



Atomic-layer-deposited buffer layers for thin film solar cells using earth-abundant absorber materials: A review



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ABSTRACT

Atomic layer deposition (ALD) is not just a thin film deposition technology limited to the semiconductor IC industries to grow high-*k* gate dielectric or a Cu diffusion barrier layer. In recent times, it has found plenty of applications in the field of renewable energy due to its precise thickness control up to few angstroms and its unique feature of conformal and uniform coating on any randomly shaped 3D structure. ALD has far-reaching applications in this field, including electrochemical storage, fuel cells, solar photovoltaics (PV), and catalysis for water splitting to produce H₂ as a green fuel. In solar PV technology, ALD is now being extensively used as an efficient tool to deposit surface passivation layers, absorber or sensitizer, transparent conducting oxide, and barrier and buffer layers in several kinds of solar cells. Out of all the different layers associated with a solar cell, ALD is majorly used for the development of a very thin *n*-type buffer layer. This review article presents a systematic chronological study on such ALD-grown buffer layers for thin film solar cells (TSFCs). The study is carried out in detail based on different earth-abundant absorber materials, such as Cu₂ZnSn(S,Se)₄ (CZTSSe), Cu₂O and SnS, for which ALD is successfully used to deposit the buffer layer.

1. Introduction

One of the biggest challenges in the 21st century is to meet the ever-rising demand for energy in every sector of life. While the conventional energy sources like coal, oil and natural gas still provide the maximum portion of the total energy produced worldwide (Fig. 1(a)), these sources pose a huge drawback in terms of the environmental pollution. Burning of fossil fuels produces CO₂, a greenhouse gas, which contributes to global warming and threatens the very existence of mankind. On the other hand, the limited availability of all these depletable energy sources adds on to the search for non-conventional and renewable energy sources. Another potential alternative to fossil fuels is nuclear energy. However, it also poses serious environment safety issues and hence has to abide by several policies related limitations.

Considering these issues, the use of environmentally clean and safe renewable energy sources has received great attention from scientists and technologists. As a result, the exponential increase in the cumulative installed capacity of the renewable energy sources has been observed for at least last fifteen years (Fig. 1(b)). Of the several promising renewable energy sources like wind, solar, H₂ and bio-mass *etc.*, solar energy can be considered as one of the most benign energy sources on

earth. The abundance of sun's energy in the form of light and heat can meet the energy demands of generations to come, if captured and stored in a suitable way. Therefore, the solar thermal and solar photovoltaic (PV) technologies were developed and are continuously being researched upon to improve their performance and sustainability. In the case of solar PV technology, the sunlight is directly converted into electricity with the help of a large area *p-n* junction semiconductor known as a solar cell. The incident photons generate electron-hole (e-h) pairs in the semiconductor material (absorber) in the device and then get separated with the help of a potential barrier that exists at the *p-n* junction. Silicon (Si) is the most well-established semiconductor material for this application and hence has been successfully commercialized. Though mostly crystalline Si (c-Si) is used for fabricating the solar cells, amorphous-Si (a-Si) has also been adopted for the same purpose to some extent. Not only have huge numbers of standalone solar PV stations been installed in several countries, but also a good number of grid-connected solar PV plants have been established, and more of these plants are going to come up in the near future. However, the huge cost and energy involved in deriving Si from SiO₂ drew researchers' attention towards other materials and technologies for solar PVs. As a result, a handful of different solar cell technologies have evolved and

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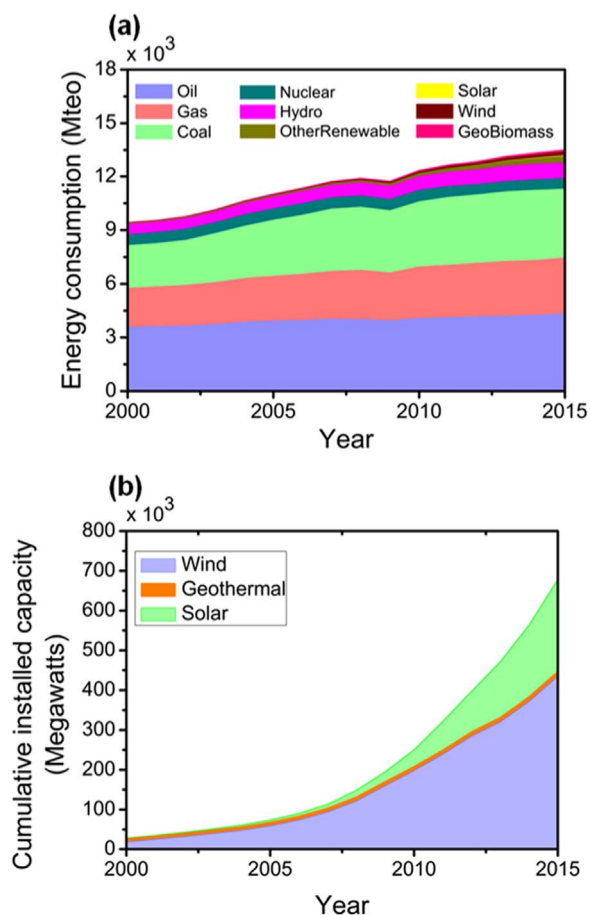


