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Academic Progress Report

Recent Development of P-Tunnel Oxide Passivated Contact Solar Cells

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Abstract: Crystalline silicon solar cells have attracted great attention for their various advantages, such as the availability of raw materials, high-efficiency potential, and well-established processing sequence. Tunnel oxide passivated contact (TOPCon) solar cells are widely regarded as one of the most prospective candidates for the next generation of high-performance solar cells because an efficiency of 26% has been achieved in small-area solar cells. Compared to n-type TOPCon solar cells, the photo conversion efficiency (PCE) of p-type TOPCon is slightly higher. The highest PCEs of p-type TOPCon and n-type TOPCon solar cells are 26.0% and 25.8%, respectively. Despite the highest efficiency in small-area cells, limited progress has been achieved in p-type TOPCon solar cells for large are due to their lower carrier lifetime and inferior surface passivation with the boron-doped c-Si wafer. Nevertheless, it is of great importance to promoting the p-type TOPCon technology due to its lower price and well-established manufacturing procedures with slight modifications in the PERC solar cells production lines. The progress in different approaches to increase the efficiencies of p-type TOPCon solar cells has been reported in this review article and is expected to set valuable strategies to promote the passivation technology of p-type TOPCon, which could further increase the efficiency of TOPCon solar cells.

Keywords: TOPCon, Solar cell, p-type silicon wafer, Passivation quality, Efficiency

1. INTRODUCTION

The crystalline silicon solar cells have the advantages of the high potential of the feedstock of silicon, which is the 2nd most abundant element in the earth's crust, high and stable efficiency, and mature manufacturing technology, occupying an excess of 90% of the market share [1]. Many high-efficiency c-Silicon solar cell designs have been reported, including the Passivated Emitter and Rear Cell (PERC) [2], interdigitated back contact solar cell (IBC) [3], silicon heterojunction solar cell (SHJ) [4], heterojunction back contact solar cell (HBC) [5], and tunnel oxide passivated contact solar cell (TOPCon) [6], etc. So far, the efficiency of mainstream PERC solar cells, which are the most commercialized, is approaching their limit, hence it is urgent to find a higher efficiency structure for solar cells to replace

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them. SHJ, IBC and HBC solar cells exhibit higher efficiency, however, they are limited to commercialization due to their complex manufacturing process or relatively expensive fabrication cost.

TOPCon solar cells are highly promising for large-scale high-efficiency c-Si solar cells due to their selective carrier passivation technology, which involves ultrathin SiOx and highly doped poly-Si [7]. This structure has attracted widespread attention owing to the solar cell with a power conservation efficiency of 25.7% fabricated at Fraunhofer ISE in German [8,9]. The TOPCon structures could be divided into two parts: n-type TOPCon (highly phosphorus-doped poly-Si) and p-type TOPCon (highly boron-doped poly-Si). To our best knowledge, it is found that the majority of previous research

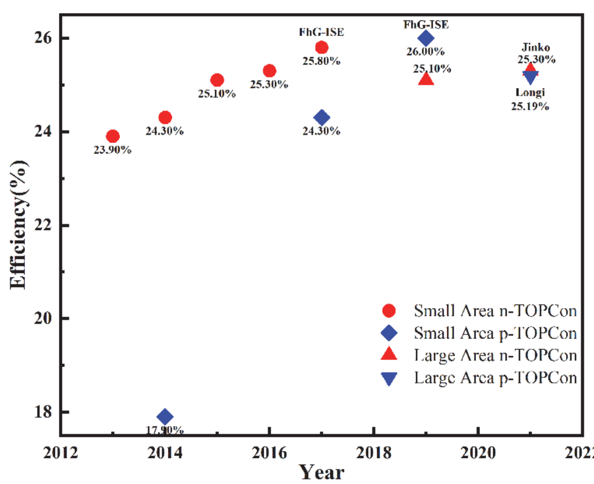


Fig. 1. Comparison of p-TOPCon and n-TOPCon solar cells efficiency.

