Applications of atomic layer deposition in solar cells

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Abstract
Atomic layer deposition (ALD) provides a unique tool for the growth of thin films with excellent conformity and thickness control down to atomic levels. The application of ALD in energy research has received increasing attention in recent years. In this review, the versatility of ALD in solar cells will be discussed. This is specifically focused on the fabrication of nanostructured photoelectrodes, surface passivation, surface sensitization, and band-structure engineering of solar cell materials. Challenges and future directions of ALD in the applications of solar cells are also discussed.

Keywords: atomic layer deposition, solar cells, surface passivation, surface sensitization, band-structure engineering

(Some figures may appear in colour only in the online journal)

1. Introduction

Atomic layer deposition (ALD) is a low-temperature, vacuum, vapor-phase thin film growth technique that allows precise control in film thickness on an atomic scale and uniformity. It distinguishes itself from chemical vapor deposition (CVD) in that the precursors in an ALD process are injected into the reaction chamber in sequenced deposition cycles [1]. In this way, the precursors will not pre-react in the chamber before anchoring the substrate surface. With ALD, nearly 100% step coverage is possible especially for most binary oxides, but also depends on the gas flow mechanism. Recent attention to ALD is being focused on the deposition of smooth and uniform thin (from 10 down to 1 nm) films on non-planar three-dimensional (3D) structures. As summarized by several recent reviews and books, ALD has become a popular and powerful tool for the template-assisted fabrication of complex nanostructures and tailoring of physical properties of nanomaterials [1, 2].

For applications in energy-related research, the reader is encouraged to refer a few recent review articles [3–6]. Application in improving the cyclic stability and energy density of electrochemical energy storage devices (lithium-ion batteries and supercapacitors) [5, 7, 8], will be discussed in another review of this special issue. In this review, our focus is directed on solar cells, including dye-sensitized solar cells (DSSCs), quantum dot sensitized solar cells, organic–inorganic hybrid solar cells, thin-film solar cells (Si and Cu(In,Ga)Se₂ (CIGS)), and photoelectrochemical (PEC) cells. The role of ALD thin
films in solar cell functions can be classified into three major categories: (1) fabrication of nanostructured active electrodes or charge transporters (e.g., ZnO, ZnS, TiO2, Fe2O3, Cu2O); (2) forming heterojunction (e.g., Al2ZnO, TiO2, CdS or CdSe); (3) inert surface passivation of trap states (e.g., Al2O3, HfO2); and (4) catalytic noble metals (e.g., Pt, Pd, Ru, Ir, and composite metals) [9].

This article discusses typical application of ALD in solar cells. It starts with the fabrication of nanostructured electrodes, followed by electrode surface passivation, electrode surface sensitization by quantum dots and metal nanoparticles, and finally band-structure engineering in dye-sensitized and CIGS solar cells.

2. Nanostructured cell electrodes fabricated via ALD

2.1. Inverse opal-based photoelectrode

Inverse opal is a replicated shell structure of face-centered-cubic opal, with high specific surface area and porosity (74% void volume). The periodical 3D inverse opal exhibits photonic crystal properties, thereby providing additional avenues to enhance light–matter interactions by controlling the propagation of light via mirror reflections, slow photons, and surface resonant modes [10–13]. As such, the inverse opal structure is an ideal electrode architecture for energy conversion applications. TiO2 inverse opals have attracted a lot of attention in DSSCs as optical elements that impart the light harvesting and conversion efficiency of a PEC cell is a function of template filling using opal structures. Controlled filling was demonstrated [16]. Subsequently, as-fabricated high quality inverse opals with different pore sizes on fluorine-doped tin-oxide-coated glass substrate were studied as a photoanode for DSSCs application as shown in figure 1. These structures were found possessing several advantages as conformity and high filling fractions ensure robust interfacial contact with the substrate, thereby providing good electron transport paths. The power conversion efficiencies of 2.22%, 1.81% and 1.42% (AM1.5) were achieved using electrodes with pore sizes of 288 nm, 390 nm and 510 nm, respectively [17]. When compared to the conventional nanocrystalline TiO2 type of photoanode in DSSCs, inverse opal electrode showed weaker absorption due to its low surface area for dye loading. Tetreault et al resolved this issue by filling the voids of inverse opal (Al/ZnO, TiO2) fabricated using ALD with high surface area nanocrystalline TiO2. Highest power conversion efficiency of 4.9% was reported using non-optimized electrodes due to enhanced surface area from nanocrystalline TiO2 and improved electron mobility from highly conductive Al/ZnO layer [12].

