

# State-of-the-art passivation strategies of c-Si for photovoltaic applications: A review

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## ABSTRACT

The carrier recombination is a major bottleneck in enhancing the power conversion efficiency of first-generation solar cells. As a remedy, passivation minimizes the recombination at the surface and bulk by either neutralizing the dangling bonds or creating a field-effect. The review describes the evolution of the different cell structures based on passivation and classifies the passivation schemes according to the mechanism. The two ways of passivating the crystalline Si are either by reducing the minority carrier concentration at the surface or decreasing the intermediate density of states. Field-effect passivation is achieved by creating an electric field at the surface of Si to repel the minority carriers. The paper compares the typical and emerging dielectric layers in terms of substrate compatibility, effectiveness, interface qualities, and carrier-selective emitters for contact passivation. The effective lifetime of solution-based chemical passivation is compared for various electrolytes. In addition to surface passivation, it describes the advanced hydrogen passivation for bulk defects, such as shielded-hydrogen passivation and laser passivation. Further, the recent developments in the passivation strategies for trending solar cell architectures are discussed from the perspective of challenges.

## 1. Introduction

The demand for energy produced by solar photovoltaics is increasing due to the scarcity of conventional energy sources. Industries and academics are looking for ways to improve cell efficiency and lower manufacturing cost [1]. First-generation photovoltaic devices, dominated by Silicon (Si) wafer-based technology, show remarkable technical and economic advancements to lower the cost per unit. The single-junction terrestrial Si solar cell achieves the highest efficiency of 26.7% [2,3]. Commercial crystalline Si solar cells with a record efficiency of 22.8% [4], amorphous cells with 10.2% [5] and hetero-junction cells with 22.2% [4,6]; together account for 93% of the current solar cell market [7,8]. Approaches such as improved cell architecture, increasing the number of cell junctions, and using efficient materials [9] are under investigation to increase efficiency [10]. Reducing the semiconductor layer thickness, replacing bulk Si with Si-nanostructures [11], adapting affordable coating processes, and replacing expensive materials with low-cost alternatives are significant ways to lower production costs.

The efficiency of the solar cell is a fraction of the incident power as expressed in equation (1), where  $V_{oc}$ ,  $I_{sc}$ ,  $FF$ , and  $P_{in}$  are the open circuit

voltage, short circuit current, fill factor, and incident power, respectively. Thus,  $FF$  determines the maximum power of the solar cell in conjunction with  $I_{sc}$  and  $V_{oc}$  [12,13].  $I_{sc}$  depends on the area of the cell, the spectrum of the incident light, optical properties of the cell surface (absorption and reflection), and minority carrier collection probability. Carrier collection probability is the significant parameter to affect the cell efficiency for a constant area of the cell and the spectrum of the incident light. On the other hand, with an increasing band gap,  $I_{sc}$  decreases and  $V_{oc}$  increases, leading to band gap optimization for maximum efficiency. Hence, cell architectural modification is the sole remedy for improving the carrier collection probability, light absorption, and band gap optimization.

$$\eta = \frac{V_{oc} I_{sc} FF}{P_{in}} \quad (1)$$

Architectural improvement is one of the practical approaches to enhance cell efficiency. The conventional solar cell structure (Al-back surface field structure) has been used for decades. However, it suffers from low efficiency and high material utilization and is space inefficient [14,15]. The efficiency of Al-back surface field-based (Al-BSF) mono-crystalline and polycrystalline Si solar cells is 19.8% and 18.5%,

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respectively [16,17]. Passivated Emitter Rear Cell (PERC) structure was first reported in 1980 and was commercially unsuccessful. In recent decades, the PERC (Fig. 1(a)) and modified PERC structures, such as Passivated Emitter Rear Locally-diffused (PERL) and Passivated Emitter Rear Totally-diffused (PERT) (Fig. 1(b)), together share more than 50% of the solar cell market [18]. The PERL cell possesses diffused layers (heavily doped) at the rear metal contact only, whereas the whole rear surface is diffused in the PERT cell. PERC has reached a commercial efficiency of 21.6% and laboratory efficiency 25% [3,18,19]. The primary reason for shifting from the conventional structure was the increased efficiency due to the introduction of the dielectric layers on the rear surface to minimize the recombination and antireflecting coating (ARC) to reflect heat-generating wavelengths [19,20].

Absence of metal fingers on the front side, the Interdigitated Back Contact (IBC) solar cell (Fig. 1(c)) is an attractive contender for high-efficiency solar cells [21,22] which outperformed PERC with a record efficiency of 26.7% [2,3]. Opening the rear side contact grooves through the dielectric layer in a PERC structure leads to substrate degradation [23]. Tunnel Oxide Passivated Contact (TOPCon) solar cells with a complete area rear side metallic contact (refer to Fig. 1(d)) abstain from difficulties such as the need for laser-aided contact apertures or charge carrier congestion at localized contacts [24,25]. Table 1 lists the passivation-related problems associated with different cell structures and the developments to resolve the issues.

The photo-generated charge carrier recombines on the surface and contact terminals instead of contributing to the current output, reducing the output power and hence the efficiency. The structural evolution of the solar cell figures out the stumbling block to efficiency enhancement-recombination at the surface and the contact region. The review classifies the passivation based on the various recombination reduction techniques. The comparison explains the efficient and effective ways of passivating the c-Si surface (and the bulk) and purpose-based appropriate techniques. Further, it outlines the mechanisms and respective fabrications for each strategy.

### 1.1. Recombination

In solar cells, charge carrier generation takes place as the result of sunlight absorption. Recombination is the opposite of generation, where the generated carriers within a semiconductor combine with the opposite charge carriers (annihilation). In thermal equilibrium, the generation and recombination rates are identical. The loss of carrier releases energy either as phonons (lattice vibrations) or as photons. Three types of recombination mechanisms are possible in semiconductors, namely, i. Auger recombination, ii. radiative recombination, and iii. Shockley-Read-Hall (SRH) recombination.

When an electron and a hole recombine, the energy is transferred to

**Table 1**

Advancement of cell structures from the passivation point of view.

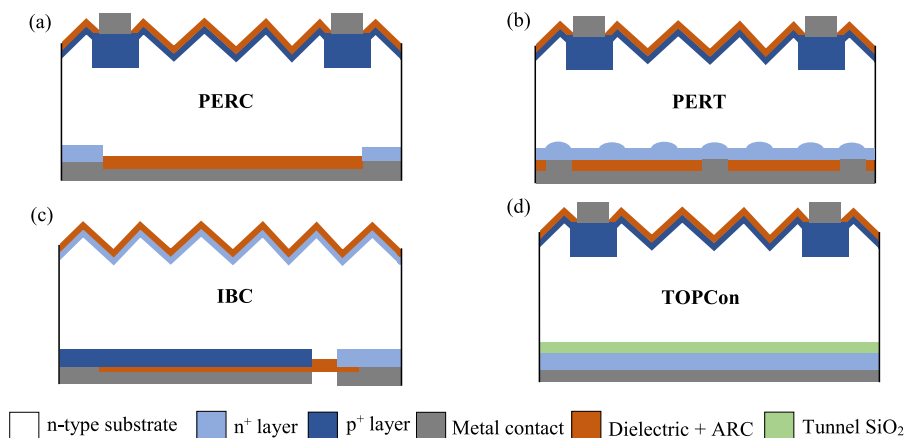
Solar cell structure	Passivation related limitations	Resolving development and corresponding cell structure
Al-BSF	A weaker electric field at the rear surface and increased rear surface recombination [26]	Deposition of a suitable dielectric layer and capping layer on the rear (PERC) [27]
PERC	Laser ablation of the dielectric layer for rear contact formation causes defects in the substrate, leading to recombination centers [28]	Full area rear metal contact, tunneling layer separates the substrate and the carrier selective passivation layer (TOPCon) [29]
PERT/PERL	Front contact through passivation ARC causes defect leading to bulk recombination and optical shading [29]	All rear contact leads to minimizing front surface defect-related recombination loss and optical shading loss (IBC) [30]
IBC	Interdigitated rear contacts by laser ablation increase rear recombination, and consecutive opposite doping narrows the current carrying path [31]	Full area rear metal contact, tunneling layer separates opposite doping layers for carrier selective contact passivation (Tunnel-IBC) [32]

another electron in the conduction band [33], termed Auger recombination. Auger recombination is highly effective in the heavily doped Si-substrates or at high injection levels under concentrated sunlight. During radiative recombination, an electron from the conduction band falls back into the valence band to recombine with the hole. The energy released from the radiative recombination is in the form of a photon having energy equal to the band gap. Radiative recombination is dominant for direct band gap semiconductors [34] and extremely low for indirect band gap c-Si solar cells.

SRH recombination (also known as recombination through defects) takes place through a trap or defect energy level in the band gap [35]. An energy state in the forbidden area traps an electron (or hole), recombining with a hole (or an electron) that climbs to the same energy level. SRH recombination is possible both at the surface and the bulk Si due to dangling bonds and defects, respectively. Surface recombination requires additional attention than bulk recombination due to the high surface-to-volume ratio of a solar cell. Various parameters that indicate the recombination levels are Surface Recombination Velocity (SRV), effective lifetime ( $\tau_{eff}$ ) and the surface saturation current density ( $J_0$ ). Either SRV or the  $\tau_{eff}$  describes the degree of passivation for non-diffused n-type or p-type c-Si. However,  $J_0$  explains the same as a function of sheet resistance for excessive dopant-diffused c-Si surfaces.

### 1.2. Characterization of recombination

The lifetime measurement evaluates the material quality by indicating the possible recombination at the surface and the bulk. Contact-



**Fig. 1.** Structure of n-type (a) PERC, (b) PERT, (c) IBC, and (d) single junction TOPCon cell.

less photoconductance decay or transient measurements are used to determine the  $\tau_{eff}$  [36,37]. The conductance measurement (photoconductance decay) using the inductive coupling method describes the change in minority carrier concentration [38]. Effective lifetime measurement considers the recombination in bulk and at the surface—termed as bulk lifetime ( $\tau_b$ ) and surface lifetime ( $\tau_s$ ).  $\tau_b$  includes the contributions of Auger ( $\tau_{Aug}$ ), radiative ( $\tau_{rad}$ ), and SRH ( $\tau_{SRH}$ ) recombination as expressed in equation (2) [39].

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{1}{\tau_s} = \left( \frac{1}{\tau_{Aug}} + \frac{1}{\tau_{rad}} + \frac{1}{\tau_{SRH}} \right) + \frac{1}{\tau_s} \quad (2)$$

SRV ( $S_{eff}$ ) is a derived quantity and is expressed in terms of  $\tau_s$  as given in equation (3), where  $W$  is the substrate thickness, and  $D$  is the ambipolar carrier diffusion coefficient [40]. The surface recombination depends on the carriers generated at the bulk and the surface. The carriers generated at the bulk travel to the surface to recombine, whereas the surface-generated carriers recombine instantaneously at the surface or diffuse to the bulk. Hence the SRV is a function of decaying exponential terms (infinite sum) of the surface lifetime, and the dominant first term is expressed in equation (3), which is further simplified with the assumptions—i. same recombination velocity at the front and rear surface, and ii.  $(S_{eff}W)/D < 0.25$  [41]. The assumptions put a limitation for the substrate with textured surface, and measurement accuracy decreases to 96% [42]. Further, an assumption of the infinite bulk lifetime results in the maximum  $S_{eff}$ .

$$S_{eff} = \sqrt{\frac{D}{\tau_s}} \tan\left(\frac{W}{2} \sqrt{\frac{1}{D\tau_s}}\right) \approx \left(\frac{1}{\tau_{eff}} - \frac{1}{\tau_b}\right) \frac{W}{2} \quad (3)$$

The determination of the  $\tau_s$  requires both  $\tau_b$  and  $\tau_{eff}$  and the measurement of the accurate  $\tau_b$  is a challenging task due to the significant value compared to  $\tau_{eff}$ . Fig. 2 depicts the effect of changing  $S_{eff}$  on  $\tau_{eff}$  for specified  $\tau_b$  values [43]. SRV must be reduced below  $1 \text{ cm s}^{-1}$  to get the effective lifetime below 10% of the for  $\tau_b > 2 \text{ ms}$ . The accurate measurement of bulk lifetimes requires excellent surface passivation, particularly in high-efficiency solar cells with  $\tau_{eff} > 10 \text{ ms}$ . Similarly, for the  $\tau_{eff}$  value below 20% of the  $\tau_b$  SRV should be less than  $1 \text{ cm s}^{-1}$  for  $\tau_b > 3 \text{ ms}$ .