has focused on an n-type crystalline silicon wafers with P-doped n^+-poly Si/SiO_x for their advantages of excellent passivation effect and high efficiency [10]. According to Fig. 1, it is obvious that p-TOPCon solar cells dominate in small-area cells, however, n-TOPCon solar cells are superior to their counterparts from a commercial point of view [11,12]

Based on ITRPV 2023 (Fig. 2) [13], it is predicted that the silicon solar cells utilizing p-type wafers will remain to be the working horse among the photovoltaic community and the trend will continue for the next 5 years. It would be much easier and cost-efficient if the production lines of TOPCon could integrate into existing PERC lines and p-type TOPCon would be an ideal structure because only small modifications are needed in the rear passivation and most of manufacture progress sequence can be left unchanged [14]. Hence, it is of great significance for the photovoltaic industries to develop high performance of p-type TOPCon technology.

The passivation quality and the efficiency of p-type TOPCon structure have achieved significant achievements through the research activities conducted all over the world in recent years. Recent advances regarding p-TOPCon solar cells are reported in this article. In order to enhance the surface passivation technology of p-type TOPCon, many efforts have been made, for instance, enhancing the layer superiority of thin SiO_x and doped poly-Si, thermal treatment after crystallization, etc. However, p-type TOPCon solar cells are still limited. In the coming years, efforts will be directed toward the development of an outstanding p-type TOPCon technology for highly commercialized TOPCon solar cells.

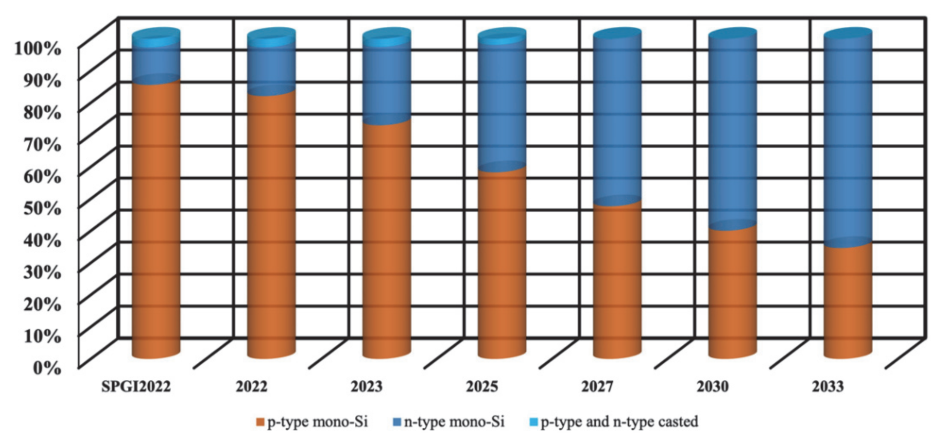


Fig. 2. Projected market share for different wafer types [13].

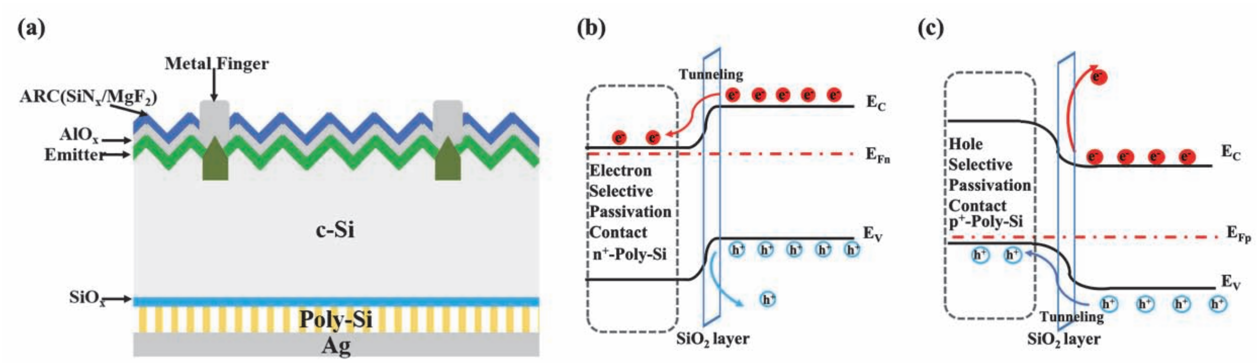


Fig. 3. (a) Schematic diagram of TOPCon solar cell, (b) band diagram of n-type TOPCon cell, and (c) band diagram of p-type TOPCon cell.