Very similar to DSSCs, PEC splitting of water into H2 and O2 by using sunlight holds promise to convert intermittent solar energy into stable and storable chemical fuel. Crucial to the light harvesting and conversion efficiency of a PEC cell is a nanostructured photoanode where the incident photons are captured, electron hole pairs are generated and the subsequent electron transfer takes place [18–20]. Inverse opal based electrodes holds promise as they possess several favorable intrinsic characteristics for efficient solar energy conversion such as direct electron transport pathways for longer electron diffusion length, light scattering to promote the light harvesting ability by confining the light within the cell and intimate contact with the electrolyte for faster oxidation and reduction reaction kinetics.

Cheng and Karuturi et al investigated CdS quantum dots sensitized TiO2 inverse opal electrodes (figure 2(a)) for the first time for PEC hydrogen generation. While TiO2 inverse opals with three different pore sizes of 288, 510 and 900 nm
were fabricated using ALD based template replication of polystyrene opal templates, photosensitization of CdS quantum dots was achieved using SILAR method [20]. A promising photocurrent density of 4.84 mA cm\(^{-2}\) and an incident photon to current conversion efficiency (IPCE) maximum of \(~30\%\) have been attained for the 288 nm inverse opal as photoanode at 0 V versus Ag/AgCl bias under AM1.5 solar light illumination. The light harvesting efficiency of the TiO\(_2\) inverse opal electrode could be further improved by forming a bilayer structure where ZnO nanowire arrays are grown directly on top of TiO\(_2\) inverse opal. Upon TiO\(_2\) infiltration of opal template by ALD, a ZnO seeding layer is deposited using ALD to allow the subsequent solution growth of ZnO nanowire arrays (figure 2(c)). Upon CdS sensitization, the bilayer electrode showed a photocurrent of \(~5\) mA cm\(^{-2}\) at 0.75 V versus Ag/AgCl, which is two times higher than that of the pure ZnO nanowire array electrode [21]. The improved photocurrent is ascribed to the photonic crystal serving as a ‘dielectric mirror’ that increased the optical path and improved light–matter interactions, thus enhancing the overall light harvesting efficiency. ALD was further employed to develop a 3D ordered hierarchical nanobushes, using TiO\(_2\) inverse opal as a 3D host template for facile solution growth of networks of ZnO nanowires. In this work, TiO\(_2\) inverse opals were coated with \(~10\) nm conformal ZnO film on TiO\(_2\) shells using ALD and utilized as a 3D seed surface to grow the networks of ZnO nanowires using solution growth method and form nanobushes structure (figure 2(d)) [22]. The highest photocurrent density for nanobushes-CdS photoanode was observed to be 6.2 mA cm\(^{-2}\) at 0 V versus Ag/AgCl with an IPCE maximum of 60\%, which is also the highest reported photocurrent density value for CdS/TiO\(_2\) electrodes for PEC hydrogen generation.

2.2. Other types of electrodes

ALD has also been used to fabricate improved photocathode nanostructures for DSSCs via templated growth approach. It is possible to select an optimal template with desirable combination of nanostructure and physical properties for photocathodes without worrying about the chemical composition as ALD can be used to incorporate necessary material compositions. This approach was used to fabricate nanostructured electrodes for DSSCs from silica aerogel templates and depositing either ZnO or TiO\(_2\) layers using ALD to impart the desired semiconducting properties (figure 3(a)) [24–26]. Similarly, anodic aluminum oxide
(AAO) has been used to template ZnO-based DSSCs, which exhibited excellent photovoltages as a result of efficient charge transport through the 1D ZnO nanotubes [27]. The ease of fabrication and the flexibility of design make ALD based templated electrodes a promising candidate to advance DSSCs. In a conventional photoanode, photoelectrons need to diffuse through the entire thickness of the semiconducting photoanode before they are collected. During this diffusion process, electrons recombine with holes in the electrolyte resulting in energy losses. However, by depositing a transparent conducting material underneath the semiconducting layer, the electrons need only traverse the thicknesses of the order of few tens of nanometers to be collected. Using this technique, DSSCs were fabricated by depositing an ALD layer of TiO2 onto transparent conducting indium tin oxide (ITO) [28, 29]. Figure 3(b) shows a cross-sectional SEM image of a single concentric TiO2/ITO nanotube in 200 nm AAO pore. The underlying ITO was estimated to improve the photocurrent density by up to 60 times, clearly demonstrating the advantage of radial charge collection enabled by ALD.

