REVIEW

Prospects of metal-insulator-semiconductor (MIS) nanojunction structures for enhanced hydrogen evolution in photoelectrochemical cells: A review

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KEYWORDS

H₂ evolution; Metal-insulator-semiconductor (MIS); Water splitting; Photocatalysts

Abstract

This review paper discussed recent developments in and prospects of metal-insulator-semiconductor (MIS) nanojunctions for hydrogen evolution from water splitting in photoelectrochemical (PEC) cells. The basic principles of MIS that functionalise upon the critical intermediate ultrathin insulator layer in the sandwiched MIS structure are explained in detail, which is followed by a summary and discussion on the generalised approaches for synthesising MIS-based nanojunctions, including specific details on the preparation of metal, insulator and semiconductor layers. Key challenges associated with the application of MIS nanojunctions in semiconductor photocatalysts for water splitting are also addressed in addition to the technique’s advantages and disadvantages. Recent developments of photovoltaic cell structures based on MIS principles are also reviewed because PEC cells are usually coupled with photovoltaic cells and electrolysers for enhanced efficiency in water splitting. Finally, the prospects of MIS nanojunctions for water-splitting applications in the context of addressing energy and environmental concerns are discussed.

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Introduction

Due to increasing energy and environmental concerns, there has been considerable attention devoted to the development of clean and renewable energy sources [1-3]. Utilisation of solar energy has the potential to create a green, environmentally friendly and sustainable society. Much research has been devoted to enabling the practical conversion of solar energy into usable renewable energy sources. Hydrogen is a good potential candidate as a renewable energy source because the final combustion products are water and heat without producing any environmentally deleterious greenhouse effect gases. In 1972, Fujishima and Honda proposed a green approach to hydrogen energy production using solar-assisted photoelectrochemical (PEC) cells [4]. To date, hydrogen energy production via solar-assisted PEC water splitting is still an attractive means of converting intermittent solar radiation into storable and non-polluting chemical energy in the form of hydrogen.

Recent techno-economic analysis showed that to produce cost-competitive hydrogen energy via the solar-assisted PEC approach, the solar-to-hydrogen (STH) efficiency of photocatalysts used should be at least 15%, preferably greater than 20% [5]. Based on recent developments in PEC semiconductor photocatalysts for water splitting, however, the route to practical adoption and realisation is still significantly impeded by the low efficiency and stability of photocatalyst issues. To make the PEC process more economical, both the issues of low efficiency and of stability of PEC semiconductor photocatalysts must be addressed and improved significantly.

Many previous studies have focused on introducing foreign dopants [6-11], p-n junctions [12-16] and phase junctions [17-21] to improve the photo-efficiency of PEC semiconductor photocatalysts but have found limited success. Of late, one promising approach to achieving higher STH efficiency and stability is through a metal-insulator-semiconductor (MIS) nanojunction design for a PEC water-splitting application [22-26].

The most important characteristic of MIS nanojunction design is that the stability and light-harvesting characteristics of semiconductor photocatalysts are decoupled. This enables semiconductor photocatalysts with a narrower band gap, which are well suited for absorbing solar radiation to be used without being corroded by the electrolyte. Within the MIS nanojunction structure, the ultrathin insulator layer, which is typically a metal-oxide layer, plays a critical role in protecting the semiconductor from corrosive electrolyte, as well as efficiently mediating the minority carrier transport across the MIS junction with minimal recombination [27]. In this instance, the MIS nanojunction presents a conceptually simpler approach when compared with photovoltaic cells. In the past, photovoltaic cells attracted much interest due to their more economical approach to solar cell production. In principle, the structuration of a MIS nanojunction resembles the illuminated side of a photovoltaic junction, allowing for better solar radiation collection. This is especially true for short wavelength solar radiation compared with standard p-n junction solar cells [28].

