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Advanced Laser Processing towards Solar Cells Fabrication

Jhantu Kumar Saha and Animesh Dutta

Abstract

The ultra-short pulse laser has the potential in selective nano-structuring of thin-films layers by adjusting the wavelength of laser radiation depending on optical properties of the thin-film and the substrate that will solve its efficiency and stability issues in a one-step process, which is a promising methodology for thin-film solar cell fabrication that are fabricated through a sequence of vapor deposition and scribing processes. The review is performed to further understand the structure of the laser modified surface and the nature of dopants and defects in the crystalline grains. Using low temperature studies, the electronic levels of the dopant and its configuration with the lattice could be probed. The review is also explored the concept of using thin films of silicon as the laser irradiation substrate and for enhanced the visible and infrared absorption of films of silicon with thicknesses of few micrometer. Although the review is made good progress studying the properties of new material and incorporation into device but there are many unanswered questions and exciting avenues of research are also explored with femtosecond laser irradiated silicon.

Keywords: femtosecond laser, photovoltaics, silicon, thin-film, intermediate band solar cells

1. Introduction

Photovoltaics (PV), the conversion of sunlight to electricity, is a promising technology that could allow for the generation of electrical power on a very large scale and contribute considerably to solving the energy problem that the next generation must face. The factors motivating the solar cell research are not only to reduce cost of the manufacturing cost of solar cell technology but also increase to the efficiency of solar cell.

Research on solar cells falls into two general categories, both aimed at reducing the cost per kilowatt-hour. The first category (eg. single crystalline Si and GaAs solar cells) involves using expensive materials and advanced processing techniques to obtain the highest possible efficiency. The increased efficiency will hopefully offset the extra cost. The second category (Poly and thin-film Si, CdTe, and CuInSe₂ solar cell) involves using cheaper materials and cheaper processes [1–5]. The lower quality material sacrifices efficiency, but this is hopefully offset by its low cost.

Crystalline silicon solar cells are transparent to wavelengths of light longer than 1.12 μm , due to their electronic band gap of 1.07 eV means they are transparent to 23% of solar energy. Whereas thin film amorphous silicon solar cells have a larger band gap of 1.75 eV and are transparent to light longer than 0.71 μm means they loss 53% of solar energy.

From a photovoltaic standpoint, the most attractive property of femtosecond laser irradiated silicon is that it absorbs nearly all light that is emitted by the sun. This offers an opportunity to tap into that lost energy and, therefore, appears to be an attractive option for solar cells. The ultra-short pulse laser has the potential to improve the optical properties of different layer of solar cell. There are many defects in the laser modified surface, thus, it is unlikely that femtosecond laser irradiated silicon will be able to improve upon the already high efficiency of single crystal silicon solar cells (25%) or even improve upon the lower efficiency of polycrystalline silicon solar cells (14%).

Thin-film solar cells have stimulated enormous research interest as a cheap alternative to bulk crystalline silicon solar cells [6–9]. The limitation of all thin-film solar cells, made from a variety of semiconductors, is that the absorbance of the near band gap is small, especially for the indirect band gap semiconductor silicon. Therefore, structuring the thin-film solar cell so that light is trapped inside to increase the absorbance is very important. On the other hand, femtosecond laser irradiated silicon can be used as a photovoltaic device; it can convert wavelengths of light that are not normally absorbed by silicon into an electrical signal. Over the past several decades ultra-short, pulsed laser irradiation of silicon surfaces has been an active area of materials science research [10–17]. The ultra-short duration of the laser pulses leads to extremely high energy densities in the material. The real advantage of femtosecond laser irradiated silicon is that it not only absorbs nearly all the wavelengths of light but does so in a laser modified surface film that is less than 500 nm thick. This makes it ideal for incorporation with thin film silicon. However, since thin film silicon already contains a large number of defects and exhibits a much lower efficiency (typically 10%), it would seem to be a good candidate for use with our femtosecond laser irradiation process [12]. There are few high-efficiency PV concepts, photon management for photovoltaics as well as several ways to increase the performance in solar cells such as isotropic acidic texturing, mechanical grooving, reactive ion etching, anisotropic silicon etching, rapid crystallization of amorphous silicon for thin-film silicon solar cell and laser processing for photovoltaics are reviewed in the following section.