3. Electrodes surface passivation via ALD

3.1. Surface passivation of photoanode in solar cells

For practical application of solar cells, long-term operation stability and high efficiency are highly required. Surface passivation could improve the photostability or viability of solar cells by isolating photoanode from surrounding environments, which is also in favor of the enhancement of efficiency by suppressing surface state recombination [12, 30, 31]. Initially, CVD technique was used to create surface passivation layer [32]. Compared with CVD, ALD provides a unique technique for the growth of passivation layer with excellent thickness and conformality control.

For DSSCs, its viability depends on the stability of surface-bound molecular chromophores. Detachment of molecular dyes from photoelectrode is one of the major limitations for the long-term operation stability. Recently, Son et al demonstrated the stabilization of small dye molecules on TiO2 photoanode surfaces in OrgD-sensitized solar cells (OrgD = (E)-2-cyano-3-(5'-((p-(diphenylamino)phenyl)thiophen-2'-yl)thiophen-2'-yl)-acrylic acid) through post-
assembly ALD of additional TiO₂ layer (figure 4) [33]. The deposited TiO₂ layer covered anchoring-groups of OrgD molecules and protected them from water molecules and hydroxide ions, thus decreasing detachment from TiO₂ photoanode surface. In comparison with untreated film, ALD TiO₂ layer reduced desorption rate of dye molecules by more than 50 times [33]. When increasing the thickness of ALD TiO₂ overlayer, desorption rate exponentially decreases [31, 33]. Although increasing the deposited oxide layer increases the stability of solar cells, it reduces interface electron injection efficiency from sensitizer to the conduction band of photoanode oxide, due to either the increase of conduction band potential of TiO₂ and/or the weakening of electronic coupling between electrons in dye and TiO₂ [34–36], which would reduce the overall efficiency. Therefore, it is important to find a balance between them to optimize device performance. As the ALD deposited oxide layer isolated anchoring-groups from water molecules or hydroxide ions, this method has been used to improve the stability of various dye sensitizers (such as [Ru(bpy)₂(4,4′-′PO₃H₂)bpy])²⁺, N719, N3 and Z907) in aqueous conditions [12, 33, 34, 37, 38], and various oxide passivation layer such as Al₂O₃ and Ga₂O₃ have also been ALD deposited [12, 33, 34, 37, 38].

In addition to improved stability, ALD treatment of DSSCs converts the initially dye-coated hydrophobic surface into a hydrophilic surface. The initial TiO₂/dye surface is usually hydrophobic due to the phenyl and/or alkyl terminating groups of adsorbed dyes. After ALD, TiO₂ or other oxide layers extend to near the dye termini, resulting in the hydrophilic TiO₂/dye/ALD layer surface, which is in favor of the permeation of aqueous electrolyte into photoelectrode mesopores, thus decreasing the limitation of photocurrent output due to constraining dye/aqueous solution and electrode/aqueous solution contact [31, 33].

Apart from DSSCs, ALD layer was also reported for the surface passivation of Si solar cells to reduce surface recombination and improve efficiency [39–41]. For example, Wang et al reported the improved efficiency of Si solar cells by suppressing surface recombination as well as reflection through ALD Al₂O₃ passivation layer [42]. The results revealed the improvement of short-circuit current density and efficiency by 8% and 10.3% respectively, realizing up to 18.2% conversion efficiency. In other works, the conversion efficiency as high as 23.2% was achieved in n-type Si solar cell with Al₂O₃ passivation layer [43–45], and surface recombination velocities below 10 cm s⁻¹ was obtained in p-type Si solar cell [46]. Similarly, ALD application in emergent perovskite solar cells for the growth of a highly compact TiO₂ layer for efficient hole-blocking has also been demonstrated [47].