The semiconductor crystal lattice abruptly discontinues at the surfaces, disrupting the band structure and the emergence of a semi-continuum of energy states. The strained and unterminated intermediate states are due to the surface dangling bonds. The well-known SRH

recombination is the most effective way to characterize recombination mediated by band gap states. When estimating the recombination activity of the interface states, a density of interface traps ( $D_{it}$ ) is approximated at single energy in the middle of the gap ( $E_t - E_i = 0$ ). The electron recombination velocity and the hole capture velocity at the approximated states are  $S_{n0} = \nu_{th} D_{it} \sigma_n$  and  $S_{p0} = \nu_{th} D_{it} \sigma_p$ , respectively [44]. Where  $\nu_{th}$  and  $\sigma$  are the carrier mean thermal velocity and the capture cross-section of the state, respectively. The effective recombination at the surface is given by equation (4) [45] where  $\Delta n_d$  is the minority carrier concentration at the edge (of width  $d$ ) of the space charge region. Further,  $n_s$ ,  $p_s$  and  $n_i$  are the steady-state electron, hole, and intrinsic electron concentration, respectively.

$$S_{eff} = \frac{U_s}{\Delta n(x=d)} = \frac{1}{\Delta n_d} \frac{n_s p_s - n_i^2}{(n_s + n_i)/S_{p0} + (p_s + n_i)/S_{n0}} \quad (4)$$

The saturation current density ( $J_0$ ) considers all the recombination mechanisms and heavy doping effects, such as band bending.  $J_0$  characterizes the recombination at the surface for heavily doped emitters and is independent of dopant concentration for undiffused surfaces [46]. Assuming  $\tau_{SRH}$  to be infinite,  $J_0$  is given by equation (5) [47], where  $n_{i,eff}$  is effective intrinsic concentration. Quasi-steady-state photoconductance (QSSPC) or Quasi-steady-state photoluminescence (QSSPL) technique measures  $J_0$  in terms of  $\tau_s$  [48]. Kimmerle et al. reported a detailed analysis of the  $J_0$  using QSSPC lifetime measurement [49].

$$J_0(\Delta n) = \frac{d}{d\Delta n} \left( n_{i,eff}^2 \sqrt{D \left( \frac{1}{\tau_s} \right)} \tan \left( \frac{W}{2} \sqrt{D \left( \frac{1}{\tau_s} \right)} \right) \right) \quad (5)$$

$\tau_{eff}$  varies with the injection level of the substrate; however, the review considers the maximum  $\tau_{eff}$  (for comparison) which exists in the injection range of  $10^{14}$  to  $10^{16} \text{ cm}^{-3}$  for non-diffused substrates [49].  $J_0$  indicates the passivation level for excessive diffused substrates (with an injection level of  $\geq 10^{19} \text{ cm}^{-3}$ ).  $J_0$  is expressed in terms of sheet resistance, and the lower the  $J_0$  value, the better the passivation quality. Both  $\tau_{eff}$  and  $J_0$  characterize the passivation level at the interface of the excessive diffused substrate and the dielectric layer. However, the interface of the excessive diffused substrate and metal contact is characterized by  $J_0$  only.

### 1.3. Passivation strategies

Various approaches, such as improvement of deposition technique [50,51], utilization of defect-free semiconductor grade wafers [52,53], and passivation, are the primary remedies to reduce the recombination from the surface and the bulk. The recombination is reduced by neutralizing the dangling bonds or restricting the minority carriers. Depending on the recombination mitigation region, the process may be either surface passivation or bulk passivation. State-of-the-art deposition techniques such as atomic layer deposition (ALD) and pure semiconductor grade wafers increase the manufacturing cost in multiple folds [54]. Hence, the economic approach of passivation is preferred to minimize the recombination to increase efficiency and limit the manufacturing cost of the solar cell.

Reducing the minority charge carrier concentration near the surface restricts the recombination, as the maximum possible recombination rate depends on the available minority charge carrier. Minority charge concentration at the surface is reduced by creating an electric field to repel the minority carriers from the surface. Electric field formation at the surface restricts the minority carriers from facilitating recombination at the surface. The two ways of creating the electric field are i. by forming a heavily doped layer and ii. by introducing a dielectric layer.

The carrier difference between the excessive diffused (heavily doped) layer and the normally diffused layer creates the electric field to repel the minority carriers, whereas an external field is applied to charge the dielectric coating—called corona charging. Corona charging enhances

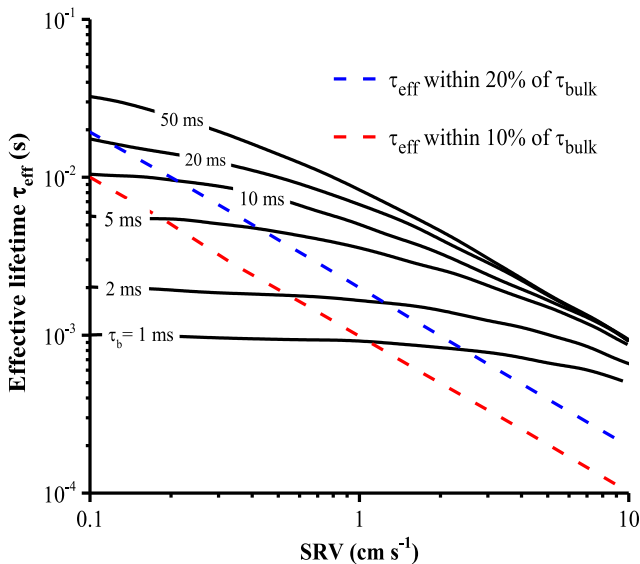


Fig. 2. Impact of varying  $S_{eff}$  on  $\tau_{eff}$  for specified  $\tau_b$  [43].

field-effect passivation exclusively on a dielectric-coated Si surface, whereas the phrase ‘field-effect passivation’ encompasses both heavily doped layers and dielectric coatings [55]. Corona charging controls the charge concentration at the interface of c-Si and the dielectric layer to improve the passivation through field-effect passivation [56]. The polarity of the corona charging differs depending on the interface and substrate type. For example,  $\text{Al}_2\text{O}_3$  is preferable for p-type substrates with negative polarity corona charging, and the  $\text{SiO}_2$  dielectric layer passivates a heavily doped n-type emitter with positive polarity charging [57–59]. The other way of passivation is neutralizing the Si surface dangling bonds by hydrogen atoms or oxygen-containing functional groups.

Surfaces (and interfaces in general) create a band of electronic states in the band gap due to broken bonds and impurities, like dislocations and planar defects. The Si surface possesses highly active recombination due to the abundance of band gap states originating from dangling bonds. The strategies for reducing the SRV are mainly of two categories, i. by reducing the carrier concentration at the surface and ii. by reducing the intermediate density of the states (DOS). In practice, both phenomena work together to passivate c-Si on the surface and in bulk. Fig. 3 represents the comprehensive classification of the passivation strategies based on the intrinsic concept and the materials used.

In addition to surface recombination, bulk defects decrease cell efficiency, and conventional passivation techniques complicate the mitigation of bulk defects. The conventional heat treatment for hydrogen passivation through the dielectric layer fails to enhance the effective efficiency of the cell due to the freshly heat-generated defects [60,61]. Shielded hydrogen passivation suggests the formation of atomic hydrogen for passivation without exposing the substrate to excessive temperature ( $>400^\circ\text{C}$ ) [62,63]. Bulk passivation requires specific techniques, such as LASER-based hydrogen passivation, to eliminate selective bulk defects using different charge states of the atomic hydrogen [64]. In the last decade, several reports explained the chemical passivation in the liquid medium [65–67]; however, applying such chemical passivation in practical fabrication still lacks clarity [43].

## 2. Field-effect passivation

Field-effect passivation shields the semiconductor interface from minority carriers through an electric field created by either doping profile below the surface or introducing electrical charges in a dielectric layer or a gate electrode [57,68,69]. A heavily doped region forms a high-low junction (such as  $p^{++}/p$ ) either on the front or rear of the c-Si. The inherent electric field across the junction prevents recombination,

thereby repelling the minority carriers towards the bulk part of the c-Si [70,71]. Fig. 4(a) shows a typical both-side-contacted cell structure with the back-surface field (BSF). Electrons and holes from the p-type and n-type c-Si flow away from the respective surfaces towards the bulk due to the intrinsic field formed by the heavily doped regions. The heavily doped layer restricts the minority carriers by increasing the energy level for the valence band of the p-type substrate to the conduction band of the  $p^+$  layer, as shown in Fig. 4(b).

On the other hand, dielectric films combine a chemical reduction of defects states and a sufficient charge concentration for field-effect passivation. Band bending occurs at the c-Si surface, which creates the field to repel the minority carriers towards the bulk portion, thereby preventing them from recombining at the surface [72]. Fig. 4(c) shows the cell structure with front and rear dielectric passivation layers. Depending on the substrate doping type, the field-effect passivation introduces a specific polarity charge into the dielectric layer via corona charging to restrict the recombination at the surface. The band bending concept is the alternative means of representing the dielectric field-effect passivation, as depicted in Fig. 4(d). The extremely wide band gap of the dielectric layer restricts the recombination on both surfaces [42,72].

### 2.1. Simulation of field-effect passivation

Solar cell modeling using state-of-art simulation software reduces manufacturing costs. The software packages such as Sentaurus TCAD, EDNA 2, and Quokka 2.2.4 include the Fermi-Dirac model, Schenk’s model, and Klaassen’s mobility model [73–75]. Schenk’s model analyzes the band gap modifications derived from a non-self-consistent finite-temperature full random-phase approximation formalism [75]. Klaassen’s first model analyzes carrier mobility, impurity screening, carrier-scattering, impurity-clustering, and the temperature dependence of carrier mobility [73]. Klaassen’s second model is especially suitable for complete device simulation, as the carrier mobility is expressed as an analytical function of the carrier concentrations. The model also determines the temperature-dependent carrier lifetime [74]. The SRH model estimates the surface recombination and considers the interface traps distributed across the band gap of the Si [76,77]. The SRH modeling uses equation (4) to estimate the SRV and  $\tau_{eff}$ . The modeling uses various substrate and dielectric layer parameters, as listed in Table 2. The simulation adapts the QSSPC technique to determine the  $\tau_{eff}$ . The homogeneous photogeneration of electron-hole pair is considered in a broad wavelength spectrum to study the injection dependent  $\tau_{eff}$ .

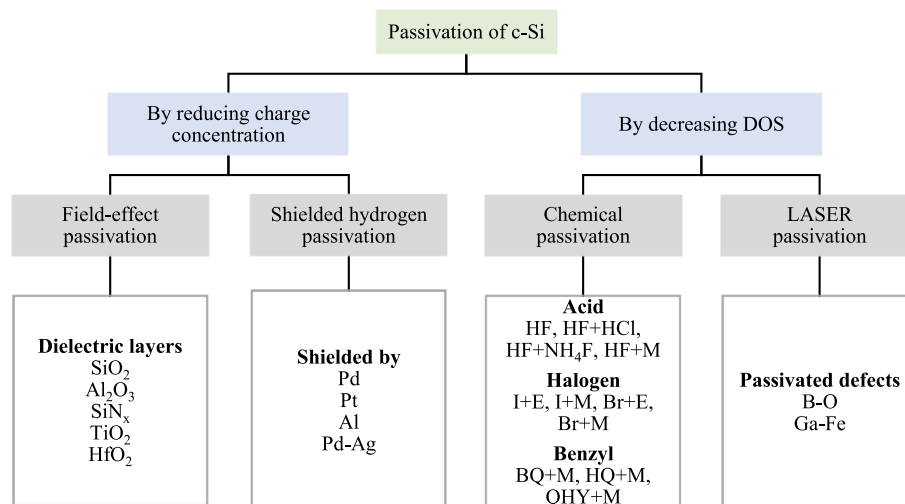
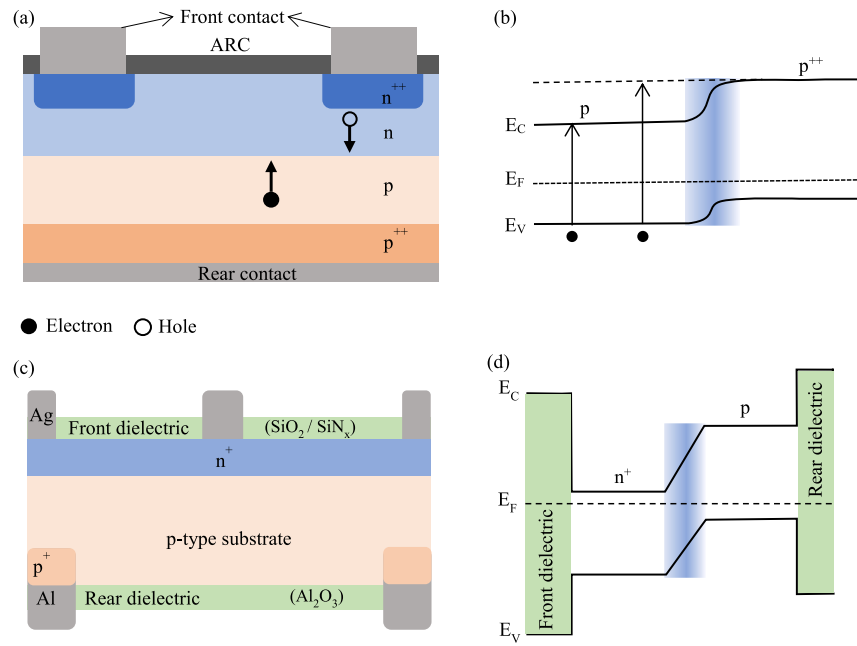


Fig. 3. Classification of passivation strategies; where M – Methanol, E– Ethanol, I- Iodine, Br- Bromine, BQ-*p*-Benzoquinone, HQ- Hydroquinone, QHY- Quinhydrone, B-O- (Boron–Oxygen) defect, Ga-Fe- (Gallium–Iron) defect.