2. THE CARRIER TRANSPORTATION MECHANISMS OF TOPCon

The TOPCon solar cell features a Poly-Si/SiO_x passivation contact structure at rear side as shown in Fig. 3(a). It could realize the selective carrier collections and interface passivation of silicon substrate. The report was first published in 2013 by institute for Solar Energy Systems (Fraunhofer ISE). There are currently two theories regarding the carrier transport mechanisms of TOPCon Solar cells.

On one hand is the tunneling effect. Owing to their difference in work function between silicon substrates and n^+-Poly-Silicon. The hole barrier layer is generated at the interface between the heavily doped n^+-Poly-Silicon and the silicon substrate. The holes (minority carriers) are repelled and the electrons could easily pass through the SiO_x layer to the n^+-Poly-Si layers. Moreover, due to the high barrier level of SiO_x, few or almost no holes could reach the oxide layers. In addition, there is a potential barrier at the interface of n^+-Poly-Si/SiO_x/n-Si passivation contact, which prevents the minority holes from reaching the interface of metal-semiconductor contact for recombination. Thus, the collections of selective carriers could be realized. Similarly, the collections of holes could be achieved through p-type TOPCon structure [15]. The tunneling mechanism is depicted in Figs. 3(b) and (c).

On another hand is the 'pinhole' effect (Fig. 4). It is reported that high temperature may cause the partial tunneling oxide layer to decompose. The 'pinhole' structure could be formed in the ultra-thin SiO_x layer, so the silicon layer could contact the doped Poly-Si layer directly. The carriers could transfer to the doped Poly-Si through the 'pinhole' and reach to the metal electrodes instead of tunneling through the SiO_x layer, thereby

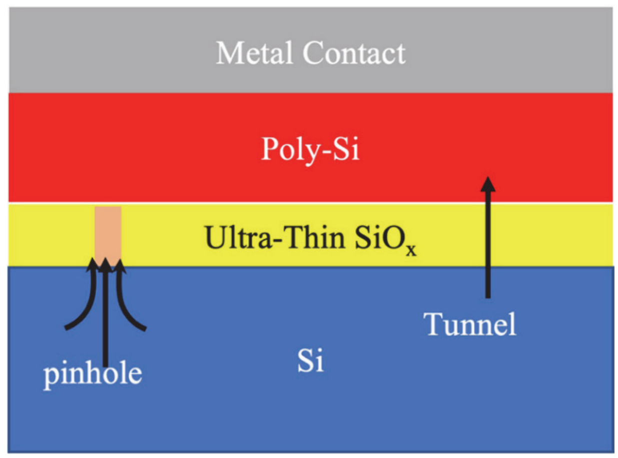


Fig. 4. Schematic diagram of carrier transport through 'pinhole'.

the current is formed. The quality of SiO_x is crucial under this transport mechanism, when the quantity of 'pinhole' is too small, the carrier transport is limited. It indicates that there are too many defects in the oxide layer if too many 'pinholes', which could result in poorer passivation effect.

The tunneling and the 'pinhole' effect both exist in the TOPCon configuration. If the tunnel oxide layer is <1.7 nm thick, the tunneling effect dominates and the 'pinhole' effect accounts for less than 35%. If the thickness is over 2 nm and the temperature of annealing is over 100℃, the predominant carrier transportation is 'pinhole' effect.