3.2. Surface passivation of photoabsorber for solar water splitting

As PEC cell is based on a semiconductor/liquid junction, the semiconductor photoelectrodes must be stable in aqueous environments. However, many of the semiconductors used for PEC water splitting, such as Si, Cu₂O, InP, ZnO, are not stable at the highly oxidative potentials required for water oxidation [48–52]. Fortunately, the stability of these semiconductors can be improved with a thin protectively insulating layer. The thickness of the protective layer should be very thin, for example several tens nanometers, otherwise the charge transfer between the semiconductor and liquid will be blocked. In addition, to function as a protective layer, it should be very dense and have excellent conformality. Among various thin film deposition methods, only ALD can meet these demands. Indeed, the ALD TiO₂ thin films have been used to improve the stability of photoelectrodes of solar water splitting. For example, Thomsen et al demonstrated that the photocurrent of electrodeposited Cu₂O photocathode only drops to 78% to the initial photocurrent with 11 nm ALD TiO₂ as protective layer after 20 min, while without ALD TiO₂ protective layer it shows no photocurrent at all [50]. It has also been reported that the ALD TiO₂ can be used as a corrosion-resistant layer to protect the Si based photoanode without inhibiting charge carrier (electron or hole) transport and photon absorption. The sample with the corrosion-resistant ALD TiO₂ (2 nm) layer remained operational for at least 24 h, whereas the sample without the TiO₂ layer failed within 0.5 h [51]. Jeol et al reported that the ALD TiO₂ can be used as protective layer to improve the stability of InP nanopillar photocathodes [52]. Very recently, Hu et al reported ALD TiO₂ films (4–143 nm thick) to protect Si, as well as GaAs and GaP photoanodes for efficient water oxidation from photocorrosion [49]. For example, in conjunction with Ni oxide electrocatalysts, ALD TiO₂–Si photoanodes exhibited continuous oxidation for more than 100 h at photocurrent densities of >30 mA cm⁻² in 1.0 M KOH solution. And ALD TiO₂–protected GaAs and GaP photoelectrodes exhibited photovoltages of 0.81 and 0.59 V, and photocurrent densities of 14.3 and 3.4 mA cm⁻², respectively [49]. Meyer and coworkers reported the enhanced surface binding stability of a phosphonate-derivatized water oxidation catalyst over a wide pH range (1–12) by ALD TiO₂ [53]. Increased stabilization of surface binding allows use of basic solutions where a rate enhancement for water oxidation of ~10⁶ is observed compared with acidic conditions. These experiments suggest that the stability of photoelectrodes can be significantly enhanced by an ALD thin film, which may be suitable for long-term PEC applications.

Among various photo-absorber materials for PEC, hematite (α-Fe₂O₃) is one promising photoanode material due to its favorable optical band gap (~2.1 eV), chemical stability in aqueous environments, elemental abundance and low cost [54, 55]. However, the overall water splitting efficiency of hematite photoanodes is still lower than the theoretically maximum efficiency, which is primarily attributed to short hole diffusion length (~10 nm) compared to the light penetration depth of several hundred nanometers [56]. One possibility to overcome the drawback is to have non-conventional photoelectrode design, i.e. nanorods or nanowires, which is characterized by both short charge-collection distances and high surface areas. However, the surface traps at the surface of nanostructured
water splitting hematite photoanodes may reduce the efficiency due to an increase in charge recombination rate at the surface [57]. Despite the nanostructuring efforts, a second crucial drawback of hematite remains: an additional high over potential (0.5–0.6 V) required to initiate water oxidation represents a significant energy loss [58]. Attaching co-catalyst materials on the nanostructured hematite photoanodes can lower the over potential [59, 60]. The passivation of the surface states and catalyst loading require a good technique to provide uniform coating on nanostructured hematite photoanodes. For this purpose, ALD stands out to be the most suitable method due to its capability of conformal coating on arbitrary-shape surfaces and atomic level control in film thickness. For example, a 100 mV photocurrent onset cathodic shift was observed on cauliflower-like silicon-doped hematite grown by atmospheric pressure chemical vapor deposition, through a very thin ALD Al2O3 (0.1–2 nm) coating [58]. The cathodic shift afforded by the Al2O3 overlayer is due to the passivation of surface states. Martinson and their co-workers reported that the ALD-coated sub monolayer catalysts using Co(Cp)2 and O3 as precursors on hematite photoanode results in a significant decrease in the applied potential required to drive water oxidation [58].

