metal oxide thin film is formed when a metal complex (e.g metal halide, metal alkoxide, etc.) and an oxygen source reacts [17]. The metal oxide is obtained via hydrolysis and condensation steps. Although, research is still on for atomic layer deposition of Ge, Si, Si₃N₄ and other multicomponent oxides. Table 1 outline an overview of major atomic layer deposition in solar cells.

Table 1. Summary of major ALD applications in solar cells.

Author	Material	Application	Thickness (nm)	Solar Cells Classification
[53-56]	Cu _x S	Absorber	unspecified	Nanostructured heterojunction
[57, 58]	CuInS ₂			
[59]	ZnO	TCO		
[60, 61]	Al ₂ O ₃	Barrier Layer	0.1–25	Dye-sensitized
[62]	TiO ₂			
[63]	HfO ₂			
[64]	ZrO ₂			
[65]	AZO			
[66]	TiO ₂	Photoanode	5–90	
[65]	SnO ₂			
[67, 68]	ZnO			
[69]	TiO ₂ : Ta			
[61, 69-71]	TiO ₂			
[60]	SnO ₂			
[72]	HfO ₂			
[72]	In ₂ O ₃ :	Compact layer	7	
[73]	Sn			
[74]	Pt	TCO	5	
[75]	In ₂ S ₃			
[76]	ZnSe	Buffer layer	10 - 70	CIGS
[77]	ZnS			
[78-80]	O (Zn,			
[81-84]	Mg)			
[85]	Zn (O,			
[86-88]	S)			
[85]	TiO ₂			
[77]	In ₂ S ₃			
[89, 90]	Al ₂ O ₃			
[91]	GaS			
[91]	Zn-Sn-O	Diffusion barrier layer	100 – 300	
[92]	Al ₂ O ₃	Encapsulation layer	10 – 55	
	Al ₂ O ₃			

[93]		TCO	400	a-Si: H
[94-96]	ZnO: B	Surface passivation layer	5-30	c-Si
	Al ₂ O ₃			
[97]	AlAs	Absorber	30 - 400	AlGaAs/GaAs multijunction
[97, 98]	AlGaAs			
[97, 98]	GaAs			

Atomic layer deposition can be used in several aspects of solar cells. ALD provides better control over CBD, PVD and CVD in terms of material growth and conformality. Material growth and conformality are vital for the development of new and low-cost solar cells. Atomic layer deposition has shown an advantage over other techniques for solar cells deposition. Atomic layer deposition technique has been established for forming barrier layers [99], an absorber layer and a passivation layer in crystalline silicon cells [100]. This has been shown in different categories of emerging solar cells especially nanostructured metal oxide solar cells.

Banerjee, Lee [64] did ALD deposition of Al-doped ZnO films. The film thickness was ~100 nm and deposited at 150 °C on a quartz substrate. The study observed 17.7 cm²V⁻¹s⁻¹ maximum mobility and 4.4 x 10⁻³ Ωcm resistivity. The carrier concentration was obtained to be 1.7 x 10²⁰ cm⁻³ at 3% Al. A band gap of 3.23 eV and optical transmittance of 80% was achieved.

Nguyen, Resende [101] deposited Al-doped ZnO films on borosilicate glass substrate using atmospheric pressure spatial ALD. A transparency of 90% and a tunable band gap in the range of 3.30 and 3.55eV was achieved. Also, the electron mobility of 5.5 cm² V⁻¹s⁻¹ was recorded. A resistivity of 5.57 x 10⁻³ Ωcm was achieved which compared favourably with 3.0 x 10⁻³ Ωcm obtained using RF Sputtering [102]. Also, a carrier density of 4.25 x 10²⁰ cm⁻³ was recorded.

Also, Muñoz - Rojas, Sun [71] used atmospheric pressure spatial ALD to deposit TiO₂ as a hole blocking layers for P3HT-PCBM-based solar cells. Glass and ITO substrates were used for the films deposition. The longest deposition took 50cycles and the thinnest took 10cycles at 100 °C in 37 s. The study concluded that fast deposition, low processing temperature, material usage, and condensed energy input makes ALD effective method for layer blocking [103, 104].

Muñoz-Rojas, Jordan [105] deposited Cu₂O films on both glass and polymer substrate at 225 °C using rapid atmospheric ALD. The study achieved a carrier concentration of ~10¹⁶ cm⁻³ and mobility of 5 cm²V⁻¹s⁻¹ with a thickness in the range of 50 – 120 nm using area >10 cm².

Poodt, Cameron [106] did an overview of spatial ALD. The study summarized the concept of spatially separating the half-reactions, with separate precursor inlets and exhausts. Several applications of spatial ALD was mentioned with thin film encapsulation and light management for PV explained. The process is an improvement on conventional ALD where the use of shields of inert gas to separate the half-reaction zones. The gas shield width is designed wide to avert diffusion and cross-reactions between the precursors. Quantum dot sensitizers with precise size have been grown using ALD [107]. The absorption coefficient of about 1.7 x 10⁷ cm⁻¹ has been achieved on plasmonic nanostructures using ALD.

4. Atomic Layer Deposition Demerit

There are a couple of demerits associated with Atomic layer deposition of solar cells. A major demerit is the temperature range of 80 – 300 °C of most ALD. The elevated surface-volume ratio causes nanostructured materials to have substantial melting point depression when combined with the vacuum in the atomic layer deposition reactor chamber [108]. Also, the formation of the nanostructured film at low temperature causes quantum dot solar cells to lose their quantum confinement. This demerit can be overcome by depositing at a low temperature. A different solution is deposition of barrier layer material grown at low temperature around the quantum dot and the second material at elevated temperature.

Also, the non-uniformity of ALD deposition of some porous structure of the thin film is a demerit. A third demerit is the inadequate commercial precursors for ALD deposition in existence. This continues to restrict the deposition for targeted material and application [49].

5. Conclusion

This review successfully shed light on Atomic layer deposition, the chemistry of ALD, previous ALD deposition of solar cells and demerit of ALD. Atomic layer deposition has been shown to be the solution for conformal, precise thickness control and barrier layer formation for thin film solar cells, especially nanostructured solar cells. It offers affordability, ease of control of film growth and improvement on the deposition of solar cells. Despite the demerits, ALD is poised to be the deposition technique of choice for modifying interfaces of the film for improved performance.

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