**Fig. 4.** (a) Generalized concept of field-effect passivation by increasing doping level, (b) band structure of doping level increment, (c) cell structure showing dielectric layers, (d) band structure of dielectric passivation.

**Table 2**

Typical values of the parameters used in the simulation extracted from experimental studies.

	Parameters	Typical reported value	Ref.
Substrate parameters	Thickness (μm)	100–300	[42]
	Resistivity (Ω.cm)	1–5	
	Doping level for undiffused substrate (cm <sup>-3</sup> )	(1–5) × 10 <sup>15</sup>	[78,79]
	Doping level for heavily diffused substrate (cm <sup>-3</sup> )	(1–6) × 10 <sup>19</sup>	
	Surface crystalline structure	{100}	[80]
Dielectric layer parameters	Electron/hole capture density (cm <sup>-2</sup> )	10 <sup>16</sup>	
	Fixed charge density at the interface (cm <sup>-2</sup> )	Al <sub>2</sub> O <sub>3</sub> -(10 <sup>12</sup> –10 <sup>13</sup> )	[76,79,81]
		SiO <sub>2</sub> 2 × 10 <sup>11</sup>	[82]
		SiN <sub>x</sub> 3.6 × 10 <sup>12</sup>	[83]
		TiO <sub>2</sub> -4.9 × 10 <sup>12</sup>	[84]
		HfO <sub>2</sub> 1.64 × 10 <sup>12</sup>	[85]

Dumbrell et al. reported that the effect of single-side metalization of the substrate decreases the lifetime due to excessive recombination at the contact area [48]. The lifetime decreases from 2 ms to 0.5 ms due to the elimination of the dielectric layer from one side of the p-type substrate, followed by Al deposition (500 nm). Ma et al. investigated the effect of polarity inversion of the corona charging of the Al<sub>2</sub>O<sub>3</sub> layer on the n-type and p-type substrate [80]. Maximum  $\tau_{eff}$  drops from 1.7 ms to 0.45 ms for n-type and 1.8 ms–0.3 ms for p-type substrate while reversing the polarity from negative to positive for a 15 nm Al<sub>2</sub>O<sub>3</sub> layer. The inversion of the corona charging polarity modifies the fixed charge density in the dielectric layer and generates additional interface traps at the surface of c-Si (surface damage), leading to a decrement in the lifetime. Table 3 presents the insight of simulated passivation of c-Si with various dielectric layers.

Anand et al. [25] optimized the TOPCon cell performance by varying

the tunnel oxide (SiO<sub>2</sub>) thickness (ranging from 0 to 1.1 nm) and BSF doping level (ranging from 10<sup>15</sup> cm<sup>-3</sup> to 10<sup>21</sup> cm<sup>-3</sup>) using the numerical tool AFORS-HET. The tunneling efficiency decreases with increasing oxide thickness and rises with increasing doping concentration. The increase in oxide thickness improves the passivation, lowers the contact resistivity, and allows selective passage of the charge carrier via tunneling. The high BSF doping lowers the recombination current and improves the overall cell performance. With optimized BSF doping level (= 10<sup>19</sup> cm<sup>-3</sup>) and tunneling oxide layer thickness (= 1 nm),  $V_{oc}$  increases by 5.5%,  $I_{sc}$  increases by ~13%, and 25% efficiency improvement is observed.

## 2.2. Dielectric layers deposition techniques for field-effect passivation

The dielectric layer deposition depends on substrate doping type,

**Table 3**

Simulated lifetime measurement of field-effect passivation.

Substrate doping type and Resistivity (Ω.cm)	Substrate thickness (μm)	Dielectric layer	Dielectric layer thickness (nm)	Maximum $\tau_{eff}$ (ms)	Mathematical tool	Ref.
p, 2	275	Al <sub>2</sub> O <sub>3</sub>	15	2	Sentaurus TCAD	[80]
n, 1.9	300			2.5		
n, 5	710	Al <sub>2</sub> O <sub>3</sub> /SiN <sub>x</sub>	–	2	Quokka	[48]



post-deposition processes, and substrate roughness (plane or textured). The substrate doping type and level decide the dielectric material as a specific dielectric layer is compatible with a particular substrate type. The post-deposition processes include Al etching, laser ablation for contact formation, heavily diffused Si layer deposition, and antireflecting layer coating (ARC).

The dielectric layer deposition on a plane Si substrate is compatible with all possible deposition techniques, whereas a textured surface needs sophisticated deposition techniques such as ALD and Plasma Enhanced Chemical Vapor Deposition (PECVD) (because of effectiveness and material purity). The textured front surface enhances the photon trapping capability; however, the recombination increases due to the high surface area (an upright pyramidal structure is a commonly reported texture with an area  $\sim 1.73$  times the flat surface) [86]. The texturing converts the surface orientation to {111} compared to a flat surface with {100} orientation, creating excess dangling bonds and interface defects [87]. Instead of the double-side polished substrate, the textured surface results in high  $I_{sc}$  due to low reflection; however, the  $V_{oc}$  decreases because of higher recombination [67]. Hence the passivation of a textured surface is a challenging task to achieve the  $\tau_{eff}$  comparable to a flat surface.

Deligiannis et al. [67] studied the  $\tau_{eff}$  of textured c-Si with three consecutive nitric acid oxidation cycles (NAOC) after standard cleaning and PECVD-grown intrinsic hydrogenated amorphous Si. The NAOC enhances the  $\tau_{eff}$  of the textured surface equivalent to that of a flat surface. With surface texturing and field-effect passivation ( $SiO_2$ ), the efficiency of the Si solar cell increases from 9.8% to 15.04%, as reported by Qiu et al. [88]. Table 4 lists the passivation of the rear and front surface with different dielectric layers with the highest reported  $\tau_{eff}$ .

One of the simple and cost-effective ways of back surface passivation is the screen printing of Al, followed by annealing at high temperatures to form a  $p^+$  layer called an aluminum back surface field (Al-BSF). However, Al-BSF is possible only for p-type substrates, and the field (formed because of the  $p^+$  layer) is weaker than the field developed across the dielectric layer after corona charging. Hence, high-efficiency PERC uses dielectric surface passivation and local contact formation, unlike the conventional Al-BSF [42]. Various dielectric layers, mainly thermally grown  $SiO_2$  [95], Si nitride ( $SiN_x$ ) by PECVD [92], and an atomic layer deposited  $TiO_2$  [93] lead to SRV of less than  $200 \text{ cm s}^{-1}$  at the injection level of  $10^{14}$ – $10^{15} \text{ cm}^{-3}$ . The commonly reported dielectric materials for the surface passivation of c-Si are  $SiO_x$ ,  $SiN_x$ ,  $Al_2O_3$ ,  $TiO_2$ , and the stacking of multiple dielectrics.

**$SiO_x$ :** The conventional way of oxide layer formation is thermal oxidation performed in an oxygen environment (temperature  $>1000^\circ\text{C}$  for at least 30 min), followed by cooling under an argon atmosphere

[95]. The passivation obtained by the oxide layer formation is further improved by forming gas (95%  $N_2$ , 5%  $H_2$ ) annealing ( $425^\circ\text{C}$  under forming gas for 25 min).

The *alneal* is improved annealing, whose main objective is to passivate the dangling bonds of the surface by the atomic hydrogen. During *alneal*, the sample is annealed (at  $400$ – $450^\circ\text{C}$  in the forming-gas atmosphere) after a thermally evaporating aluminum layer ( $0.1 \mu\text{m}$ – $1 \mu\text{m}$  thick) on thermally grown  $SiO_2$  [97]. Finally, the Al layer is etched using hot phosphoric acid ( $80^\circ\text{C}$ ) [97]. The reaction between the Al and the hydroxyl ions (or water molecules in the  $SiO_2$  layer) produces atomic hydrogen [98] that diffuses through the  $SiO_2$  layer and passivates the dangling bonds [99]. Hydroxyl ions are the prominent source of atomic hydrogen, as heating at  $100^\circ\text{C}$  removes the water molecules, whereas hydroxyl ions require vacuum heating at  $600^\circ\text{C}$  [100]. The presence of the Al on the oxide surface creates an electric field that causes injection of the atomic hydrogen into the oxide and improves the drift towards the Si– $SiO_2$  interface [101]. The driving field is due to the lower work function of the Al ( $4.2 \text{ eV}$ ) [102] compared to  $SiO_2$  ( $5.05 \text{ eV}$ ) [103,104]. The importance of the Al coating was verified by Collett et al. [101] by coating Au (with a work function of  $5.1 \text{ eV}$ ) and proved the inability of Au to introduce the ions into the oxide layer. The enhanced *alneal* reduces the overall processing time and charge introduction during the Al deposition, and hydrogenation takes place simultaneously [101]. Instead of only phosphoric acid, enhanced *alneal* uses a mixture of phosphoric acid (60%), acetic acid (3.5%), and nitric acid (2.5%).

**$SiN_x$ :** High effective lifetime of  $\sim 4.3 \text{ ms}$  is possible by forming  $SiN_y/SiN_x$  double layers on the rear side of the p-type Si [92]. Firstly,  $SiN_y$  passivating layer and, after a wet chemical RCA process,  $SiN_x$  capping layer is deposited by direct plasma and remote plasma PECVD, respectively. In both processes,  $NH_3$  content is varied in the  $SiH_4 + NH_3 + H_2$  gas mixture to control the refractive index of passivating and capping layers. Nguyen et al. used HF-methanol solution to wash the wafer prior  $SiN_x$  deposition by catalytic chemical vapor deposition (cat-CVD) to improve the passivation by increasing the wettability of the fine-textured n-type c-Si and reported the  $\tau_{eff}$  of  $\sim 7.8 \text{ ms}$  with SRV of  $\sim 0.6 \text{ cm s}^{-1}$  [91].

The thermally grown  $SiO_2$  layer was the commonly adapted technique for passivation in 1980–90 because of the ease of the deposition [105,106]. Low-temperature PECVD-coated  $SiN_x$  is used as one of the alternatives to thermal oxidation to avoid the high-temperature process.  $SiN_x$  outperforms the passivation properties of  $SiO_2$  and is also suitable for both normally doped and heavily doped c-Si [107–111]. The factors that popularize the PECVD-grown  $SiN_x$  are its antireflecting property and the excellent passivating property (comparable to thermally grown  $SiO_2$ ) even after high-temperature firing. The ‘*alneal*’ and ‘enhanced *alneal*’ were parallel development to the  $SiN_x$ , which again proved the

**Table 4**  
Summary of significant field-effect passivation materials.

Surface fields	Dielectric material	Substrate doping type, Resistivity ( $\Omega\text{cm}$ )	Wafer thickness ( $\mu\text{m}$ )	Fabrication process	Maximum $\tau_{eff}$ (ms)	SRV ( $\text{cm. s}^{-1}$ )	Ref.
BSF	$Al_2O_3$	p, 1–4	190	ALD	0.01	–	[89]
				ALD + front and rear $SiN_x$	0.175	–	
				ALD + front and rear $SiN_x$ + firing	0.895	–	
				ALD + front and rear $SiN_x$ + firing + Al removal	0.765	–	
	$SiO_x/SiN_x$ $SiO_x/SiN_x/SiO_xN_y$	p, 1	250	PECVD + annealing	0.15	$\sim 70$	[90]
					0.2	$\sim 60$	
FSF	$SiN_x$	n, 1–5	280	Catalytic-CVD	7.8	0.6	[91]
	$SiN_y/SiN_x$	p, 2–3	290	PECVD	$4.53^a$	3.2	[92]
	$TiO_2$	p, 10	140	ALD	$\sim 0.85$	$\sim 14$	[93]
		p, 1			$\sim 0.2$	$\sim 54$	
		n, 1000	500		$\sim 0.9$	–	
	$SiO_2$	p, 1.25	–	Thermal oxidation	–	$\sim 10$	[94]
			–		–	$\sim 24$	[95]
			–		–	–	
		n, 1	265		4	$\sim 2.6$	[96]

<sup>a</sup> Calculated considering infinite bulk lifetime.

effectiveness of the thermally grown  $\text{SiO}_2$  [101].

**$\text{SiO}_x/\text{SiN}_x/\text{SiO}_x\text{N}_y$ :**  $\text{SiO}_x\text{N}_y$  capping layer improves the defect passivation and prevents the interaction between the Al contact and  $\text{SiO}_x/\text{SiN}_x$  passivation on the rear side [90]. PECVD-coated  $\text{SiO}_x\text{N}_y$  layer improves the passivation by 30% compared to  $\text{SiO}_x/\text{SiN}_x$  passivation. The thickness of the layer must be more than 200 nm for better protection of the  $\text{SiO}_x/\text{SiN}_x$  stacking layer.