Recently, Li et al have found that an ultrathin amorphous FeTi1−xOx layer on the hematite nanorod surface results in significant increase of the photocurrent density, which can go up to 1.9 mA cm−2 at 1.23 V versus RHE in 1 M NaOH solution, while the reference sample without FeTi1−xOx layer shows negligible photocurrent (figure 5). The ultrathin amorphous FeTi1−xOx layer was obtained by annealing the ALD TiO2 coated hematite sample at 650 °C. The amorphous FeTi1−xOx layer thickness plays an important role to the overall photocurrent. If the amorphous FeTi1−xOx layer is too thin, it cannot provide sufficient passivation of the surface states. While it is too thick, the hole transfer from hematite to liquid will be blocked. The optimized passivation layer was obtained from ALD TiO2 thickness ~2.5 nm (40 ALD cycles) and 1 h post annealing at 650 °C.

Figure 5. (a) Schematic of the hematite nanorods array coated with an ultrathin FeTi1−xOx layer for efficient water oxidation (b) Photocurrent–potential (J–V) curves for PEC water oxidation reaction hematite nanorod arrays photoanodes with and without the FeTi1−xOx layer.

4. Surface sensitization

4.1. Quantum dots sensitization

Surface sensitization is a fundamental and important approach to improve light harvesting and conversion efficiency of solar energy in various light-harvesting devices. Quantum dots sensitization provides potential for the design of next generation solar cells as their high theoretical conversion efficiency. Conventional methods for depositing quantum dots photosensitizers such as dip coating, electrochemical deposition and CVD suffer from poor control in thickness and uniformity. By employing ALD for quantum dots sensitization, excellent infiltration and conformity could be achieved, and the size of quantum dots can be controlled simply by tuning the number of ALD cycles. For example, Brennan et al realized ALD CdS quantum dots sensitized solid-state solar cells, using dimethyl cadmium and in situ generated H2S as cadmium and sulfur precursors respectively [61]. Results showed the performance of solar cells was dependent on the number of ALD cycles, and the maximum photocurrent was obtained in five ALD cycles. Further increasing ALD cycles resulted in the decrease of cell efficiency. This is may be due to the overgrowth of CdS increased the aggregation of nanoparticles, which increases the recombination sites and decreases the filling efficiency of hole-conductor [61].

PbS, as narrow bandgap quantum dots, was also reported via ALD in the sensitization of Si solar cell using bis(2,2,6,6-tetramethyl-3,5-heptanedionato)lead(II) and H2S as precursors [62]. The deposited PbS was uniformly coated onto the surface of Si wires in the form of isolated nanoparticles. The size varied from 5 to 25 nm with increasing the number of ALD cycles from 10 to 80 as shown in figure 6. It is indicated that ALD is a unique and powerful tool to conformally coat a single layer of QDs with controlled size. Other sulfides sensitizer such as In2S3 was also deposited for solar energy conversion [63]. During processing of In2S3, ALD displayed a nucleation period of 60–70 cycles on initial surface, and the growth per cycle decreased from 0.28 Å 130 °C to 0.15 Å per cycle at 170 °C due to the incomplete self-
limiting In(acac)\textsubscript{3} reaction. Though many papers have reported ALD sulfides as sensitizer for solar energy conversion, we note that all those sensitizers were deposited using H\textsubscript{2}S as sulfur precursor. It is known H\textsubscript{2}S is a highly toxic and corrosive gas, which expose users to huge safety risk when use it. Thus, developing safe and eco-friendly sulfur precursors is highly required.