Since the inception study on MIS nanojunction structure reported on Si solar cells in 1976, many studies have explored both the fundamental and application aspects of MIS structuration in solar-related devices [24]. In the past, MIS-based solar cells have received much attention due to their facile low-temperature fabrication process and the potential for achieving high solar conversion efficiency [29]. To date, however, few studies have reported on the application of MIS nanojunctions for hydrogen production from a water-splitting reaction in PEC cells. This review paper discusses recent developments and prospects of MIS nanojunctions for hydrogen evolution from water splitting in PEC cells. The basic principles of MIS that functionalise upon the critical intermediate ultrathin insulator layer in the sandwiched MIS structure are explained in detail. This is followed by a summary and discussion of the generalised approaches for synthesising MIS-based nanojunctions including specific details on the preparation of metal, insulator and semiconductor layers. Key challenges associated with the application of MIS nanojunctions in semiconductor photocatalysts for water splitting are also addressed along with its advantages and disadvantages. Recent developments of photovoltaic cell structures based on the MIS principles are also reviewed because the PEC cells are usually coupled with photovoltaic cells and electrolysers for enhanced efficiency in water splitting. Finally, the prospects of MIS nanojunctions for
transparent insulator layer (i.e., approximately 20 Å of SiO2).

The MIS nanojunction structure was initially proposed as a voltage-controlled varistor (i.e., variable capacitor) in 1959 by Moll and Garrett [30]. Subsequently, the characteristics of MIS were analysed by Frankl and Lindner [31]. The first successful MIS nanojunction structure was made of silicon dioxide (SiO2) grown thermally on a silicon surface by Ligenza and Spitzer [32]. The first application of MIS-based diodes as photosensitive devices was solar cells. Within the MIS nanojunction structure, it was discovered that by using a tunnel-transparent insulator layer (i.e., approximately 20 Å of SiO2 in silicon Schottky-barrier solar cells), both the energy conversion efficiency and electromotive force could be increased. The net effect of enhancing energy conversion efficiency is mainly due to the potential barrier of insulator layer that reduces the recombination current of majority charge carriers, whereas the electromotive force increases because of the built-in charge by the insulator layer. For instance, the structure of an MIS-based diode consists of an intermediate insulator layer on the bottom wide-band semiconductor (MIS) nanojunction structures for enhanced hydrogen evolution [33].

**Basic principles of metal-insulator-semiconductor (MIS) nanojunctions**

The MIS nanojunction structure was initially proposed as a voltage-controlled varistor (i.e., variable capacitor) in 1959 by Moll and Garrett [30]. Subsequently, the characteristics of MIS were analysed by Frankl and Lindner [31]. The first successful MIS nanojunction structure was made of silicon dioxide (SiO2) grown thermally on a silicon surface by Ligenza and Spitzer [32]. The first application of MIS-based diodes as photosensitive devices was solar cells. Within the MIS nanojunction structure, it was discovered that by using a tunnel-transparent insulator layer (i.e., approximately 20 Å of SiO2 in silicon Schottky-barrier solar cells), both the energy conversion efficiency and electromotive force could be increased. The net effect of enhancing energy conversion efficiency is mainly due to the potential barrier of insulator layer that reduces the recombination current of majority charge carriers, whereas the electromotive force increases because of the built-in charge by the insulator layer. For instance, the structure of an MIS-based diode consists of an intermediate insulator layer on the bottom wide-band semiconductor layer and a highly doped amorphous or polycrystalline semiconductor metal top layer [33]. In the early version [29], the MIS-based diode consisted of a continuous low-work-function metal that sandwiched an intermediate insulator layer with a p-type semiconductor bottom layer. With the structuration of a MIS nanojunction, a collecting barrier is induced at the semiconductor surface due to the difference in work function. However, the major disadvantage of a MIS-based solar cell is that a very thin metal layer must be used. In this instance, the thickness of the transparent metal layer is a compromise between the degree of transparency and voltage drop caused by the serial resistance. To overcome the issues with the thin metal layer, the structuration of the MIS nanojunction was restricted to the contact grid where the active area between grid fingers was covered by a transparent dielectric layer (e.g., grating-type MIS solar cells). If an inversion layer is induced by the presence of insulator charges, the device is called a MIS-inversion layer (MIS-IL) solar cell. Previously, different thermally assembled SiO2 and titanium oxides (TiOx) materials, as well as chemical vapour-deposited SiO2, silicon oxide (SiO) and tantalum oxide (Ta2O5) materials were used as the transparent dielectric for inversion layer formation at the silicon surface [34,35]. A major shortcoming of early MIS-IL solar cells was that they suffered from rapid degradation of the inversion layer. This could be overcome via the introduction of silicon nitride as the charged dielectric and anti-reflection layer, with its highly stable positive charge densities achieved by the incorporation of alkaline species [27].