2. High-efficiency PV concepts

The current state of the art of high efficiency single-junction monocrystalline silicon (c-Si) based solar cells are the PERL (Passivated Emitter, Rear Locally diffused) cell, the SunPower A300 cell, and the Sanyo HIT cell [18–20]. There are also few high-efficiency PV concepts as reviewed in the following section.

The intermediate band (IB) solar cell concept can be used to increase the efficiency of current of solar cells, ideally is above the limit established by Shockley and Queisser in 1961 but fabricating IB is difficult and no current design has demonstrated the theoretically predicted efficiency improvements [21–24].

Quantum dots (QDs) are nanocrystals of a material immersed in a matrix material usually with a higher bandgap. Quantum dots are also used to make the cells but the efficiencies that have been achieved so far are not yet satisfactory [24]. QDs can also be used in IB solar cell [25].

3. Photon Management for Photovoltaics

Photon management for photovoltaics (PV) is focused for increasing the solar absorbance of solar irradiance through some modification of the photovoltaic

material. Very small sized (micrometer-sized) photovoltaic material (eg. silicon) spikes decrease geometric light trapping for reflection. The extent of geometric light trapping enhances optical path length. The light trapping depends on the height, spacing, and subtended angle although structures with large, graded density and the spike heights will not play for visible and near-IR light. Multiple reflection on the surface is the dominant effect of light trapping [26–30]. Treating the case of spikes subtending a cone angle of 42° , observed on a silicon surface after irradiation in pulsed-laser hyper doping and surface texturing as shown in **Figure 1a**. Incident light undergoes four reflections before escaping as illustrated in **Figure 1b** of the optical path of light incident on laser-textured silicon surfaces, with cones subtending 42° .

There are also several ways to increase the performance in solar cells as reviewed in the following section.

3.1 Isotropic acidic texturing

The novel technique of isotropic texturing of the multi-crystalline surface basically use acidic solution (such as HNO_3 – HF – CH_3COOH) followed by a simple chemical treatment to make the surface more uniform in terms of roughness [31]. Due to high reflectivity of acid textured surface helps to improve the open circuit voltage but gives lower short circuit current of the multi-crystalline silicon (mc-Si) solar cell [32].

3.2 Mechanical grooving

The mechanically texturized structures created by anisotropic etching of mono-crystalline silicon, resulted the first silicon solar cell to exceed 20% energy conversion efficiency at 1-sun illumination because of positive trend of improvement in the electronic quality of the c-Si substrates [33].

3.3 Reactive ion etching (RIE)

Texturing surface have been developed using the reactive ion etching (RIE) method, which is expected to form a low reflectance surface on various crystalline orientations of grains [34, 35].

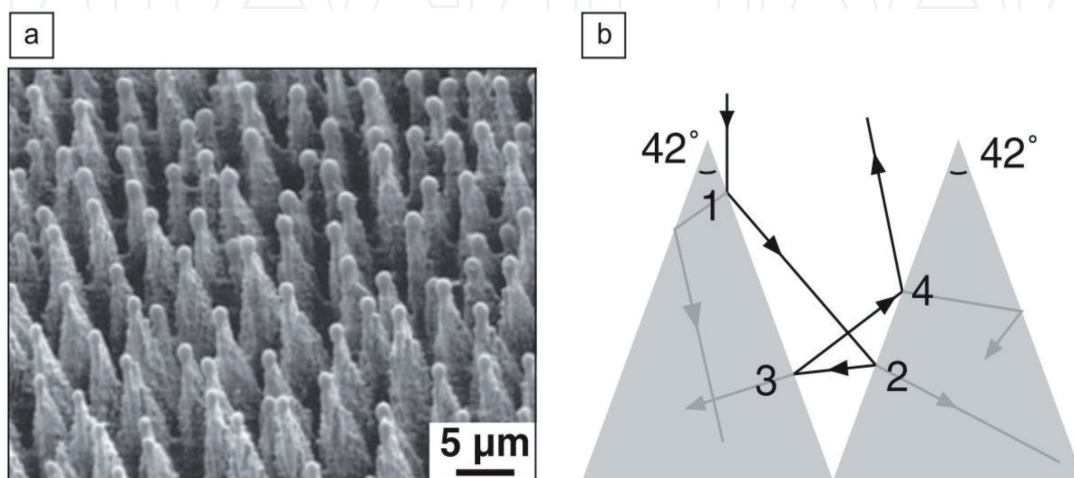


Figure 1. Pulsed-laser hyper doping and surface texturing, Cambridge (2001) (ref. R. Younkin, PhD dissertation, Harvard University), (a) scanning electron micrographs, (b) illustration of the optical path (adapted from [31] with permission).