Alternatively, ALD also provides an indirect approach for the sensitization of quantum dots etc. Luo and Karuturi et al demonstrated CdSe quantum dots photosensitization method by ALD depositing sacrificial ZnO thin films on various TiO\textsubscript{2} nanostructures, anion solution exchange of ZnO layer to ZnSe, and finally cation solution exchange of intermediate ZnSe to CdSe. PEC performance tests to CdSe-sensitized TiO\textsubscript{2} inverse opal photoanodes revealed a drastically improved photocurrent level, up to 15.7 mA cm\textsuperscript{-2} at zero bias (versus Ag/AgCl), more than double that by conventional techniques such as SILAR (figure 7) [64]. Moreover, ALD was applied as an effective technique to integrate the up-conversion nanomaterials in photoelectrodes for efficient solar energy conversion by broadening the spectral photoresponse. A heteronanostructured photoanode was developed by encapsulating up-conversion nanoparticles with electron transporting TiO\textsubscript{2} using ALD. The resultant heteronanostructure was sensitized with CdSe quantum dots and demonstrated for near-infrared PEC hydrogen generation through an in situ photon up-conversion of near-infrared light to visible wavelengths [65].

4.2. Metal nanoparticles sensitization

Similarly, ALD metal nanoparticles sensitization provides a promising approach to improve the conversion of solar energy by catalysis in PEC water splitting. Dasgupta et al revealed that Si nanowire arrays with ALD sensitized Pt nanoparticles exhibited the current densities from 7 to 21 mA cm\textsuperscript{-2} at 0 V versus RHE (AM 1.5) with increasing the number of ALD cycles from 1 to 10 [66], while there was no photo-activity with Si alone, indicating the tunability of catalytic activity of Pt nanoparticles by varying the number of ALD cycles. And an onset voltage of 0.15–0.25 V versus RHE and current densities of ~30 mA cm\textsuperscript{-2} were shown for all photoanodes [66]. All samples exhibited comparable PEC performance to previous reported standard Pt sensitization technique. Importantly, the corresponding surface loadings of ALD Pt nanoparticles were as low as 13–105 ng cm\textsuperscript{-2}, it is indicated
that ALD is an effective tool for the ultralow loading of Pt nanoparticles without reducing catalytic performance, thus potentially reducing the use costs of noble-metal catalysts.

In addition, Pt nanoparticles catalyst deposited by other techniques predominantly reside on the tips of Si nanowire arrays, which increases the diffusion distance for the collection of electrons (figure 8) [67]. On the contrary, ALD-deposited Pt nanoparticles uniformly covered on the surface of Si nanowire arrays, achieving the efficient collection of photogenerated charges, thus improving PEC water splitting efficiency. Analogously, this technique could easily be extended to the preparation of metal-plasmon enhanced solar cells, however, the relevant information is rarely reported up till now.

Figure 7. A new method for the fabrication of chalcogenide semiconductor photosensitizers enabled by ALD. (a) Fabrication process based on TiO2 inverse opal photoanode. (b) SEM image of the TiO2 inverse opal sensitized by CdSe particles using conventional SILAR method. (c) SEM image of the TiO2 inverse opal sensitized by CdSe particles using ALD-assisted method. (d) Photocurrent versus potential for the TiO2 inverse opal PEC anode. Reprinted with permission from [64]. Copyright 2012 Nature publishing.

Figure 8. (a) TEM and (b) HRTEM images of Pt nanoparticles deposited on Si nanowire by ALD Pt, and (c) polarization curves of various electrodes in hydrogen evolution reaction environments. 1, 2 and 3 represent bare Si nanowires, Si nanowires with electroless-deposited Pt, and Si nanowires with ALD Pt, respectively. Reprinted permission from [67]. Copyright 2013 Wiley.
5. Band-structure engineering via ALD

5.1. Band-structure engineering in DSSCs

Much effort has been put into band gap engineering in DSSCs so as to improve the conversion efficiencies of the cells. Conventionally, wide band gap semiconductors nanoparticles are being used as the photoanode material due to their inherent high surface area [68]. Recent developments to enhance the absorption capability of the photoanode include employing 3D hierarchical nanostructures such as inverse opals in place of conventional TiO2 nanoparticles [69]. However, the adsorption band gap needs to be tuned in order to achieve higher conversion efficiencies. The adsorption band gap is determined by the inherent property of the photosensitizer. Conventional photosensitizers that are used are based on Ru complexes, which typically have conversion efficiencies over 10% and absorption of around over 500 nm [70]. However, due to the high cost of ruthenium, alternative photosensitizers such as metal free dyes are currently being explored.