**Fig. 1** shows the typical MIS-based photoelectrode structure consisting of a metallic collector layer situated at the surface of an insulator-covered semiconductor layer. When the MIS photoelectrode is illuminated, photogenerated minority carrier electrons are created and subsequently diffused (tunnelling) through the insulator-to-metal collector to initiate the hydrogen evolution reaction [33]. As shown in Fig. 1, the photocurrent may only be produced when the photogenerated electrons are created within a distance less than the sum of the depletion width (W) and effective minority-carrier diffusion length (Ld) of the collector. In this instance, the potential barrier of an insulator layer can reduce (or block) the recombination current of majority carrier electrons, as the minority charge carriers are able to flow through the thin insulator layer via quantum mechanical tunnelling [36]. This was observed for the Si-based MIS solar cells when a thin SiO2 layer was inserted in-between the metal and Si semiconductor layers [37]. In a well-behaved p-type MIS nanojunction, the photogenerated minority electrons pass directly from the semiconductor conduction band edge (Ec) to the Fermi level of the metallic collector (Ef,metal), as illustrated in Fig. 1b. The key advantage of MIS-based photoelectrode design is that the semiconductor stability and light-harvesting efficiency are decoupled, enabling narrower bandgap semiconductors typically used for absorbing solar radiation to be applicable in pH-extreme electrolyte without causing corrosion problems. This is achieved by the critical insulator layer in the MIS structure, which is typically an ultrathin metal oxide.

![Fig. 1](image-url)
layer that protects the semiconductor from corrosive electrolyte. The insulator layer will also efficiently mediate the minority carrier electron transport across the MIS nanojunction with minimal recombination.

To understand the physics behind a MIS-based diode, it is useful to analyse the band diagram of the MIS structure. In general, it was found that reverse applied bias (i.e., which gives rise to the depletion layer) was distributed between the insulator layer and space charge region. The height of the potential barrier on the semiconductor–insulator interface (SII) consists partly of the applied bias and is partly determined by the differences in (i) work functions between the metal and semiconductor layers; (ii) summary charge of the interface states; and (iii) built-in insulator charge and the charge of minority carriers accumulated near the SII. Once the reverse bias is applied to the MIS structure, the regime of non-equilibrium depletion is established [33].

For example, Scheuermann et al. [38] synthesised a MIS structure based on Si with uniform TiO\textsubscript{2} films of thickness between 1 nm and 12 nm through the ALD method on a degenerately doped p-type Si semiconductor wafer substrate (Fig. 2). They reported that the ALD-TiO\textsubscript{2} thin films yield water oxidation overpotential between 300 mV and 600 mV at 1 mA/cm\textsuperscript{2} in aqueous solution. Subsequently, an analysis of an electrical equivalent circuit of MIS structure based on the admittance measurements can be carried out [39]. Kochowski et al. [39] proposed electrical equivalent circuit designs for the analysis of a MIS structure based on Al-SiO\textsubscript{2}-(n) Si. Fig. 3 shows the electrical equivalent circuit designs capable of measuring the frequency dispersion of admittance characteristics in a broad range of signal frequencies and gate voltages from inversion to accumulation. The elements in these circuits for different gate voltages are illustrated in Fig. 3. The serial resistance generally is from the resistances of the semiconductor materials as well as of the contacts and electrical connections. The origin of the additional bias-dependent capacitance \( C_D \) is not currently clear. The estimated space charge
Table 1  Summary of recent developments of MIS nanojunction structures.