Bonilla et al. simulated the Si– $\text{SiO}_2$  interfaces using the TCAD software package for PERC cells and reported a 1% improvement in power conversion efficiency [112]. The interface trap density of the Si– $\text{SiO}_2$  and Si– $\text{SiN}_x$  are  $4 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$  and  $10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ , respectively [113,114]. Forming gas annealing of  $\text{SiO}_2$  and  $\text{SiO}_x/\text{SiN}_x$  improves the passivation quality by reducing the interface trap density to  $5 \times 10^{10} \text{ eV}^{-1} \text{ cm}^{-2}$  and  $10^{10} \text{ eV}^{-1} \text{ cm}^{-2}$ , respectively [112].

**$\text{Al}_2\text{O}_3$ :** Huang et al. [89] reported ALD of  $\text{Al}_2\text{O}_3$  (~10 nm) on the rear surface of the p-type c-Si at 200 °C in an  $\text{O}_3$  environment after HCl and HF cleaning. Then  $\text{SiN}_x$  layer (100 nm) is deposited on both the front and rear surface by PECVD and fired at ~760 °C.  $\text{SiN}_x$  layer acts as the ARC and capping layer on the front and rear surfaces, respectively. The dielectric layer (commonly  $\text{SiN}_x$ ) covers the major area of the front surface for effective passivation as well as ARC. The metalization typically covers 2–5% of the area to minimize the shadowing and recombination losses. However, in the case of the Al electrode, the cost-effective screen-printed Al electrode covers up to 20% of the rear side, and the  $\text{Al}_2\text{O}_3/\text{SiN}_x$  stack covers the rest area. Dingemans et al. investigated the interface quality of the Si– $\text{Al}_2\text{O}_3$  interface and reported the minimum interface trap density of  $0.4 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$  for  $\text{Al}_2\text{O}_3$  deposited by water-based ALD followed by annealing at 350 °C (SRV of  $4 \text{ cm s}^{-1}$ ), whereas maximum fixed charge density of  $5.6 \times 10^{12} \text{ cm}^{-2}$  for plasma-based ALD followed by annealing at 450 °C (SRV of  $2.8 \text{ cm s}^{-1}$ ) [115].

**$\text{SiO}_2/\text{Al}_2\text{O}_3$ :** Among the stacking of multiple dielectric layers for the passivation,  $\text{SiO}_2/\text{Al}_2\text{O}_3$  is extensively reported after  $\text{SiO}_2/\text{SiN}_x$  stacking. The  $\text{SiO}_2$  layer is grown by thermal oxidation, whereas either ALD or PECVD deposits the  $\text{Al}_2\text{O}_3$ . The significant investigation on the stacking of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  started after the report of additional ultrathin  $\text{SiO}_2$  layer formation on the c-Si surface during  $\text{Al}_2\text{O}_3$  by Stesmans et al. [116]. The forming gas annealing after the thermally grown  $\text{SiO}_2$  introduces hydrogen ions, and rapid thermal annealing ( $30^\circ \text{C} \cdot \text{min}^{-1}$ ) of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  in the  $\text{N}_2$  atmosphere passivates the Si surface [99]. Dingemans et al. showed the dependency of passivation properties on the annealing temperature, annealing duration, and the mass density of the  $\text{Al}_2\text{O}_3$  layer for ~190 nm thermally grown  $\text{SiO}_2$  and ~100 nm ALD-deposited  $\text{Al}_2\text{O}_3$  [99]. Hydrogen diffusion in molecular form is possible in low-density  $\text{Al}_2\text{O}_3$  films ( $2.9 \text{ g cm}^{-3}$ ) annealed at a temperature over 600 °C and in atomic form for a dense film ( $3.2 \text{ g cm}^{-3}$ ) annealed at a temperature between 300 °C and 600 °C. The effective SRV is drastically reduced by 60% for  $\text{SiO}_2/\text{Al}_2\text{O}_3$  stacking from  $\text{SiO}_2$  monolayer [117].

**$\text{TiO}_2$ :** Gad et al. [93] reported the deposition of  $\text{TiO}_2$  on the front surface of p-type c-Si by ALD at 150 °C and 200 °C by using tetrakis (dimethyl amido) titanium ( $\text{C}_8\text{H}_{24}\text{N}_4\text{Ti}$ ) as Ti precursor and water vapor as oxidant (plasma enhanced ALD). The alternative source of Ti for ALD is titanium isopropoxide and titanium tetrachloride (heat-assisted ALD), along with DI water as the source of oxygen [94,118].

The passivation mechanism at the Si– $\text{TiO}_2$  interface differs from other dielectric layers as the forming gas annealing cannot introduce atomic hydrogen into the ALD-deposited  $\text{TiO}_2$  layer due to the insufficient activation energy (0.37 eV) for hydrogen diffusion [119]. Further, Miyagawa et al. proved the same for post-ALD hydrogen plasma treatment [120]. The plausible passivation mechanism is forming Si–O–Ti bonds by dissociating the Si–H and Si–H<sub>2</sub> bonds [119,121].

**$\text{HfO}_2$ :** As a passivation layer for n-type c-Si, hafnium oxide ( $\text{HfO}_2$ ) is preferable due to its positive fixed charges and thermal stability [122]. ALD preferably deposits  $\text{HfO}_2$  either as a monolayer or along with a  $\text{SiN}_x$  capping layer [123]. The interface trap density of ALD-deposited  $\text{HfO}_2$

can be reduced to the order of  $10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$  and controlled to positive and negative fixed charge by deposition conditions and post-deposition treatments [123]. Zhang et al. [122] reported the deposition of the  $\text{HfO}_2$  by remote plasma ALD and simulation of PERC for rear surface  $\text{HfO}_2/\text{SiN}_x/\text{H}$  passivation and capping layer. The  $\tau_{\text{eff}}$  increases from 0.015 ms to 0.074 ms with post-deposition annealing temperature from 400 °C to 500 °C and a further increase in temperature (650 °C) reduces the  $\tau_{\text{eff}}$  to 0.019 ms. The interface quality investigation proved the reason for  $\tau_{\text{eff}}$  variation trend. The interface trap density reduces from  $50 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$  to  $5 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$  for annealing temperature of 500 °C (as a result  $\tau_{\text{eff}}$  improves), and further elevation of temperature increases the defect density (as a result  $\tau_{\text{eff}}$  degrades). The other plausible cause for the  $\tau_{\text{eff}}$  degradation is the rapid decrease in fixed charge density above 500 °C of post-deposition annealing temperature.

Although ALD and PECVD are effective and commonly used techniques for dielectric layer deposition, both ALD (plasma-assisted) and PECVD cause bulk defects in c-Si due to high-energy charged particles and UV rays in the plasma. The shielded hydrogen passivation (SHP) is an extended version of field-effect passivation to mitigate the harmful effect of plasma and introduce atomic hydrogen (using PECVD) to the bulk for defect passivation.

### 2.3. Field-effect passivation at different interfaces

The schematic of a typical commercial bifacial structure is given in Fig. 5 to explain the passivation at the four different interfaces [72] for field-effect passivation at interface I. excess dopant-diffused c-Si, II. non-diffused c-Si, III. the interface of metal contact and the electron selective region, and IV. the interface of metal contact and hole selective region.

#### 2.3.1. Interface I: excess dopant-diffused c-Si

Thermally grown  $\text{SiO}_2$  effectively passivates the  $\text{n}^+$ ; however, owing to several design constraints, including the high manufacturing cost and the sensitivity of the silicon bulk material to high temperatures, high-temperature oxidation is not ideal for industrial solar cells [72]. The alternative low-temperature passivation scheme, chemical-vapor-deposited  $\text{SiN}_x$ , outperforms  $\text{SiO}_2$  passivation and is preferable for industrial solar cells due to the tunable refractive index and ease of screen-printed contact formation [124]. As shown in Fig. 6(a), annealed- $\text{SiO}_2$  further decreases the  $J_0$  (compared to  $\text{SiN}_x$  passivation) due to atomic hydrogen introduction [101].

However, to avoid the Al deposition and chemical cleaning involved in the anneal, the  $\text{SiO}_2$  and  $\text{SiN}_x$  layer stacking provides the same effective passivation as the annealed  $\text{SiO}_2$  [125]. Considering the simplicity of

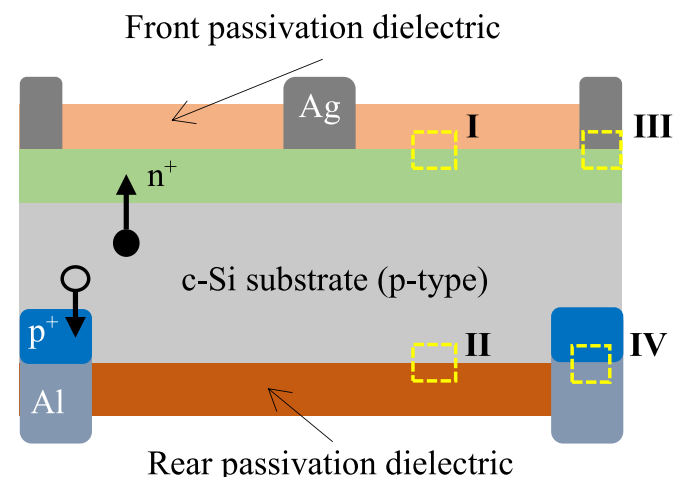


Fig. 5. Standard cell structure with possible interfaces for passivation.

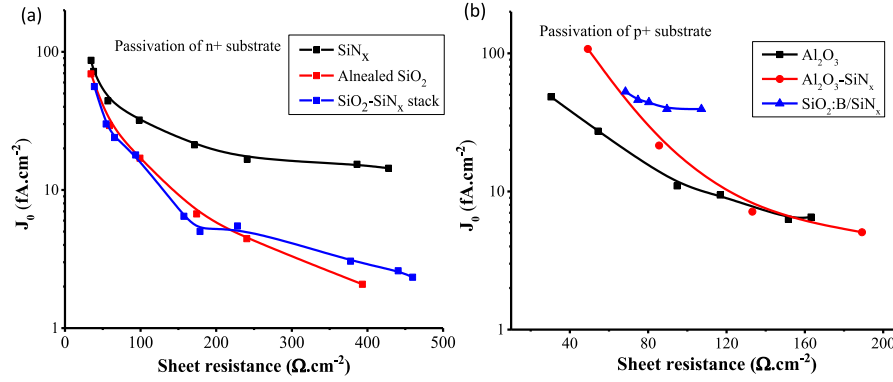


Fig. 6. Comparison of saturation current density of passivation with various materials for (a)  $n^+$  substrate [125], (b)  $p^+$  substrate [126–128].

$\text{SiO}_2$  deposition and the antireflecting property of  $\text{SiN}_x$ , stacking of the  $\text{SiO}_2$  and  $\text{SiN}_x$  ( $\text{SiO}_2/\text{SiN}_x$ ) is the preferable passivating method for the  $n^+$  emitter. The high hydrogen concentration in the PECVD- $\text{SiN}_x$  layer contributes to the improved passivation performance of the  $\text{SiO}_2/\text{SiN}_x$  stack. Fig. 6(a) shows the saturation current density of the  $n^+$  substrate passivated by different dielectric layers.

For boron-diffused  $p^+$  emitter, passivation through thermally grown  $\text{SiO}_2$  is unstable and causes degradation in the voltage output. The instability is due to the permeability of the  $\text{SiO}_2$  layer, which forms a moisture barrier and restricts passivation [129–131].  $\text{SiN}_x$  is detrimental for  $p^+$  emitter due to the high positive fixed charge density and asymmetric electron-hole capture cross-section ratio of the interface states [132]. The passivation level for the  $p^+$  substrate is lower than that of the  $n^+$  emitter with either  $\text{SiO}_2$  or  $\text{SiN}_x$  layer.

However, due to high negative fixed charge density,  $\text{Al}_2\text{O}_3$  deposition on the  $p^+$  layer results in excellent passivation [126] and stability (even under prolonged UV radiation) performance [113]. Richter et al. reported that the  $\text{Al}_2\text{O}_3/\text{SiN}_x$  stacking layer passivation outperforms pure  $\text{Al}_2\text{O}_3$ -based passivation for substrates with sheet resistance greater than  $130 \Omega \text{ cm}^2$  [127]. The modified PERC cell structure uses PECVD grown boron silicate glass (BSG) layer instead of the  $\text{Al}_2\text{O}_3/\text{SiN}_x$  stack (PERT). Though the BSG results in inferior passivation quality compared to  $\text{Al}_2\text{O}_3/\text{SiN}_x$  stacking (Fig. 6(b)), it acts as the source of boron for the  $p^+$  emitter and a passivation layer, thus making it favorable for industrial cell fabrication.