3.4 Anisotropic silicon etching

Textured silicon surface with 100% pyramid density can be obtained on the surface texturization of monocrystalline wafers with solutions containing sodium-hydroxide and isopropanol [36].

3.5 Rapid crystallization of amorphous silicon for thin-film silicon solar cell

The novel crystallization technique for synthesizing crystalline Si film from a-Si film utilizing a VHF thermal micro-plasma jet is used as shown in **Figure 2** [37]. **Figure 3** shows the photocurrent–voltage characteristics and collection efficiency for p–i–n Si thin-film solar cells with crystallized Si films as an intrinsic layer [37].

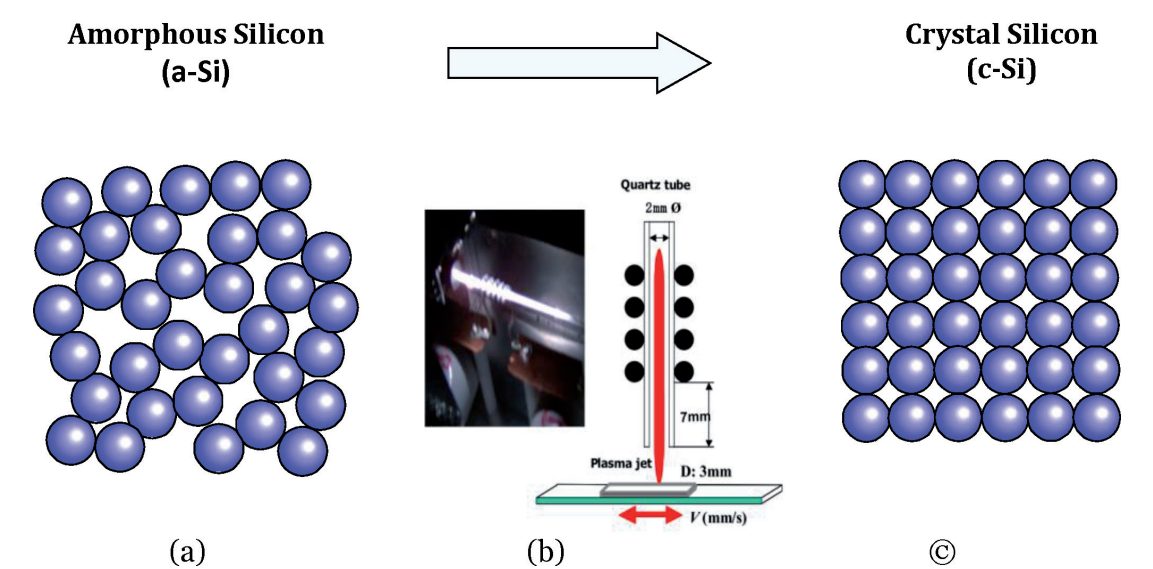


Figure 2.
Rapid crystallization of amorphous silicon utilizing a very-high-frequency micro-plasma jet.