<table>
<thead>
<tr>
<th>No.</th>
<th>Figure</th>
<th>Synthesis method</th>
<th>MIS Devices Characterisation</th>
<th>Materials/thickness /efficiency/ stability</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| 1   | ![Image](98x93 to 151x160) | 1. SiO<sub>2</sub> grown in a furnace by annealing at 500 °C for 2 min 30 s in an oxygen atmosphere  
2. F<sub>3</sub>T<sub>1</sub>CuPc and CuPc deposited on SiO<sub>2</sub> from Knudsen cells under high vacuum  
3. Al<sub>2</sub>O<sub>3</sub> deposition in ALD reactor without exposure to air  
4. Au deposited on top of the Al<sub>2</sub>O<sub>3</sub> through electron-beam deposition | The threshold voltage of resonant tunnelling can be controlled according to the energy levels of the molecules. The carriers were injected into the respective molecules at corresponding threshold voltages in the binary molecules. These findings point to a new multilevel operation of resonant tunnelling through organic molecules in a practical MIS device structure | Materials: F<sub>3</sub>T<sub>1</sub>CuPc; CuPc  
Thickness: SiO<sub>2</sub>-1.2 nm, Al<sub>2</sub>O<sub>3</sub>-3.5 nm  
Efficiency: -  
Stability: - | Incorporating organic molecules in MIS structure has many advantages: The molecules have a uniform size at the nanometre scale; These nanometre-scale sizes permit higher densities of dots; Their energy levels are tunable through the attachment of functional groups such as electron-withdrawing (or donating) groups; These features make organic molecules superior to inorganic molecules for making quantum dots | | [50] 2013 |
| 2   | ![Image](163x93 to 218x151) | 1. P-doped CZ Si(1 0 0) was cleaned and dried  
2. SiO<sub>2</sub> grown by RTO at 950 °C in 8% O<sub>2</sub>/N<sub>2</sub>, cooled to 250 °C and then annealed to 1000 °C for 60 s in a pure N<sub>2</sub> followed by 60 s in 10% H<sub>2</sub>/N<sub>2</sub>  
3. Ti and Pt were evaporated through shadow masks onto oxide-covered wafers at 1 A/s by e-beam evaporation in a Denton infinity 22 thermal evaporator system with a base pressure of 1.0 × 10<sup>−7</sup> Torr | Recombination within the inversion layer is significantly reduced, allowing electron transport over very long distances \( E_g \). The LSV for the MIS photodetector with 23 nm diameter collector is characterised by a photodetector efficiency of 2.9%, assuming an ideal counter-electrode. This efficiency is about 15 times larger than previous reports for p-Si MIS photocathodes | Thickness: SiO<sub>2</sub>-2 nm; Pt-20 nm; Ti-30 nm  
Efficiency: 20 mA at applied potential 0.15 V in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution  
Stability: Excellent stability over 2 h of continuous operation | 1. High-quality thermal SiO<sub>2</sub> layer  
2. Both photo- and electrolyte-induced formation of an inversion channel beneath the SiO<sub>2</sub>/Si interface can extend the transport distance of minority carriers | Although it proposed a quite new method that incorporates organic molecules in an MIS structure, there are no test results describing STH efficiency or the stability of this new-type MIS structure. Further research could be developed on this new method | [27] 2013 |
| 3   | ![Image](222x93 to 277x151) | 1. Ni films were deposited on as-received phosphorous-doped (100) n-type Si wafers (0.3 0.5 2 cm) at a deposition rate of \( \sim 0.2 \) A/s  
2. Ohmic contact was made to the backside of the Si wafer by e-beam deposition of Ti. Copper tape was used to contact the Ti to the backside for electrochemical experiments | High photocurrent density was measured at approximately 1.07 V without sign of decay even after 80 h of continuous PEC water oxidation. The high photovoltage was attributed to the high built-in potential in a MIS-like device with an ultrathin, incomplete screening of Ni/NiO<sub>2</sub> layer from the electrolyte. In 1 M aqueous KOH, the Ni/n-Si photocathode exhibited high PEC activity with a low onset potential \( (\sim 1.07 \) V vs RHE) and high photocurrent density \((60 \) mA/cm<sup>2</sup>) | Thickness: Ti-20 nm; SiO<sub>2</sub>-native; Ni-2 nm  
Efficiency: In 1 M aqueous KOH, the photocathode exhibited high photocurrent density \((60 \) mA/cm<sup>2</sup>) with a low onset potential \((\sim 1.07 \) V vs RHE) under 225 mW/cm<sup>2</sup> | 1. Form MIS junction, favouring charge separation and motion of photoexcited holes toward the OER catalyst-electrolyte interface  
2. Ni served as the active electrocatalyst for OER  
3. Ni/NiO<sub>2</sub> film provided excellent protection to Si | 1. The bandgap (1.1 eV) of Si limits the amount of photovoltage that can be generated for water splitting, although it is a low-cost and abundant earth material  
2. The use of semiconductors with wider band gaps than Si under similar surface protection/electrolyte conditions should result in a shift of the OER photocurrent onset to more negative potentials | [96] 2013 |
### Table 1 (continued)