3. FABRICATION OF TOPCon SOLAR CELLS

The fabrication process of p-TOPCon and n-TOPCon solar cells is similar. Both are fabricated via a combination of

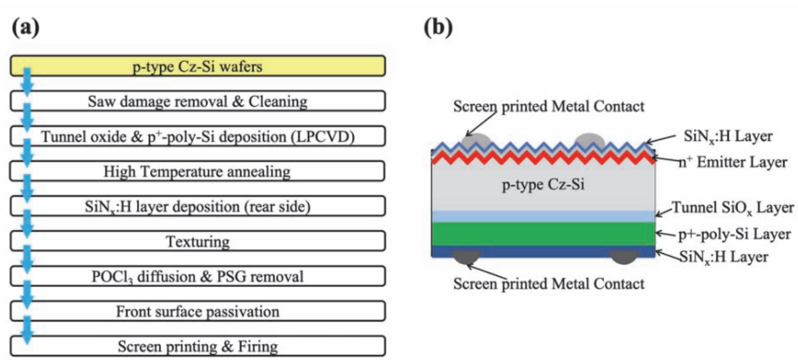
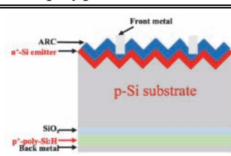
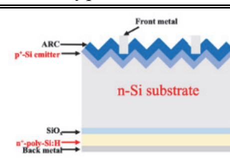


Fig. 5. (a) Process flow for the fabrication of p-type TOPCon solar cells and (b) Schematic cross section of the fabricated solar cells [16].

Table 1. Comparison of n-type TOPCon and p-type TOPCon.

Type	p-type TOPCon	n-type TOPCon
Structure		
Transport property	Dominated by holes	Dominated by electrons
Fabrication process	Different doping process and p^+-poly Si	Different doping process and n^+-poly Si
Efficiency	Dominated in small area	Dominated in large area
Advantages	Lower cost: using the upgraded PERC production line p-type wafer: more common	Higher lifetime Better stability
Disadvantages	Lower lifetime High defect density	Costly

standard silicon processing techniques, including wafer cleaning, texturing, diffusion, surface passivation, thermal SiO_x and poly Si, screen printing and firing. Figure 5(a) illustrates the fabrication process of p-type TOPCon solar cells fabricated by Mack et al [16]. The manufacturing process of p-type TOPCon solar cells based on boron-doped crystalline Si wafers starts with removing saw damage and then chemical cleaning. Subsequently, an ultra-thin SiOx layer (approximately 1.2~1.4 nm) and an in-situ B-doped poly-Si layer are deposited via low pressure chemical vapor deposition (LPCVD) in a tube furnace to form a rear surface field (BSF) passivation contact. The following step of thermal treatment in a nitrogen atmosphere causes the activation of dopant, and the profile of rear dopant is formed below the silicon oxide. Then, only SiN_x: layer (~75 nm) is deposited on the rear side. Next, etching in an alkaline solution promotes the formation of random pyramids on the unprotected front side. In order to obtain appropriate sheet resistance, $POCl_3$ diffusion is followed. Following are the PSG removal and chemical cleaning procedures. Subsequently, combined with thermal treatment and SiNx: H deposition is carried out for front-surface passivation. Metallization is achieved by screen printing and co-firing silver pastes in a conveyor belt furnace to create electrodes on both sides of the substrate. Figure 5(b) illustrates a cross-section view of the p-type TOPcon solar cell.

N-type TOPCon and p-type TOPCon are two types of high-efficiency solar cells that exhibit similarities and notable differences, as shown in Table 1. They both have similar structures, however, n-type TOPCon is doped with 5-valent impurities such as phosphorus or arsenic. In contrast, p-type TOPCon uses 3-valent dopants such as boron. In addition, the transport of charge carriers in n-type solar cells is dominated by electrons, while it is dominated by holes in p-type solar cells. Based on the above discussion, it is known that the highest efficiency of p-type TOPCon and n-type TOPCon solar cells are 26.0% and 25.8%, respectively. Despite dominating in small size, p-type TOPCon solar cells have made limited progress in large areas due to their lower carrier lifetime and inferior surface passivation. However, it is more cost-effective to promote p-type TOPCon solar cells due to the low price of p-type wafers and the utilization of the upgraded PERC production line with minor modifications. In fact, the n-type TOPCon solar cell has received more attention for its advantages of higher efficiency in large-scale cells, superior passivation quality and stability. However, p-type TOPCon should receive more commercial attention from the point of view of mass production and potential high efficiency for c-Si solar cells.