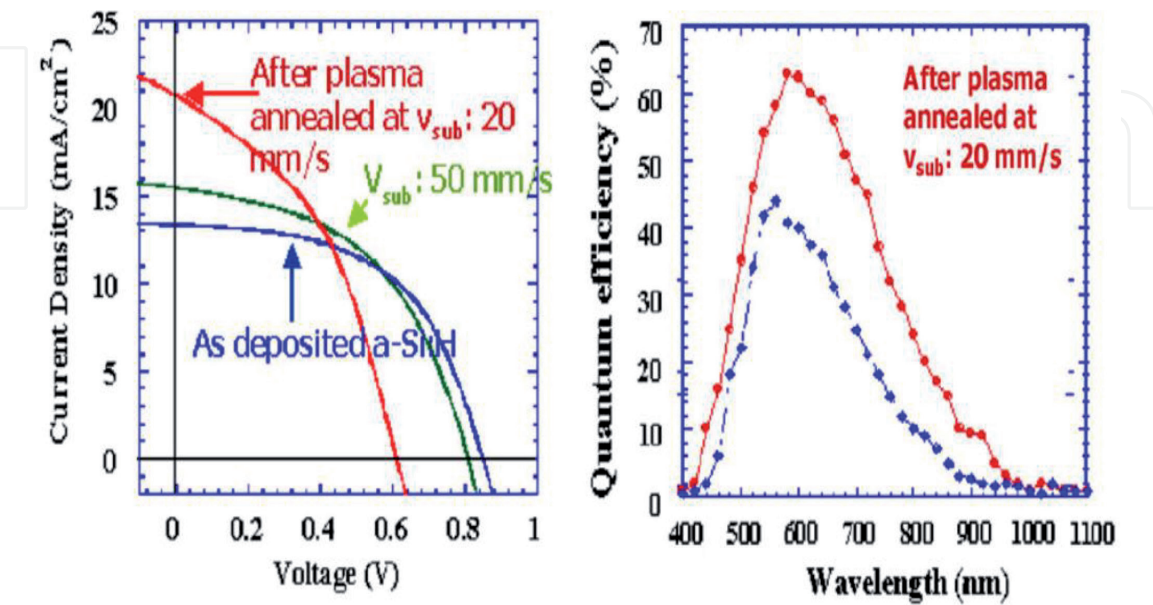


Figure 3.
(a) Photocurrent–voltage characteristics, (b) collection efficiencies spectra of solar cells [adapted from [37] with permission].

4. Laser processing for photovoltaics

The laser modified surface and the nature of dopants and defects in the crystalline grains are crucial to improve the performance of solar cells. Pulsed-laser hyper doping & surface texturing for photovoltaics, laser processing for thin-film (TF) photovoltaic, Light trapping for thin silicon solar cells by Femtosecond Laser Texturing, Patterning of Transparent Conducting Oxide (TCO) layers by Femtosecond Laser as well Solar cells based on laser-modified materials are discussed in the following section.

4.1 Pulsed-laser hyper doping and surface texturing for photovoltaics

The two different approaches eg. pulsed-laser hyper-doping and surface texturing are used to enhance photon absorption enhancement from the pulsed-laser processing of semiconductors with nanosecond, picosecond, or femtosecond laser pulses. The absorbance A is obtained from the expression $A = 1 - R - T$, where R and T are reflectance and transmittance, respectively, measured with an integrating sphere to collect both specular and diffuse light. **Figure 4a** shows the untreated crystalline silicon (c-Si) which has negligible absorption of light with a wavelength longer than 1.1 μm due to its energy bandgap. **Figure 4b** shows the pulsed-laser hyper-doping with sulfur enables absorption of sub-bandgap light. **Figure 4c** shows the pulsed laser texturing that enhances above-bandgap light absorption with geometric light trapping. **Figure 4d** shows the broadband near-unity absorption is achieved with both pulsed-laser hyper-doping and surface texturing.