### 2.3.2. Interface II: passivation of normally-doped c-Si

The passivation of the rear p-type substrate is one of the technological advancements to achieve higher efficiency. As explained earlier,  $\text{SiN}_x$  passivation replaces the high-temperature thermal deposition of  $\text{SiO}_2$ . The high density of the fixed positive charge of the  $\text{SiN}_x$  creates an inversion layer on the c-Si, and the connection of the inversion layer to the base contact causes a considerable reduction in short-circuit current density (known as ‘parasitic shunting’) [133]. Annealing of the  $\text{SiN}_x$  passivated c-Si reduces  $\tau_{\text{eff}}$  for annealing duration longer than 200 min, unlike  $\text{SiO}_2$  passivation ( $\tau_{\text{eff}}$  saturates for prolonged annealing) [125]. Schmidt et al. prove that an intermediate thermally grown  $\text{SiO}_2$  layer between p-type c-Si and  $\text{SiN}_x$  prevents parasitic shunting [125]. The hydrogen diffusion occurs from PECVD-grown  $\text{SiN}_x$  to the c-Si and oxide interface to neutralize the dangling bonds, which improves the passivation of the  $\text{SiO}_2/\text{SiN}_x$  stack.

$\text{Al}_2\text{O}_3$  removes the parasitic shunting due to the fixed negative charges [134,135]; however, the firing ( $\sim 800^\circ\text{C}$ ) of industrial solar cells after applying the screen-printed metal paste (Al) degrades the passivation layer (ultrathin  $\text{Al}_2\text{O}_3$ ). The  $\text{SiN}_x$  capping layer improves the stability [136], protecting the  $\text{Al}_2\text{O}_3$  layer from Al contact [137]. From Fig. 7,  $\text{Al}_2\text{O}_3/\text{SiN}_x$  results in  $\tau_{\text{eff}}$  of almost two times that of  $\text{SiO}_2/\text{SiN}_x$  for the p-type substrate.

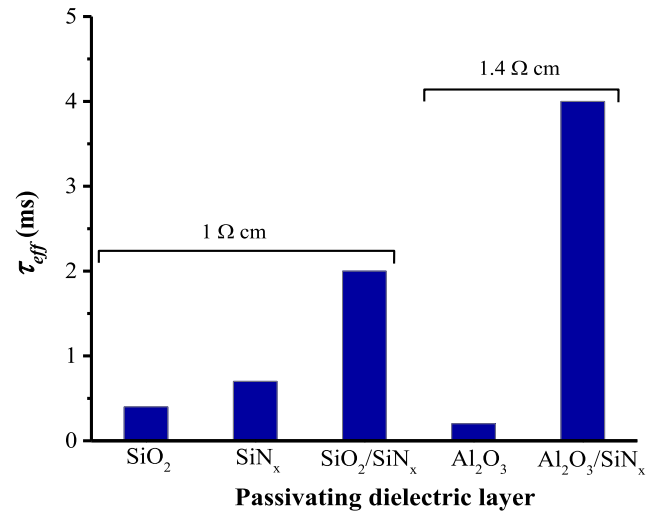


Fig. 7. comparison of  $\tau_{\text{eff}}$  of passivation of p-type substrate [125,137].

Table 5

Effectiveness of the dielectric layer with the substrate (based on  $\tau_{\text{eff}}$ ).

Dielectric layer	Doping type			
	p	n	$p^+$	$n^+$
$\text{SiO}_x$	✓	✓	×	✓✓
$\text{SiN}_x$	✓	✓✓	×	✓
$\text{Al}_2\text{O}_3$	✓✓	×	✓✓	×
$\text{TiO}_2$	✓✓	✓	✓	✓
$\text{HfO}_2$	✓	✓✓✓	✓	✓✓
$\text{SiO}_2/\text{SiN}_x$	✓✓	✓✓✓	✓	✓✓✓
$\text{SiO}_2/\text{SiN}_x/\text{SiO}_x\text{Ny}$	✓✓	✓✓	✓	×
$\text{Al}_2\text{O}_3/\text{SiN}_x$	✓✓✓	✓	✓✓✓	✓
$\text{SiO}_2/\text{Al}_2\text{O}_3/\text{SiN}_x$	✓	✓	✓✓✓	✓✓

× - ineffective, ✓ - less effective, ✓✓ - moderately effective, ✓✓✓ - highly effective.

Though a single dielectric layer passivates the c-Si surface, the  $\text{SiN}_x$  layer further improves the lifetime both for the  $\text{SiO}_2$  with a positive fixed charge and  $\text{Al}_2\text{O}_3$  with a negative fixed charge.  $\text{SiN}_x$  layer acts as the positive charge introducer ARC [124] for  $\text{SiO}_2$  and the protective capping layer for  $\text{Al}_2\text{O}_3$  [136]. The typical PERC structure (p-type substrate) with the  $n^+$  emitter on the front and either p or  $p^+$  on the rear surface requires  $\text{SiO}_2/\text{SiN}_x$  and  $\text{Al}_2\text{O}_3/\text{SiN}_x$  as the front and rear passivation layer [138]. The detailed analysis in Table 5 summarizes the compatibility and effectiveness of the dielectric layers with the substrate



type.

### 2.3.3. Interface III and IV: Carrier selective contact passivation

The metal-semiconductor interface suffers from strong recombination, restricting the enlargement of the metal contact area on the cell structure. A highly doped  $n^+$  (or  $p^+$ ) region underneath the metal contact allows electrons (or holes) from the c-Si reducing recombination velocity [139]. An electron-selective  $n^+$  emitter at the negative-metal contact permits electrons to flow from the c-Si wafer to the contact. The poor hole conductivity of the  $n^+$  emitter prevents holes from reaching the recombination sites reducing the saturation current density. As shown in Fig. 5, the photo-generated electron flows towards the screen-printed Ag electrode (front surface) through the electron-selective P-diffused  $n^+$  emitter. The hole travels to the screen-printed Al contact (rear surface) through Al-doped hole-selective  $p^+$  region. Increasing the doping level beneath the metal contact further enhances the passivation of the emitter (selective emitter) [140]. A hole-selective zone isolates the positive contact from the c-Si wafer and is locally produced by Al-doped back surface field during the firing. Holes can readily flow through the hole-selective zone inhibiting electrons and resulting in a low recombination current density [141]. Table 6 lists the reported carrier-selective layers for contact passivation with respective saturation current density ( $J_0$ ) and contact resistance ( $\rho_c$ ).

### 3. Shielded hydrogen passivation (SHP)

The defect elimination uses hydrogen incorporation into Si to achieve excellent passivation of surface and bulk defects [153,154]. Some of the Si PV structures, especially screen-printed cells, require high-temperature firing to release the hydrogen in dielectrics (such as  $\text{SiN}_x$  [155] and  $\text{Al}_2\text{O}_3$  [156]). The architectures based on Si heterostructures need hydrogen introduction at low temperatures to avoid heat-generated defects at the interfaces [157]. SHP introduces sufficient atomic hydrogen at low temperatures using modified PECVD with ammonia as the H source [158]. During SHP, a metallic shield, either of palladium (Pd) or Pd-alloys [159], electrically connected to the ground

to neutralize the energetic ions striking the sample [158], protects the wafer from the harmful effects of the hard UV photons [62]. Fig. 8(a) shows the schematic of the arrangement for the metal shield in the plasma chamber. An aluminum grid holds the shield, and the shield thickness depends on the chamber temperature and pressure.

According to Pick et al. [160], the Pd shield absorbs the atomic hydrogen after the dissociation of the  $\text{H}_2$ . The hydrogen atom diffuses through the shield and combines with a nearby H atom to form  $\text{H}_2$  on the opposite surface (Fig. 8(b)). Though the theory is well-referred, it fails to explain the formation of atomic hydrogen after diffusion through Pd. The Si surface receives the atomic hydrogen and gets passivated, so there may be different phenomena behind the dissociation of the  $\text{H}_2$  on Pd [159,161,162]. Lisowski et al. suggest the plasma source forms the hydrogenated palladium (Pd-H) film and post-high-temperature treatment decomposes to release atomic hydrogen [163]. Tyurin et al. raise the energy level of the H on the Pd surface by ion bombardment, and the diffused excited atomic hydrogen through Pd exhibits delays in further combination to form  $\text{H}_2$  [164].

The Pd shield should be oxide-free and sulfur-poisoned (HS-treated Pd) to improve the atomic hydrogen diffusion and molecular dissociation on the surface [165]. Palladium oxide (PdO) restricts the atomic hydrogen diffusion, and the hydrogen plasma treatment in PECVD removes the oxide layer from the Pd surface. Sulfur increases the probability of sticking and the dissociation of the  $\text{H}_2$  on the Pd surface. Although numerous hypotheses explain atomic hydrogen passivation, one plausible explanation is that Si-H bonds form at a quicker rate than  $\text{H}_2$  formation from H atoms. In addition to Pd, other metal shields such as Pt, Al, and Ni [39–42] cause hydrogen dissociation; however, no report claims any of these metals can introduce atomic hydrogen for passivation below 400 °C and as diffusive as Pd.

Bourret-Sicotte et al. performed SHP on 200  $\mu\text{m}$  thick, 1  $\Omega\text{cm}$ , n-type float zone Si samples with a 100 nm thermally grown  $\text{SiO}_2$  for 45 min at 380 °C using sulfur-poisoned Pd shield and reported the lifetime of the passivation enhanced from 12 to 1050  $\mu\text{s}$  [159]. Corona charging further enhanced the lifetime to 6.3 ms (equivalent SRV of 0.17  $\text{cm s}^{-1}$ ). The performance of the Pd-Ag alloy (3:1 and 10  $\mu\text{m}$  thick) sheet is comparable to that of Pd, and the alloy restricts the phase change of Pd in the hydrogen environment that creates pin holes [159]. Hamer et al. show the lifetime improvement with the poisoning of Pd 4.5 ms post-corona charging using a pure Pd shield [158]. The effectiveness of SHP is associated with the application of corona to the Si- $\text{SiO}_2$  interface. With only SHP, the measured lifetime of a p-type Si is  $\sim 0.5$  ms, almost half of the lifetime obtained by corona charging ( $\sim 1$  ms), and the same improves to 2.2 ms with both SHP and corona charging [62]. Table 7 lists the reported works on the SHP with the obtained maximum effective lifetime.

Though SHP is an effective passivation method, hydrogen introduction to n-type FZ Si at  $\sim 350$  °C without any dielectric layer generates hydrogen-related defects (active recombination complexes) that degrade the effective lifetime [162,166]. On the other hand, SHP does not produce defects in the case of p-type FZ Si without an additional dielectric layer [162]. Different charge states of atomic hydrogen contribute to different behavior in n-type and p-type Si. Atomic hydrogen in n-type Si exists in  $\text{H}^0$  and  $\text{H}^-$  states, whereas in p-type Si, it exists only in the  $\text{H}^+$  state [167,168]. So, the existence of the multiple charge states of atomic hydrogen in n-type Si increases the probability of defects.

### 4. Chemical passivation

The effect of heat treatment on the lifetime of the wafer can be minimized using the chemical method at room temperature. The generalized band bending concept explains the mechanism of chemical passivation, as shown in Fig. 9. The oxidation and reduction potential ( $E_{\text{ox}}$  and  $E_{\text{red}}$ ) of the electrolyte must be higher than the conduction ( $E_{\text{cs}}$ ) and valence band ( $E_{\text{vs}}$ ) of the Si substrate for effective passivation.

**Table 6**  
Carrier selective emitter for passivation of metal-semiconductor interface.

Type	Passivation layer	Deposition technique	$J_0$ (fA. $\text{cm}^{-2}$ )	$\rho_c$ ( $\Omega\text{cm}^2$ )	Ref.
Electron-selective contact passivation	$\text{MgO}_x$	Sputtering	$\sim 950$	0.018	[142]
	P-diffused $n^+$	Screen-printing	109	0.26	[143]
	$\text{SiO}_x/\text{TiO}_2$	TO/ALD	50	0.026	[144]
	$\text{SiO}_x/\text{poly-Si}$ ( $n^+$ )	TO/LPCVD	5	0.016	[145]
			2.7	0.0013	[146]
			30	0.001	[147]
	$\text{SiO}_x/\text{SiN}_x/\text{poly-Si}$ ( $n^+$ )	TO/PECVD/PECVD	3.7	0.1	
Hole-selective contact passivation	a-Si:H(i)/a-Si:H (n)	PECVD	2	0.1	[148]
	$\text{MoO}_x$ on n	TE	$\sim 300$	0.03	[149]
	Al-doped $p^+$	Screen-printing	$\sim 550$	0.005	[150]
	$\text{MoO}_x$ on p+	TE	$\sim 200$	0.0002	[149]
	$\text{MoO}_x$ on p		$\sim 200$	0.001	
	$\text{SiO}_x/\text{poly-Si}$ ( $p^+$ )	TO/PECVD	$\sim 35$	0.01	
	$\text{SiO}_x/\text{Si:C}$ ( $p^+$ )	CO/PECVD	16	0.008	[147]
			$\sim 12$	0.017	[151]
	a-Si:H(i)/ $\text{MoO}_x$	PECVD/TE	10	0.4	[152]
	a-Si:H (i)/a-Si:H (p)	PECVD	2	0.4	[148]

a-Si – amorphous silicon, a-Si:H (i) – hydrogenated intrinsic amorphous silicon, poly-Si – polycrystalline silicon, TO – thermal oxidation, TE – thermal evaporation, CO – chemical oxidation.