4. PROGRESS of p-TOPCon SOLAR CELLS

In 2014, Feldmann et al. [17] fabricated n-TOPCon and p-TOPCon solar cells using both planer and polished wafers. The authors also noted that the implied open-circuit voltage (iV_{oc}) for p-TOPCon (680 mV) was lower than n-TOPCon (725 mV). This indicates that the passivation properties of p-TOPCon are suboptimal, potentially due to a greater concentration of defects within the bulk silicon layer and at the Si/SiO_x interface. Several papers reported similar results as well: the passivation efficiency of n+-poly-Si/SiO_x (n-TOPCon) outperformed that of p+-Poly-Si/SiO_x (p-TOPCon) in quality. Various techniques have been developed to enhance the PCE of p-TOPCon solar cells, such as incorporating a poly-Si layer, implementing an ultra-thin interfacial SiO_x layer, and utilizing post-crystallization treatment.

4.1 The Ultra-Thin Interfacial SiO_x Layer

Agarwal and colleagues [18] reported that passivation quality can be enhanced by optimizing SiOx layer thickness. They investigated whether variation of SiO_x layer had an impact on the passivation performance of p^+-poly-Si/SiO_x. They also proved that p-TOPCon could achieve the highest implied V_{oc} (~700 mV) with an ultra-thin SiO_x layer of 1.4~1.6 nm.

Feldmann et al. [19] investigated the influence on passivation quality of the SiO_x layer deposited by different methods like plasma oxidation, plasma oxidation with nitridation or thermal oxidation. They found that the SiO_x grown by thermal oxidation exhibited the best passivation quality and high-temperature tolerance. They also found that the implied V_{oc} of p-TOPCon (705 mV) was lower than n-TOPCon (730 mV) in agreement with previous results. In their studies, they also pointed out that diffusion could be inhibited by applying the method of plasma oxidation with nitridation. However, the passivation quality still decreased because the incorporation of nitrogen atoms would destroy the ultra-thin SiO_x layer. Guo et al. [14] also demonstrated the SiO_x grown by different approaches would influence the passivation properties. The SiO_x layers were produced using 3 methods: hot nitric acid oxidation (NAOS-SiO_x), plasma-assisted nitrous oxide (N_2O) gas oxidation (PANO-SiO_x), and thermal oxidation (Thermal-SiO_x). The passivation quality is as follows: Thermal-SiO_x > PANO-SiO_x > NAOS -SiO_x. The best value of i-V_{oc} could be achieved at 722 mV.

Compared to SiO_x, AlO_x exhibited superior field effect passivation owing to its abundance of negative fixed charge, thus Xin et al. [20] tried to replace the conventional SiO_x by thickness-controllable and film-uniformly AlO_x to form a tunnel layer of p-type TOPCon. The highest value of i-V_{oc} could be achieved up to 723 mV with a recombination current density ($J_{0,s}$) of 6.6 fA/cm^2.

The most commonly used methods for depositing the tunnel oxide layer in TOPCon solar cells include thermal, plasma-enhanced chemical vapor deposition (PECVD), and atomic layer deposition (ALD) oxidation [21]. Various techniques have their own strengths and weaknesses when it comes to tunnel oxide layer deposition. The oxidation layer produced by thermal oxidation process showed excellent passivation, however, it required high temperature and took lots of time. PECVD-grown tunnel oxide layer demonstrated a high growth rate and economical process, but the uniformity needed to be improved in the future. Oxidation by ALD approach might form an excellent uniformity oxidation layer, but the growth rate was too low for commercialization. Lastly, the oxidation layer deposited by chemical oxidation required low temperature and ease of process, however, the quality and the stability seemed not good enough. The advantages and disadvantages of TOPCon solar cell technology are shown in Table 2. Hence, tunnel oxide layer deposited by PECVD would be an economical procedure if the uniformity was improved in the future.