Fig. 1. The schematic representation of the (a) shares from different energy sources towards total energy consumption worldwide and (b) exponentially increasing share from renewable sources like wind and solar in 15 years. (All the data obtained from the BP Statistical Review of World Energy 2016) [1].

flourished with time. Heterojunction solar cells (bi-layer and bulk), organic photovoltaic (OPV), dye- and semiconductor sensitized solar cells (DSSC and SSSC), and thin film solar cells (TFSCs) are examples of such technologies [2–8]. A TFSC is a kind of heterojunction solar cell in which mainly Cu-based *p*-type absorbers such as Cu(InGa)Se₂ (CIGS), and Cu₂ZnSn(S,Se)₄ (CZTSSe) are used. With the help of an *n*-type buffer layer, the *p*-*n* junction which can separate the photo-generated e-h pairs [9–18] is created.

Similar to other Si and non-Si-based technologies, nano-dimensions are one of the most essential parameters in TFSCs to control the performance of the device. Especially, the thickness of the buffer layer in the TFSCs varies from a few nano-meters to a few hundred nano-meters. The formation of a smooth interface between absorber and buffer layer is also extremely important in this kind of solar cells. CdS has been considered to be the gold standard for this application for a long time [19,20]. However, the conventional wet chemical synthesis method, chemical bath deposition (CBD), which is used to deposit the CdS layer, has several disadvantages. First of all, CBD is not a very compatible technique with the gas phase deposition techniques such as sputtering and co-evaporation that are usually adopted for growing the absorber material for TFSCs. Secondly, the film qualities (thickness and uniformity over the absorber surface) of the CBD grown buffer layer are bound to be affected by this technique's poor control on the material growth. Furthermore, replacing the CdS buffer layer became important because of the environmental hazards associated with Cd. Therefore, atomic layer deposition (ALD) is being considered in this field due to its well-established potential for depositing several kinds of oxide [21–25], sulfide [26–29], and ternary materials [30–32]. It is expected to be much more compatible than CBD for depositing the buffer layer on TFSC absorbers.

ALD is a gas-phase thin film deposition technique [33] in which the reactants (also known as precursors) are dosed sequentially and separated by the purging of an inert gas, such as Ar or N₂. The closest similar thin film deposition technique is the chemical vapor deposition (CVD) in which the reactants are mixed together to grow the desired film. Therefore, unlike all the other gas phase thin film deposition techniques like CVD and PVD (physical vapor deposition), ALD is unique in its feature of sequential dosing into the reactor maintained under vacuum. Fig. 2 shows such a sequential reaction scheme for the ALD growth of

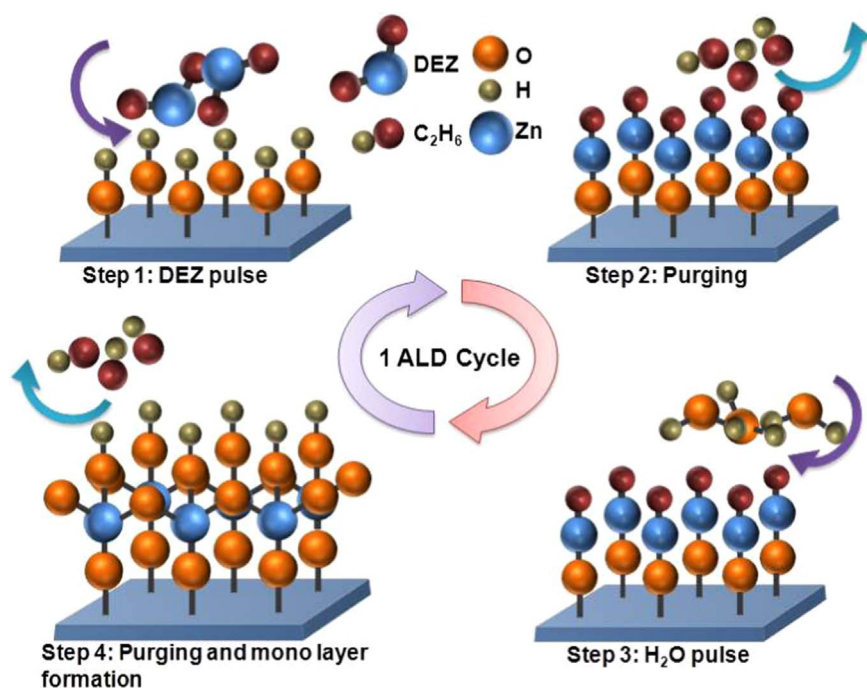


Fig. 2. Representation of one ALD cycle (ZnO) with the sequential precursor exposure.

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