Although the adsorption band gap is determined by the material type, the efficiency of the electrode is limited by carrier recombination that happens with the electrolyte. To address that issue, ALD is being employed to reduce these recombination processes. With ALD, a thin and conformal coating of a high band gap metal oxide between the photosensitive layer and the substrate can be achieved. However, with barrier layers like Al2O3, HfO2, the electron transfer efficiency to the substrate (e.g. TiO2) sometimes decreases due to the fact that the conduction band of the barrier layer is usually higher than that of the substrate. However for some other metal oxides like Ta2O5 actually improved the electron transfer efficiency. As can be seen, there is considerable potential for ALD to be employed in optimizing the charge transfer efficiency by facilitating the carrier transport between the photosensitizers and substrate with varying band structures.

5.2. Buffer layer engineering in CIGS solar cell

Buffer layer is indispensable to the chalcopyrite-type thin-film solar cells based on CIGS and related absorbers such as CuInS2, Cu(In,Ga)(S,Se)2 and CuZnSnS, as it efficient charge separation and charge transport between the absorber and the ZnO window layer. The absence of such a buffer layer will result in a drop of open circuit voltage (Voc) and poor efficiency, among others, due to the large negative conduction band offset (CBO, ΔEc) at the CIGS/ZnO interface [71]. As there are intrinsic material limitations and industrial processing drawbacks of the commonly used CdS buffer layer, to find a substitute for CdS is one of the major objectives in the field of CIGS technology.

ALD provides thin films with excellent conformality and thickness control down to atomic level, which is capable to deposit a wide variety of Cd-free materials as a buffer layer in CIGS solar cells. As the growth rate per cycle of ALD is in the atomic level, excellent composition control over the film can be easily achieved through control of the precursor pulse ratios during the co-deposition process. Thus excellent control of the band gap and CBO can be achieved (figure 9). Moreover, ALD is a gas phase process that can be easily integrated alongside other vacuum processes. ALD Cd-free buffer layers have been extensively reviewed previously [4, 72, 73]. ZnO, S), Zn1−xSnxO, (Zn,Mg)O and In2S3 have been identified as the most promising Cd-free buffer layers for CIGS solar cells.

ALD Zn(O,S) buffer can be deposited by changing the ZnO and ZnS cycles using diethyl zinc (DEZ), Zn(C2H5)2, precursor and H2O and H2S as reactants. The performance of the solar cell using ALD Zn(O,S) as buffer layer depends strongly on the S/(S + O) ratio of the buffer layer, which is controlled by the pulse ratios of H2S/H2O during the ALD process. On the one hand, when S/(S + O) ratio is too high, an ultrathin buffer layer is required to prevent charge recombination in this layer. On the other hand, the Voc of the solar cell drops if the S/(S + O) ratio is too low. Both phenomena can be explained by the ΔEc at the CIGS/Zn(O,S) interface, which has been intensively discussed by Plater-Björkman et al [74–77]. ΔEc ranging from 0 to 0.4 eV was calculated to be well suited to reach high performance (figure 10). Over 18.0% efficiency of CIGS solar cells with ALD Zn(O,S) buffer layers was reported by many groups. The absorption of these cells with Zn(O,S) buffer layers in the short wavelength range is much better than that of the reference cell using CdS as buffer layers, resulting in an increased Jsc and efficiency.