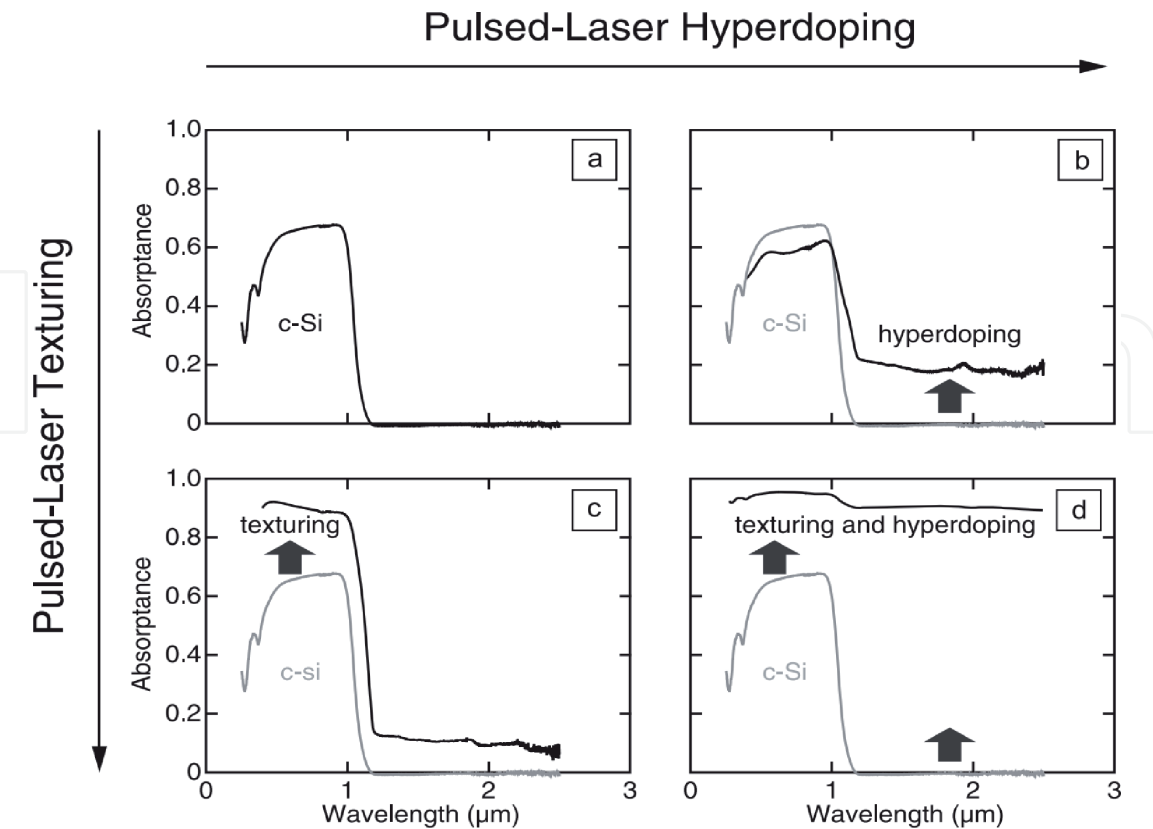


Figure 4.
(a) Untreated crystalline silicon (c-Si), (b) pulsed-laser hyper-doping with sulfur, (c) pulsed laser texturing, (d) both pulsed-laser hyper-doping and surface texturing (adapted from [31] with permission).

Table 1 compares various texturing methods and reflectivity values reported for c-Si and mc-Si wafers. While anisotropic chemical etching method using KOH or NaOH with IPA is applicable for c-Si materials, it could not be applied to multi-crystalline materials due to the anisotropic nature of the chemical etchant. Isotropic chemical texturing uses acidic mixture of HF and HNO₃ and organic additives for multi-crystalline silicon (mc-Si). On the other hand, lasers are unique energy sources and laser ablation is an isotropic process. Lasers could texture surfaces by selectively removing materials by ablation process. Texturing could be achieved irrespective of the crystallographic orientation of material surface. Under shorter pulse regimes (few nanoseconds to femtoseconds), a very different types of self-assembled micro/nano structures are formed [32].

Total reflection of as-laser-treated samples is very low and increases by a few more percentages after post-chemical cleaning as shown in reference [42].

4.2 Laser processing for thin-film (TF) photovoltaic

The serial monolithic interconnection of thin-film solar cell can be achieved by laser scribing three patterns during fabrication. The layers are numbered in the order in which they are deposited. They are micromachined by laser ablation, an established material removal process [35].

Nayak et al. [37] reported nanocrystalline Si material following femtosecond-laser-induced crystallization of a-Si:H. Despite the number of structural defects, which for the time being prohibits PV applications, the process produces remarkable light-trapping microstructures at the surface.

Author	Year	Technique	Substrate used	Applicable to	Approx. R (%) @550 nm (as textured)
Gangopadhay et al.	2017	Isotropic acidic texturing	mc-Si	mc-Si	15
Zechner et al.	1997	Mechanical grooving	mc-Si	c-Si & mc-Si	>15
Inomata et al.	1997	RIE	mc-Si	c-Si & mc-Si	<2
Vazsonyi et al.	1999	NaOH+IPA	c-Si	c-Si	10
Nashimoto et al.	2000	Na ₂ O ₃	c-Si	c-Si	10
Abbott et al.	2006	Laser texture	c-Si	c-Si & mc-Si	<5
Nishioka et al.	2009	Ag nanoparticle	c-Si	c-Si & mc-Si	<5
Branz et al.	2009	Au nanoparticle	c-Si	c-Si & mc-Si	<2
Younkin et al.	2003	Femtosecond laser-induced microstructure	c-Si	c-Si & mc-Si	<3
Nayak et al.	2010	Ultrafast laser micro/nano structure	c-Si	c-Si, mc-Si, and thin a-Si	<3

Table 1. Various Texturing Methods and Reflectivity values reported for mono-crystalline (c-Si) and multi-crystalline (mc-Si) wafers (Adapted/modified from references [32, 36-42]).