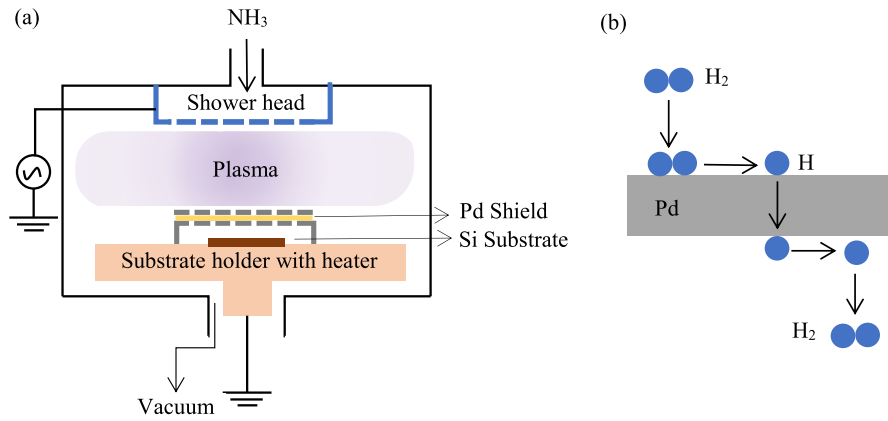


Fig. 8. (a) Set up for the metal shield in the plasma chamber, (b) possible mechanism of H diffusion on Pd.

Table 7

Summary SHP passivation (Substrate resistivity of 1  $\Omega$  cm and SiO<sub>2</sub> dielectric layer).

Substrate doping type	SiO <sub>2</sub> thickness (nm)	SHP details	Maximum $\tau_{eff}$ (ms)	Ref.
n-type	100	Pd (10 $\mu$ m)	0.012	[159]
		Sulfur poisoned Pd	1.05	
		Pd with corona charging	4.5	
		Sulfur poisoned Pd with corona charging	6.3	
p-type	10	Only corona charging	1	[62]
		Sulfur poisoned Pd	0.5	
		Sulfur poisoned Pd with corona charging	2.2	

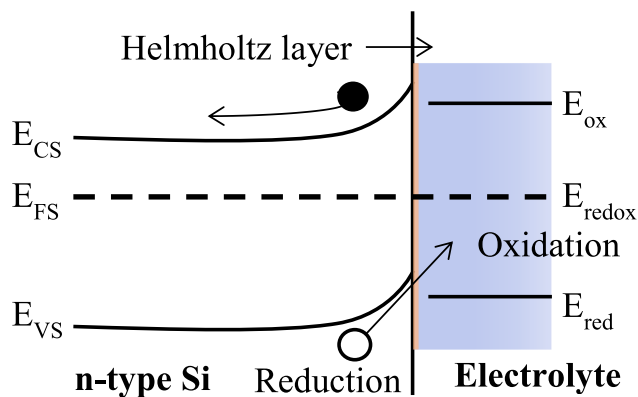


Fig. 9. The generalized band-bending concept for chemical passivation.

Electrons from the valence band of the Si cross the semiconductor-electrolyte interface to take part in the oxidation of the electrolyte, leading to the upward bending of the Si band structure. Accumulating the reciprocal charge at the interface on the electrolyte side creates the Helmholtz layer that restricts the electrons from jumping to the conduction band (during photon absorption) [43]. Chemical passivation uses electrolytes such as hydrofluoric acid (HF), (halogen + alcohol), and (benzyl + alcohol) solutions [169]. The lifetime measurement of chemical passivation is conducted by immersing the cleaned wafer in an electrolyte solution in an airtight plastic transparent container.

HF passivation is popular among all the solution-based chemical methods, where HF etches the unwanted oxide formation from the surface to passivate the dangling bonds with Si-F bonds. Due to the high electronegativity of fluorine atoms, surface Si atoms are etched out as SiF<sub>4</sub> forming a nonpolar [170] hydrogen-terminated (Si-H) surface [171–173] and leading to surface passivation (Fig. 10(a)). Michalak et al. reported the passivation of Si {111} surface with NH<sub>4</sub>F-HF solution (buffered HF) with a higher  $\tau_{eff}$  than HF passivation [174]. Grant et al. show the passivation with HF (2%): HCl (2%) is  $\sim 5$  times more effective than HF (50%), and the former improves passivation with a longer duration of treatment, whereas the latter worsens [175]. The same study also reports that bis(trifluoromethane) sulfonimide (TFSI)-pentane superacid treatment after HF (2%) + HCl (2%) immersion enhances the passivation by  $\sim 6$  times (Table 8).

Halogen-based passivation requires different solvent environments, such as ethanol, methanol, and benzene [66] and can be explained by either the halogen termination or ethoxylation of the surface. Firstly, iodine or bromine atoms replace hydrogen from the hydrogenated c-Si surface to form Si-I or Si-Br bonds due to the electro-negativity of halogen atoms [191]. Secondly, the electrons from the surface of the substrate dissociate the I<sub>2</sub> to form I<sup>-</sup>, which converts the H-terminated surface (produced by HF dip) to ethoxy-termination (Fig. 10(b)) [190]. Iodine acts as an oxidant by acquiring an electron (I<sup>-</sup>) from the Si-H surface, forming [Si-H]<sup>+</sup> ions. The ethoxy nucleophile combines with the Si atom via a coordinate bond, and protons released from the alcohol and Si surface neutralize the iodine atoms. According to Batra et al., iodine + ethanol (I + E) results in better passivation than bromine + ethanol (Br + E) [189]. Iodine produces higher saturation of dangling bonds than bromine as the dissociation of iodine (in alcohol) is higher due to lower bond strength (151 kJ mol<sup>-1</sup> as compared to 193 kJ mol<sup>-1</sup> of Br-Br).

Quinhydrone (QHY) is the equimolar charge transfer complex of *p*-benzoquinone (BQ) and hydroquinone (HQ). Two phenomena illustrate the mechanism of benzyl passivation. Firstly, BQ gains proton from methanol to form semiquinone (SQ), and due to the change in the ratio of HQ and BQ, HQ acts as a reducing agent for BQ. Thus, SQ is created both by the oxidation of HQ and the reduction of BQ. As a result, methanol retains the H<sup>+</sup> ions, and SQ formation and passivation occur in the methanol environment [195].

Secondly, BQ grabs the H atom directly from the Si-H surface to become semiquinone and reacts with the Si cation to form the Si-SQ surface. On the other hand, SQ gets H<sup>+</sup> from methanol and forms methoxide (CH<sub>3</sub>O<sup>-</sup>), combining with Si cation to become methoxy-Si [177]. Excessive SQ species lead to competition for adsorption between the active SQ and CH<sub>3</sub>O<sup>-</sup> species on the Si surface (Fig. 10(c)); however, the SQ species are grafted to the Si-H surface to maximize the coverage before the CH<sub>3</sub>O<sup>-</sup> species. Then the CH<sub>3</sub>O<sup>-</sup> replaces the

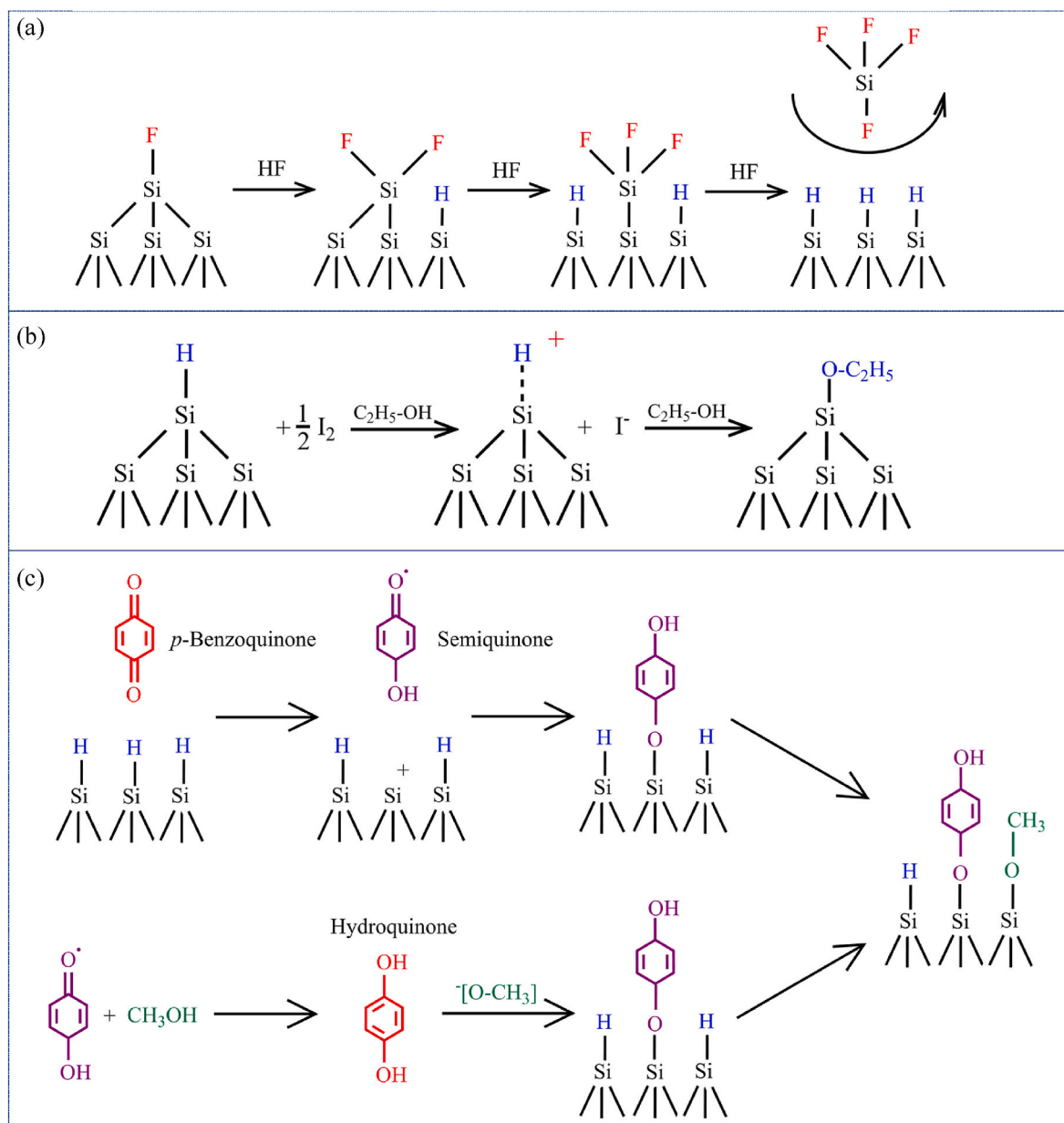


Fig. 10. Mechanism of passivations in (a) HF [176], (b) halogen + alcohol solution, and (c) benzyl + alcohol solution [177].

grafted SQ on the Si surface due to lower adsorption energies and may cause in weakening of molecular field-effect passivation [194]. Effective passivation is due to the synergistic effect of Si dangling bond saturation and the field-effect of the interface dipoles. The latter is due to the more electronegative oxygen atoms bonded to surface Si atoms [196].

For the (benzyl + methanol) or (iodine + alcohol)-based passivation, the Si wafer is cleaned by either piranha solution or RCA cleaning procedure to remove organic residues from the surface of the wafer [10]. The surface must be H-terminated by dipping the wafer into the HF solution. Finally, the H-terminated Si surface is immersed in passivating chemical solutions such as I + M or QHY + M. Before every stage, deionized (DI) water wash and N<sub>2</sub> gun drying may be followed [169, 196].

The degree of passivation depends on the electrolyte (chemical and solvent), substrate properties such as doping type, and resistivity. Fig. 11 (a), (b), and (c) represent the variation of  $\tau_{eff}$  of passivated substrates of different resistivities for acid, halogen, and benzyl passivation.  $\tau_{eff}$  is higher for the substrates with higher resistivity, and the trend is similar

for all the chemicals. The increase in resistivity restricts the flow of the charge carrier to the surface, reducing the SRV. The concept is valid for p-type and n-type substrates with similar variation trends irrespective of the chemical used for passivation. Fig. 11(d) shows the comparison of passivation of the p-type and n-type substrate (of the same resistivity) with certain chemicals at a constant concentration.  $\tau_{eff}$  of the n-type substrate is higher than that of the p-type substrate for all the passivating chemicals.