Zn1−xSnxO is a new alternative buffer layer for CIGS solar cells, which also benefit from the ability of ALD to control the film composition from pure ZnO to pure SnO, by changing the ratio between the DEZ and TDMASn, Sn(N(CH3)2)4, precursors and the H2O reactant [78, 79]. Similar to Zn(O,S), the band gap and the CBO can be controlled by the Sn/(Sn + Zn) ratio of the Zn1−xSnxO buffer layer. However, the difference is that the ALD Zn1−xSnxO buffer layers are amorphous, which is an interesting property because it reduces the amount of recombination centers at the grain boundaries in the bulk buffer layer and at the CIGS/buffer interface. The best Zn1−xSnxO buffer layer had an Sn/(Sn + Zn) ratio between 15% and 20% deposited at 120 °C. The

Figure 9. Band diagram of a CIGS thin-film solar cell with Cd-free buffer layers.
application of these 25 nm thick Zn_{1−x}Sn_xO buffer layers on coevaporated CIGS solar cell led to efficiencies up to 18.0%, which is comparable to that with CdS buffer layer [78]. The higher $J_{sc}$ obtained for the Zn_{1−x}Sn_xO compared with CdS reference samples are expected, as the band gap of the CdS is lower than that of Zn_{1−x}Sn_xO (3.0 eV) (figure 10) [78, 80]. Due to the Voc drop of the cell with Zn_{1−x}Sn_xO buffer layers, the overall efficiency is not better than the CdS reference cell.

ALD (Zn,Mg)O buffer layers are usually deposited by alternating ZnO and MgO cycles using Zn(C_2H_5)2, MgCp2 as precursors and H_2O as reactant. By tuning the Mg/(Zn + Mg) ratio, the band gap of the as deposited (Zn,Mg)O buffer layers can be controlled from 3.3 eV to 3.8 eV [71, 81]. The optimized (Zn,Mg)O buffer layers with a band gap of about 3.6 eV were deposited at 120 °C. Due to the lower Voc and fill factor values, a significant drop in cell efficiency was observed with (Zn,Mg)O buffer layers deposited at higher temperatures, which could be due to the deterioration of the interface quality. The co-evaporated CIGS cells with ALD (Zn,Mg)O buffer layer (150 nm thick) yielded efficiencies up to 18.1% [82].

ALD-In_{2}S_{3} buffer layers can be deposited using In(acac)_3 and H_2S as precursors. The deposition temperature is relatively higher compared to that of (Zn,Mg)O and Zn(O,S), typically 200–210 °C. It has been reported that the interface diffusion happens between the CIGS absorber and In_{2}S_{3} layer during the deposition process at such a high temperature [83]. If Cu is present in excess in the In_{2}S_{3} buffer layer, the p–n junction formed between CIGS and In_{2}S_{3} may be deteriorated. At the same time, the occupation of Cu vacancies by In ions will imply the inversion of the near-interface region of CIGS from p-type to n-type and form a buried junction in the CIGS layer [83]. The highest cell efficiencies up to 16.4% have been reported for cells with ALD In_{2}S_{3} buffer layers of 30–40 nm [84, 85]. As the band gap of In_{2}S_{3} (2.7 eV) is larger than CdS (2.4 eV), the quantum efficiency of the devices with In_{2}S_{3} buffer layers is higher than the CdS reference device in the short wavelength range. Compared to other alternative Cd-free buffer layers, the main advantage for In_{2}S_{3} buffer layers is that the cell does not suffer from the light soaking effect [86].

6. Conclusions

We have summarized and discussed the emergent application of ALD in solar cell research, including the fabrication of PEC photoanodes, sensitization of TiO_2 nanostructured PEC anode by semiconductor nanoparticles and Si nanowire photocathode by highly dispersed noble metal nanoparticles, and surface passivation of Si and CIGS thin film solar cells. Most solar devices materials have stability issues, either due to photocorrosion, etching, or simply dissolution into electrolyte, and thus hurdle the practical application of these high-potential materials. A uniform coated atomic thin film rendered by ALD could address this problem via various mechanisms. In the particular case of thin film solar cells and PEC cells, an ALD film in some circumstances is not simply a ‘passivation’ but constructs a thin heterojunction interface; the resulting built-in potential is beneficial to the photo charge separation. In addition, doping is highly desirable for all solar applications but this has been a challenge. Some success has been achieved mainly for Al/Ga/Ti-doped ZnO and Ta-doped TiO_2 and more intensive research is needed for materials like Fe_2O_3 and WO_3. Of particular interest is the ALD metal which naturally form well dispersed nanoparticles rather than thin films. This will be extremely useful for photocatalyst or electrocatalyst. In short, with the increasing interest in energy and environment related research, ALD will continue to play an increasingly important role and most likely become a mainstream facility.

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