4.3 Light trapping for thin silicon solar cells by femtosecond laser texturing

A variety of surface morphologies can be obtained from fs laser treatments, depending on laser parameters and the ambient gas environment. The efficacy fs laser texturing of solar cell devices is also demonstrated in ref. 26 and the problem of laser-induced damage may have significantly improved cell performance in the future by increased absorption (vs. un-textured cells) for infrared photons, due to enhanced light-trapping.

4.4 Patterning of transparent conducting oxide (TCO) layers by femtosecond laser

A method for patterning crystalline indium tin oxide (c-ITO) patterns on amorphous indium tin oxide (a-ITO) thin films is proposed by femtosecond laser irradiation at 80 MHz repetition rate. The laser patterning technique provides a versatile and highly precise means of fabricating the transparent electrode structures required in a wide range of modern optoelectronic devices. High repetition rate femtosecond (80 MHz) laser-induced crystallization and proposed laser patterning technique provides a versatile and highly precise means of fabricating TCO structures [42].

4.5 Femtosecond laser induced crystallization & simultaneous formation of light-trapping nanostructures

Femtosecond laser induced crystallization & simultaneous formation of light-trapping nanostructures is a one-step laser process, which could lead to fabricate the highly efficient solar cells [42–51]. Microstructures and small spikes have been spontaneously formed upon laser treatment. Interestingly the a-Si:H films turned completely dark from an original shiny reddish gray color. A similar effect has been extensively studied by Mazur's group and others in crystalline bulk silicon wafers [42–52].

5. Solar cells based on laser-modified materials

Solar cells based on laser-modified materials focus on three major thrusts that will lead to more efficient and economic thin-film solar cell fabrication by (i) combining femtosecond laser irradiation processing of a-Si:H surface and simultaneous crystallization occurs in a one step process [16]. Optical absorption will be enhanced by light trapping via multiple reflections through the surface geometry changes, and the formation of mixture of $\mu\text{c-Si:H}$ and a-Si:H after crystalline suggests that the overall stability will be potentially increased; (ii) Laser with a shorter, femtosecond pulse duration will be applied for nano-structuring of TCO deposited on glass as a plasmonic nanostructure for efficient light trapping; (iii) For scribing thin-film solar cells with femtosecond laser will be applied for electrical isolation, hermetic sealing of the module, glass cutting, the complete removal of all layers from the edges of fully processed thin-film solar cells on glass substrates [52]. **Figure 5** is a schematic presentation of how femtosecond laser irradiated silicon can be incorporated into the p-i-n configuration of a thin-film silicon solar cell.