Lifetime is measured when the substrate is submerged in the chemical, and removal of the substrate from the chemical reduces the stability of the passivation [198]. Fig. 12(a) shows the maximum  $\tau_{eff}$  measured after removing the substrates from QHY + M (0.01 M) solution at different time intervals. For both p-type (2  $\Omega$  cm) and n-type (100  $\Omega$  cm) substrates, with increased environmental exposure,  $\tau_{eff}$  decreases due to oxidation and removal of the passivating benzyl group [198]. The QHY + alcohol passivation is more stable than (I + E) or (I + M) passivation [197, 201] and the mechanism of the passivation degradation is depicted in Fig. 12(b).

**Table 8**

List of the solution-based chemicals used for passivation of the c-Si.

Type	Chemical (concentration)	Si doping type, Resistivity ( $\Omega\text{cm}$ )	Wafer thickness ( $\mu\text{m}$ )	Maximum $\tau_{\text{eff}}$ (ms)	SRV ( $\text{cm.s}^{-1}$ )	Ref.
<b>Acid</b>	HF (5%)	n, 100	475	0.125	184	[65]
	HF (20%)	n, 1	400	2	2.7	[178]
		n, 5	700	10	2.8	
		p, 1000	500	50	0.7	
		p, 1	400	0.2	10	[179]
	HF (40%)	p, 0.8	300	0.8	4.8	[178]
	HF (48%)	p <sup>c</sup> , 35	525	2.9	2.8 <sup>b</sup>	[180]
		p, 2	300	1.9	1.9 <sup>b</sup>	
		n, 4000-6000	500	2.2	11	[174]
		p, 22	2700	2.5	1	[181]
		p, 150	250	40	0.25	[182]
	HF (50%)	n, 5	110	0.18	194 <sup>b</sup>	[175]
	HF (50%) + SA <sup>a</sup>			1.5	23.3 <sup>b</sup>	
	HF (2%) + HCl (2%)			0.85	41.2 <sup>b</sup>	
	HF (2%) + HCl (2%) + SA <sup>a</sup>			5.5	6.4 <sup>b</sup>	
<b>Halogen</b>	I + E (0.03 M)	n <sup>c</sup> , 6.7	1190	1.82	5.5	[183]
	I + E (0.08 M)	n, 1-10	500	0.9	28	[184]
		n, 1.7-13	180	0.97	5.2	[185]
		n, 100	430	2.72	7.9	[186]
		p, 100	279	1.7	8.2	
		p, 200	220	6	1.8	[187]
		p, 5	650	0.177	192	[188]
		p, 5	650	0.78	–	[189]
	I + E (0.1 M)	n, 8-12	350	10	–	[190]
		n (111), 30	350	20	–	
		n, 5	640	8	–	[191]
		n, 3- 5	1490	46	6.2	
		n (111), 60	360	17	–	
		p, 12.8	–	0.25	–	[192]
	I + M (0.08 M)	p, 5	650	0.171	194	[188]
	I + M (0.09 M)	p, 22	2700	3.25	0.75	[181]
		n, 100	475	0.65	35	[169]
		n, 3	280	0.23	60	
		n, 1	170	0.09	89	
		n, 100	475	0.89	25	[65]
	Br + E (0.06 M)	p, 5	650	0.121	282	[188]
	Br + E (0.08 M)			0.78	–	[189]
	Br + M (0.06 M)			0.15	227	[188]
	Br + M (0.08 M)	n, 2.6-3.4	200	–	20	[181]
<b>Benzyl</b>	BQ + M (0.1 M)	n, 25	500	3.25	8 <sup>b</sup>	[193]
		p	525	1.9	14 <sup>b</sup>	
		n	280	4.5	1.6	[194]
	BQ + M (10 mM)	n, 100	450	3.39	6.64 <sup>b</sup>	[195]
	HQ + M (10 mM)	n, 100	450	0.09	250 <sup>b</sup>	[195]
	QHY + M (1 mM)	n, 0.1	300	0.47	31.9 <sup>b</sup>	[196]
	QHY + M (10 mM)	n, 100	450	2.81	8.0 <sup>b</sup>	[195]
		n <sup>c</sup> , 1	170	0.67	12.6	[169]
		n <sup>c</sup> , 3	280	1.36	10.2	
		p, 5	650	0.7	–	[197]
		p, 150	380	4.5	–	
		n, 100	460	3.3	–	[198]
		p, 2	280	1.1	–	
		n, 100	460	3.3	7	[199]
		n, 3	280	1.36	–	
		n, 1	170	0.67	–	
		n, 100	475	2.2	10.4	[65]
	QHY + M (70 mM)	p, 200	220	8.5	–	[187]
		n, 2	–	0.18	–	[177]
	QHY + E (10 mM)	p, 5	650	0.6	–	[197]
		p, 150	400	4.1	4.6	[200]

<sup>a</sup> Bis(trifluoromethane)sulfonimide (TFSI)-pentane superacid treatment.<sup>b</sup> Calculated considering infinite bulk lifetime.<sup>c</sup> Czochralski (CZ) wafer and rest are Float-zone (FZ) wafers.

## 5. Laser passivation

One of the approaches to minimize the solar cell fabrication cost is the use of upgraded metallurgical grade (UMG) wafers instead of semiconductor grade. However, the cell efficiency decreases due to the higher bulk defects such as B–O complex formation and metallic impurities at the grain boundaries. Advanced hydrogen passivation reduces the recombination due to the bulk defects using laser technology,

making the UMG wafers suitable for efficient solar cell production. Though a laser is used for the dielectric layer ablation and grooving of the semiconductor surface for the contact formation, passivation of the bulk defects is possible with a laser source by changing the charge states of atomic hydrogen with the laser parameters [202]. The hydrogen charge states play an essential role in the passivation of defects, such as the neutralization of dopant atoms ( $\text{B}^-$  by  $\text{H}^+$  and  $\text{P}^+$  by  $\text{H}^-$ ), the passivation of impurities ( $\text{Fe}^+$  by  $\text{H}^-$ ), and the permanent deactivation

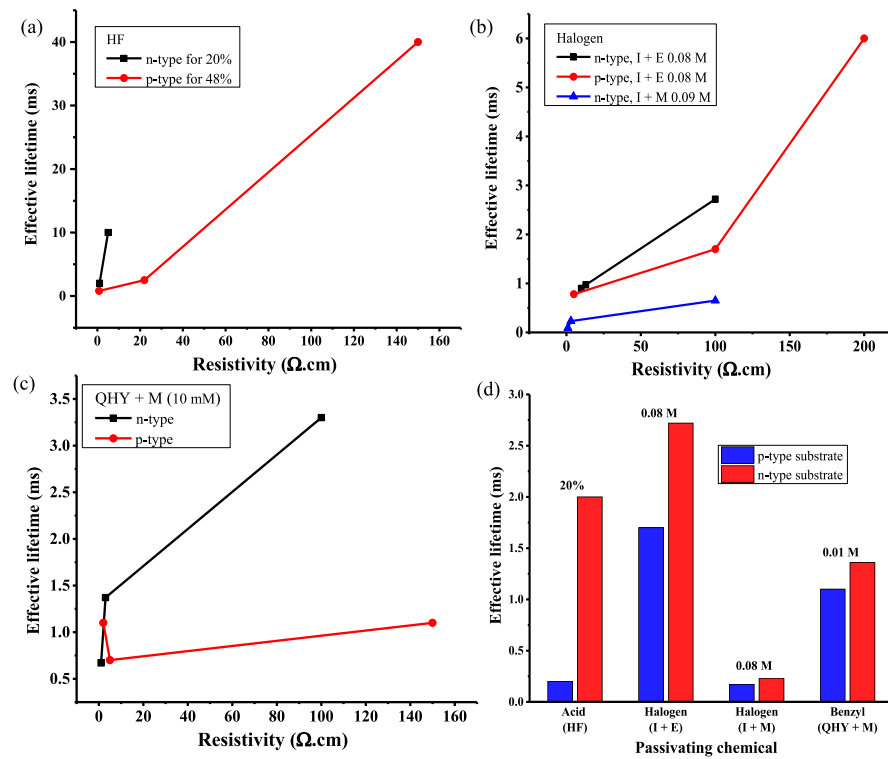


Fig. 11. Dependency of  $\tau_{eff}$  on the resistivity of the substrate passivated by (a) HF acid, (b) halogen- (I + E) & (I + M), (c) benzyl- (QHY + M) at constant concentrations; (d) Comparison of passivation of p-type and n-type substrate with different chemicals.

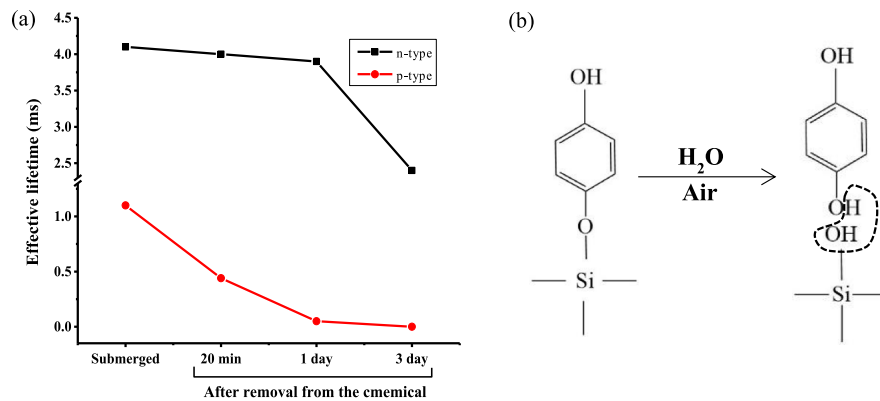


Fig. 12. (a) Variation of effective lifetime after removing the sample from the QHY + M (0.01 M) solution, representing the temporary passivation; (b) mechanism of degradation of passivation by QHY + M [198].

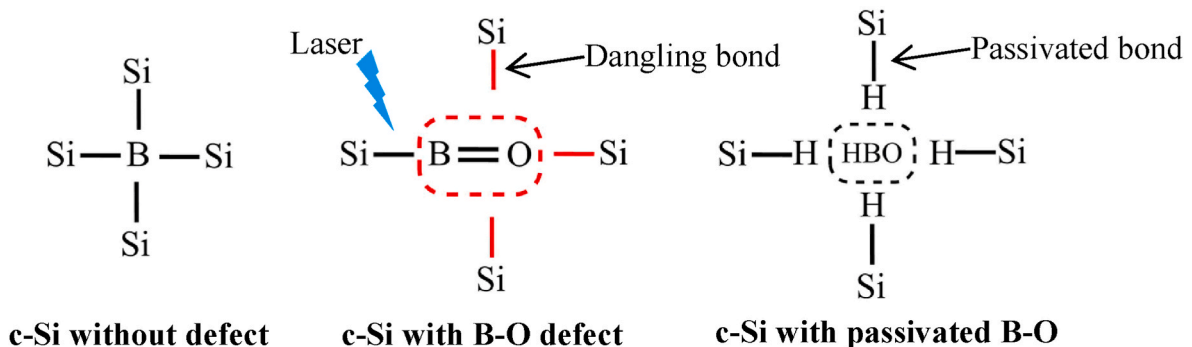


Fig. 13. Mechanism of laser hydrogen passivation of B-O defect.



of B–O complex (by  $H^+$  or  $H^0$ ).

The position of the Fermi level to the hydrogen donor and acceptor levels dominates the relative hydrogen concentration of a given charge state [203,204]. A hydrogen donor level is at 0.16 eV below the conduction band for the donor level, and a hydrogen acceptor level is at 0.07 eV below the middle band gap [204]. In p-type Si, the ionized boron atoms ( $B^-$ ) attract the  $H^+$  due to the Coulombic attraction at moderate temperatures [205]. Similarly, ionized phosphorus atoms ( $P^+$ ) retract the diffused  $H^-$  in n-type Si [206]. In contrast,  $H^0$  is unaffected by fixed charges, such as ionized dopant atoms and charged defects within the Si.

The bulk defects create dangling bonds that act as the recombination centers leading to a reduction in  $V_{oc}$ . Trapped oxygen in the B-doped substrate creates a B–O complex with Si leaving three Si-dangling bonds aside, as depicted in Fig. 13 (a possible passivation mechanism). Although the bond dissociation energy of Si–B ( $= 289 \text{ kJ mol}^{-1}$ ) is weaker as compared to the Si–H ( $= 298.5 \text{ kJ mol}^{-1}$ ), only the atomic hydrogen introduction to the defect site does not neutralize all the dangling bonds [172,207]. Laser illumination breaks the Si–B bond and alters the charge state of the atomic hydrogen to combine with the Si-dangling bonds and the B–O complex to form either borane (HBO) or hydroxyl boron (HOB). During subsequent high-temperature processes (the wafer goes through until the solar cell fabrication), the probability of breaking the Si–H bond is higher than that of the B–H bond ( $= 330 \text{ kJ mol}^{-1}$ ), leading to dehydrogenation and recreation of the recombination center [208]. Hence, trapping enough atomic hydrogen is extremely important during hydrogenation.