Table 2. Comparison of the tunnel oxide layer deposited by different approaches.

Method	Thermal oxidation	PECVD	ALD	Chemical oxidation
Advantages	Excellent passivation Ease of process	High growth rate Effective	Good passivation Uniformity	Ease of process Low temperature
Disadvantages	Low growth rate High temperature	Poor uniformity	Low growth rate	Poor quality Poor stability

Table 3. Comparison of the Poly-Si layer deposited by different methods.

Method	LPCVD	PECVD	CVD
Advantages	Mass production Mature technology	High deposition rate Cost-effective	No wrap-around issues No pollution
Disadvantages	Wrap-around issues	Small wrap-around issues Pollution	Low production Costly

4.2 Poly-Si layer

Along with the ultrathin SiO_x layer, the poly-Si layer would play a vital role in determining the passivation quality for TOPCon. Low-pressure chemical vapor deposition (LPCVD) and PECVD are commonly utilized techniques for fabricating doped silicon layers [22-24]. The former method could be applied to mass production and exhibit excellent uniformity of thickness. However, the wrap-around issues should be addressed. PECVD-grown poly-Si layer could generate higher deposition and seemed a cost-effective process, but production needed to be improved. Yan et al. [25] proposed a co-sputtering technique based on physical vapor deposition to fabricate selective passivation contact holes in p^+-poly-Si for p-TOPCon solar cells. They fabricated TOPCon solar cells with a phosphorous-diffused region on the front surface and a p-TOPCon on the back surface, achieving an impressive 23% efficiency alongside a high V_{oc} of 701 mV. The advantages of this method could solve the wrap-around related issues; however, the cost was much higher, and production needed to be improved in the future. The advantages and disadvantages of various techniques are outlined in the Table 3.

4.3 Post-crystallization treatment

In order to enhance passivation quality in the p-TOPCon structure, a post-crystallization process was employed. According to previous discussion, it is known that, compared with n-type crystalline wafers, it is more difficult to passivate the p-type wafers based on the presence of boron-oxygen complex defects [26,27] Nemeth and coauthors [28] developed a post crystallization treatment to improve the passivation quality via hydrogenation of passivated contact layer through applying atomic layer deposition (ALD) Al_2O_3 layer, which could result in an implied V_{oc} of ~700 mV for p-type TOPCon structure. Furthermore, Schnabel et al. [29] implemented similar technology to enhance passivation quality. Using atomic layer deposition (ALD) Al_2O_3 layer and post-deposition annealing in forming gas and nitrogen, implied V_{oc} could reach 710 mV. The improvement remained after the removal of Al_2O_3 layer, which meant the Al_2O_3 was primarily the hydrogen source for chemically passivating defects.

In order to minimize the influence of B-O complex defect, Young and colleagues [30] fabricated gallium-doped (Ga-doped) poly-Si/SiO_x passivated contacts that demonstrated *i*-V_{oc}>730 mV with recombination current density $J_{0,s}$ below 5 fA/cm^2, which were among the top performers for p-TOPCon. Mack et al. [31] investigated the links between wafer morphology and p-type TOPCon passivation quality. They found the passivation quality of the planar surface with shinny-etched wafer was superior to the textured wafer. The implied V_{oc} could be as high as 737 mV. Then, they fabricated a large size p-type TOPCon solar cell from a commercialized p-type crystalline silicon wafer (244 cm^2) with a PCE of 20.4%. Furthermore, they found the efficiency could be improved to 21.2% through optimizing the manufacturing process, including optimizing the thickness of poly-Si, applying the most promising metallization pastes and improved hydrogenation treatment, etc [16]. Stodolny et al. [32] reported that they could improve the passivation level of p-type TOPCon with an implied V_{oc} value of 735 mV. The high passivation quality was achieved through the following methods: optimizing the diffusion profile of boron, implementing a novel dielectric stack structure for hydrogenation and suppressing the diffusion of boron during annealing.