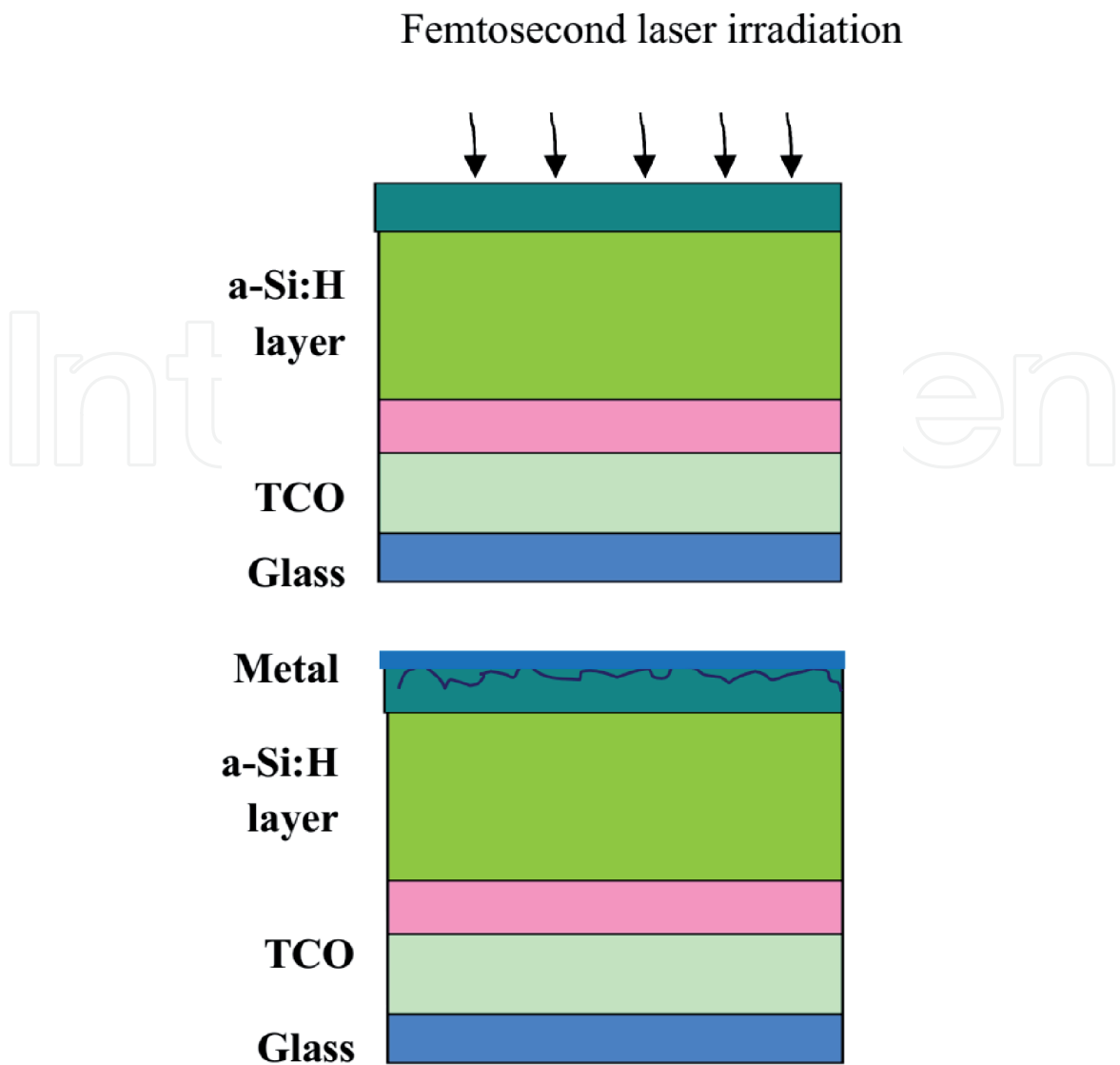


Figure 5.
Schematic cross-section of the fabrication process of a femtosecond laser irradiated thin film silicon solar cell.

6. Conclusions and outlook

Pulsed laser processing provides two routes for effective photon management: Surface texture and hyper doping process are distinct and independently achievable. Surface texture using intense pulsed-laser light to create quasi-periodic surface features reduces reflection and increases path length through the material.

The creation of femtosecond laser irradiated thin film silicon solar cells is an exciting area of research. Thin-film solar cell requires a highly efficient light-trapping design to absorb a significant fraction of the incident sunlight and material property changes to increase stability. Laser based treatment of thin-film is required for resolve efficiency and stability issues in a one-step process, which is a promising methodology for thin-film solar cell fabrication. Laser with a shorter, femtosecond pulse duration will be applied for nano-structuring of TCO deposited on glass as a plasmonic-nanostructure for efficient light trapping. The ultra-short pulse of femtosecond laser at small fluences will also overcome the parasitic losses and decreased electrical power output of the solar module resulting from the active material remaining over the active layer scribing with picosecond laser of thin-film solar cells which is critical in forming the series interconnects between cells.

Thin-film materials eg. Si, CdTe, CuInSe₂ are becoming more and more attractive based on their potential for low-cost solar modules, possibly to create tandem junctions and large-scale manufacturing. They can reduce the cost of the material at the expense of efficiency. The a-Si:H is the most popular material for use in thin film form due to its low energy economy (watt/cost). But due to their instability and low efficiency, a thin-film a-Si:H solar cell requires a highly efficient light-trapping design to absorb a significant fraction of the incident sunlight and material property changes to increase stability. On the other hand, microcrystalline silicon is one of the promising materials for thin-film solar cells of achieving high conversion efficiency. In addition, microcrystalline silicon films show enhanced carrier mobility, excellent stability against light-induced degradation and improved longer wavelength response. But deposition rate of microcrystalline silicon thin-film fabricated by conventional PECVD is lower compared with the a-Si:H. Therefore, laser-based treatment of a-Si:H is required to resolve its efficiency and stability issues in a one-step process, which is a promising methodology for thin-film solar cell fabrication.

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