The temperature and the illumination control the minority charge carrier, and the injection of the minority carrier controls the charge state of the hydrogen, enhancing the passivation [209,210]. Laser, being the source of heat and illumination and having comprehensive control over various parameters, is used for hydrogen passivation of a localized area of Si. Wang et al. showed that the laser hydrogenation temperature affects the passivation more than the illumination intensity (laser power) [211]. After a short period of 1 min, the influence of the illumination intensity saturates, whereas the process temperature affects the hydrogenation. With an increase in temperature, the diffusivity of the atomic hydrogen improves; however, the effectiveness degrades at higher temperatures due to the loose stability of the atomic hydrogen during the cooling from elevated temperatures.

The laser wavelength selection is another crucial factor for successful laser-induced hydrogenation. According to Hamer et al., irradiation with a long-wavelength laser is appropriate for hydrogenation [212]. Longer wavelengths allow homogenous carrier production over the bulk, a reduction in low energy, and the ability to manipulate the charge state of atomic hydrogen with greater temperature control. Several aspects involved in laser-assisted hydrogen passivation are i. atomic hydrogen introduction to the bulk of the substrate, ii. diffusion of the atomic hydrogen throughout the substrate, iii. activation of the appropriate charge state of the atomic hydrogen at the recombination sites, and iv. trapping of the hydrogen in the substrate to avoid the release during subsequent processes.

High temperature shifts the Fermi level towards the middle of the band gap in p-type Si, achieving a higher ratio of minority charge states of atomic hydrogen and increasing the hydrogen release rate from the

PECVD-grown  $SiN_x$  layer as the source of atomic hydrogen [213,214]. Forming gas and  $NH_3$  are the sources of hydrogen for the thermally grown  $SiO_2$  layer (introduced during annealing) and PECVD-grown  $SiN_x$  layer. High-temperature passivation also leads to rapid dissociation of hydrogen-defect complexes, which limits the effectiveness of the process [215]. On the other hand, illumination significantly increases the relative concentrations of the minority charge states of atomic hydrogen [210]. It helps in reducing defect-reactivation during the cooling phase of high-temperature hydrogen passivation [168,209]. Si surface passivated by PECVD- $SiN_x$  containing hydrogen shows degradation and regeneration with illumination, whereas passivation by low-pressure chemical vapor deposition (LPCVD)  $SiN_x$  without hydrogen shows only degradation and no regeneration of minority carrier [216].

Hallam et al. compared the conventional industrial hydrogen passivation with the laser passivation of p-type UMG Si and showed the improvement of a bulk lifetime from 8 to 550  $\mu s$  due to the minimization of the B–O defect sites in the bulk of the substrate (Table 9) [209]. The hydrogen passivation of the B–O defect is a reversible process, i.e., the B–O defect may regenerate during the subsequent high-temperature substrate processing of cell manufacturing due to the release of the atomic hydrogen [216]. Hence a sufficient amount of atomic hydrogen should be introduced into the bulk to avoid defect-regeneration during the high-temperature processes. The introduction of laser passivation into the fabrication of the PERL solar cell based on commercial grade B-doped CZ wafer results in  $V_{oc}$  of 681 mV and a bulk lifetime of 500  $\mu s$  [216]. Although laser hydrogen passivation increases the lifetime of B-doped substrates, no substantial lifetime improvement is reported in Ga-doped substrates with the  $SiN_x$  dielectric layer. Rather,  $Ga_2O_3$  dielectric layer assists the laser passivation for Ga–Fe defects [64]; however, it lags behind the  $SiN_x$  in terms of antireflecting coating.

## 6. Passivation strategies in various solar cells

The efficiency improvement is the driving factor for the evolution of various solar cell architectures, from Si-based single junction Al-BSF to multi-junction TOPCon cells. For Si-based cells, both surface and bulk passivation are the critical aspects considering substrate compatibility, photon absorption [217], contact interface [218,219], and fabrication complexities [137]. Among passivation strategies, field-effect passivation and chemical passivation are the acceptable methods for surface passivation [43,72,220] however, dielectric-based field-effect passivation is the established technique and still evolving [217,221]. Though solution-based chemical passivation results in a comparative lifetime to field-effect passivation, the use of chemical passivation in solar cell fabrication is rarely reported due to its instability [43]. For investigating impurity activity in multi-crystalline Si for solar cells, liquid-based chemical passivation, especially of the halogen- or benzyl-based solutions, is useful [222–224]. SHP and laser passivation are the improvements over dielectric-based field-effect passivation for bulk defects [63, 209]. Table 1 lists the advancement of the solar cell from the passivation point of view, and the current section summarizes the passivation strategies used in various solar cells in recent years.

**Table 9**  
List of the defects and parameters of laser passivation.

Defect passivation	Laser wavelength (nm)	Laser processing speed (m.s <sup>-1</sup> )	Dielectric layer	Si wafer, doping, Resistivity ( $\Omega$ .cm)	Max $\tau_{eff}$ (ms)	Ref.
B–O	532	0.5	$SiN_x$	B-CZ, p, 2	1.4	[209]
	–	–	$SiN_x$	UMG-CZ, p, 2	0.55	
Ga–Fe	355	~0.33	$SiN_x$ $Ga_2O_3$	p; 1.6	0.15 ~3	[211] [64]

UMG-upgraded metallurgical grade, B-CZ- Boron doped Czochralski.

## 6.1. PERC

PERC cell is the successor of the Al-BSF cell and is passivated on both the front and rear surface by a dielectric layer, unlike the heavily-doped rear surface of the Al-BSF cell. The efficiency of a standard Al-BSF solar cell is constrained by poor light absorption and rear-side recombination losses [225]. The direct contact of metal-Si recombination loss is caused by a significant number of metal-induced surface state densities [226]. PERC uses a dielectric layer + ARC on the front side, whereas a dielectric layer + capping layer on the rear side, as depicted in Fig. 1 (a). The dielectric layer on the front and rear side may be  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{HfO}_2$  [227] and the substrate compatibility is listed in Table 5.  $\text{SiN}_x$  is a versatile dielectric which can act as an independent dielectric layer, ARC, and rear capping layer [228–230]. The dielectric layer on the front surface is optional for  $\text{SiN}_x$  ARC; however, the dielectric layer + ARC combination surpasses in terms of performance [89,228].

Though  $\text{SiO}_2/\text{SiN}_x\text{:H}$  is the convenient passivation stacking layer for both the front and the rear surface of the PERC cell, the combination of the CZ substrate and  $\text{SiO}_2/\text{SiN}_x\text{:H}$  passivation is prone to surface-related defects caused by illumination [231]; whereas the PERC cells with  $\text{Al}_2\text{O}_3/\text{SiN}_x\text{:H}$  is safe. Similar passivation schemes are also applicable to PERL and PERT cells; however,  $\text{Al}_2\text{O}_3/\text{SiN}_x\text{:H}$  is preferred for rear surface passivation [232,233]. Though dielectric-based field-effect passivation is the only strategy used in PERC cells, laser passivation is also used for localized doping for the selective emitter and rear contacts for hydrogen defect passivation to reduce the device's dark saturation current [233,234].

## 6.2. IBC

The front surface of the IBC cell is fully coated with the dielectric layer + ARC, and the rear surface possesses all the contact terminals, as shown in Fig. 1 (c). As the front surface is fully utilized for photon absorption, ARC plays a significant role in efficiency improvement; however, a monolayer of ARC ( $\text{SiN}_x$ ) or  $\text{Al}_2\text{O}_3$  dielectric layer is inefficient (Table 5). The preferable passivation scheme for the front surface of the n-type substrate-based IBC cell is  $\text{SiO}_2/\text{SiN}_x$  followed by  $\text{SiO}_2/\text{Al}_2\text{O}_3/\text{SiN}_x$  [235,236].

Yang et al. reported ion-implanted polysilicon as a carrier selective passivated contact on the rear side for both BSF and emitter, resulting in a well-passivated gap to minimize the shunting loss [237]. An advanced ARC was obtained by layering an ultrathin  $\text{SiO}_2$  layer above traditional micro-textured pyramids and passivated with a-Si/ $\text{SiN}_x$ .  $\text{SiO}_2/\text{SiN}_x/\text{SiO}_2$  acts as excellent passivation and ARC on the front (random pyramidal textured) and the rear surfaces to achieve 25% cell efficiency [238]. Apart from field-effect passivation, IBC cells use a thin polymer film (polystyrenesulfonate-a water-based solution spin-coated and dried) as an ARC on the front surface for surface passivation [239]. For a 150 nm thick polymer layer, a minority carrier lifetime of 2.5 ms was achieved for an n-type (280  $\mu\text{m}$  thick), which showed a new technology roadmap for organic solution-based chemical passivation. Though no literature reports the hydrogen passivation via laser in IBC cells, contact passivation is possible by laser doping on  $n^+$  and  $p^+$  regions to optimize the contact resistance for  $\text{SiO}_2/\text{a-Si:H}$  passivation layer [240,241].

## 6.3. SHJ

Silicon heterojunction (SHJ) cell is one of the cell architectures with an efficiency of >25% and an open circuit voltage of >0.7 V [3]. SHJ cell uses hydrogenated intrinsic amorphous Si as the passivating layer, separating the amorphous emitter layer from crystalline substrate and indium tin oxide (ITO)/ $\text{SiO}_2$  as the front ARC and passivating layer [242]. Parasitic absorption at the front ITO and amorphous emitter interface is the main limitation for the SHJ with both side contacts, which can be solved by the IBC structure [243]. Ding et al. reported the passivation effect of intrinsic ZnO and Al-doped ZnO, which can replace

the phosphorous-doped a-Si on an n-type c-Si substrate [244]. Solution-based ZnO and Al-doped ZnO were spin-coated and annealed to result in 17.13% and 18.46% cell efficiency, respectively, whereas the primary purpose of the layers is the electron-selective transport layer. Instead of  $\text{SiO}_2$  and hydrogenated a-Si, as chemical passivation, spin-coated carbon nanotube passivates n-type substrate and results in 21.4% efficiency [245].

## 6.4. TOPCon

TOPCon cell architecture possesses two passivation schemes-surface passivation by conventional dielectric-based field-effect passivation and rear surface contact passivation by tunnel-oxide (Fig. 1 (d)). The front surface uses  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  as the dielectric layer and ITO or  $\text{SiN}_x$  as the ARC [29]. Both-sided TOPCon solar cell uses the ultrathin  $\text{SiO}_2$  layer as the contact passivation on both surfaces [246]. The front passivation mechanism is similar to that of conventional PERC cells, i.e., the compatibility of the dielectric and ARC layer depends on the heavily-doped emitter, as listed in Table 5. However, the contact passivation through the tunnel oxide is the prime attraction for the researchers. Lu et al. studied the replacement of  $\text{SiO}_2$  with ALD-deposited  $\text{Al}_2\text{O}_3$  and a combination of  $\text{Al}_2\text{O}_3/\text{SiO}_2$  [247]. Both  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3/\text{SiO}_2$  stacking fails to yield better passivation than the  $\text{SiO}_2$  due to the increased B-diffusion and accumulation of B at  $\text{Al}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3/\text{SiO}_2$  stacking, leading to higher recombinations through B–O defects. The effect of ITO deposition followed by annealing on the passivation quality of the p-TOPCon and n-TOPCon was reported by Tao et al. [248]. The passivation improves for annealing temperature up to 500 °C in p-TOPCon, whereas the passivation degrades in the n-TOPCon after ITO deposition and annealing indicating the compatibility of ITO with B-doped poly-Si.

## 7. Conclusion

Recombination is one of the major reasons that limit solar cell efficiency. As a remedy, passivation reduces recombination both at the surface and the bulk. The field-effect passivation mitigates the surface recombination by the electric field generated by the excess doping layer or by the corona charging of the dielectric layer. The electric field reduces the minority carrier concentration at the surface to minimize the possible recombination. The dielectric layer, such as ( $\text{SiO}_2$ ) and ( $\text{Al}_2\text{O}_3$ ) with a capping layer ( $\text{SiN}_x$ ), are more effective than the dielectric layer alone as the interface quality improves. Excess-diffused deposition act as selective carrier layers for contact passivation. SHP is an extended version of field-effect passivation for further improvement of the lifetime. Pd and Sulfur poisoned Pd–Ag alloy sheets act as the shield during PECVD for hydrogen passivation of surface as well as bulk defects. Alcohol-based HF, halogens, and benzyl solutions are used for chemical passivation of the c-Si surface, facilitating the bulk lifetime measurement without actual dielectric layer deposition. Laser passivation decreases surface and bulk recombination current by passivating the defects using different charge states of the atomic hydrogen. Chemical passivation and laser passivation work on the principle of DOS reduction. Effective passivation always incorporates both the carrier concentration and DOS reduction strategies regardless of strategies. The recent development shows that standard solar cells employ dielectric-based field-effect passivation, whereas solution-based chemical passivation is unstable under atmospheric exposure and hence rarely reported for solar cell applications.

## CRediT authorship contribution statement

**Sakti Prasanna Muduli:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Paresh Kale:** Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

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