Moriset et al. [33] found that the blister density of the interface between poly-Si and SiO_x could influence the passivation level and stability of TOPCon. In order to obtain blister-free and enhance the adhesion of the poly-Si layer, they tried to increase the gas flow raion (H_2: SiH_4) and deposition temperature during the progress of PECVD. As a result, the p-TOPCon with an n-type silicon wafer was able to achieve an implied V_{oc} value of 714 mV.

4.4 Both side TOPCon structure

Furthermore, the p-type TOPCon design was employed in double-sided TOPCon solar cells, as depicted in Fig. 6, to minimize manufacturing expenses associated with boron diffusion. Tao et al. [34] manufactured solar cells having p-TOPCon on the front surface and n-TOPCon on the rear surface. They described that ITO layers deposited by sputtering would degrade the passivation performance of p-type and n-type TOPCon structures, and post-annealing could recover the passivation quality. After thermal treatment, p-TOPCon exhibited a better improvement than its counterpart. The efficiencies of solar cells with a front p-TOPCon and a rear n-TOPCon increased from the improved 16.05% initially to 18.55% after thermal treatment. Besides, Lozac'h and Nunomur [35] discovered that TOPCon solar cells featuring textured substrates outperformed those utilizing polished wafers. The former exhibited a higher current density. The solar cells that used p-TOPCon on the front surface and n-TOPCon on the rear achieved the best photovoltaic conversion efficiency (PCE) of 19.1% among their peers. However, Ma and co-authors [24] predicted that the efficiency of p-TOPCon structures based on n-type wafer could reach ~25% featuring state-of-art devices simulated by Quokka. The inferior passivation performance of p-TOPCon might be responsible for the insufficient efficiency.

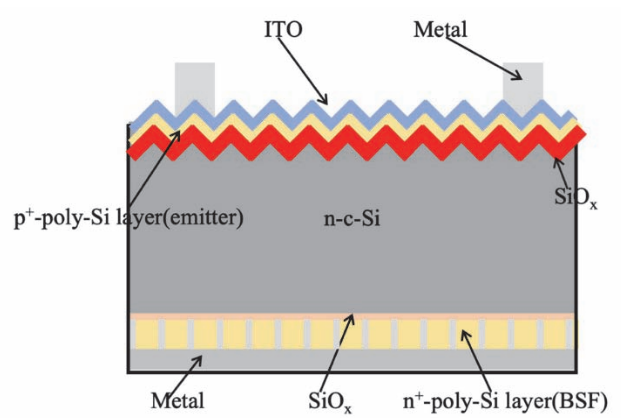


Fig. 6. Schematic diagram of both-sided TOPCon Solar cells featuring p-TOPCon at front side and n-TOPCon at rear side.

5. CONCLUSION AND OUTLOOK

It is obvious that the passivation performance of p^+-poly-Si/SiO_x (p-type TOPCon) cannot be as the same level as n^+-poly-Si/SiO_x (n-type TOPCon). Consequently, the efficiency of large-scale p-type TOPCon solar cells is inferior to their counterparts. On top of less attention on p-type TOPCon, there are several limitations such as B-O complex defects between the boron-doped poly-Si and SiO_x layers. According to extensive research to date, we notice that there are several reasons which could influence the passivation quality, including the preparation methods and quality of p^+-poly Si layer, doped SiO_x layer, the post crystallization treatment to suppress the defect of bulk silicon layer and the interface of Si/SiO_x, etc.

From the perspective of commercialization, p-type Si wafers have greater advantages over n-type Si wafers in terms of cost. It is predicted that the current mainstream p-type wafers will dominate the market share for the next five years. Additionally, the p-type TOPCon could be directly applied in upgrading the existing PERC production lines. Therefore, it seems more attractive to develop TOPCon technology based on gallium doped p-type c-Si wafers. Furthermore, the p-type TOPCon structures are applied in double-side TOPCon solar cells as well, which could further improve efficiency. Thus, improving the passivation quality of p-type TOPCon technology is crucial to promoting the commercialization of crystalline solar cells.

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