<table>
<thead>
<tr>
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<td>4</td>
<td><img src="image1.png" alt="Image" /></td>
<td>1. SiO$_2$ layer was annealed in a furnace at 500 °C under an oxygen atmosphere</td>
<td>The change in the SET (single-electron tunnelling) could be due to the alternation between open- and closed-ring isomers induced by light irradiation. This means that information about the threshold voltage in SET was memorised as a reversible change in the molecular orbitals along with the photoisomerisation and reveals that diarylethene molecules work as an optical memory in a practical device structure. These achievements represent unique features of organic molecules that strongly outweigh those of inorganic quantum dots.</td>
<td>Thickness: ITO-30 nm; Al$_2$O$_3$-3.5 nm; SiO$_2$1.2 nm; p-Si(1 0 0); diarylethene molecules</td>
<td>1. The molecules have a uniform size at nanometre scale and thus, achieving quantum dots with a large number density. The number density of the molecules can reach around 1013 cm$^{-2}$, which is two orders of magnitude higher than that of inorganic dots. 2. The tenability of the molecular orbitals. Photochromic molecules such as diarylethene and azobenzene molecules, permit the molecular orbitals to be reversibly changed by light irradiation. This is a unique feature of organic molecules that makes them very different from inorganic dots.</td>
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<td>[97]</td>
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<td>5</td>
<td><img src="image2.png" alt="Image" /></td>
<td>1. TiO$_2$ films were deposited on top of the FTO electrode</td>
<td>This MIS heterostructure for plasma-electric energy conversion is a novel architecture to harvest hot-electrons derived from plasmonic excitations. The external quantum efficiency (EQE) of 4% at 460 nm by using a Ag nanostructured electrode and EQE of 1.3% at 550 nm by a Au nanostructured electrode. The insulator interfacial layer plays a crucial role in interface passivation, a requisite in photovoltaic applications to achieving both high open-circuit voltages (0.5 V) and fill-factors (0.5). However, its introduction simultaneously modifies hot-electron injection and transport. The influence passivation has on these processes for different material configurations, and characterise different types of transport depending on the initial plasmon energy band, reporting power conversion efficiencies of 0.03% for nanopatterned silver electrodes.</td>
<td>Thickness: (anatase)TiO$_2$-50 nm; TiO$_2$ and ITO were used as control devices. Efficiency: The external quantum efficiency (EQE) of 4% at 460 nm by using a Ag nanostructured electrode and EQE of 1.3% at 550 nm by a Au nanostructured electrode. Stability: Silver devices are stable within 22% performance degradation after 2 months of storage.</td>
<td>This device is a novel architecture to harvest hot-electrons derived from plasmonic excitations. Unlike semiconductors where light is absorbed within a thickness of 1 μm (for direct band gap semiconductors) to 100 μm (for indirect-band gap semiconductors), appropriately designed metal nanostructures exhibit total light absorption within thicknesses below 90 nm or show omnidirectional coupling. The direct use of LSPRs to harvest light would open the exciting possibility of creating artificial materials with a tailored absorption, but without the band gap limitations of bulk semiconducting materials.</td>
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<td>[51]</td>
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This research introduced the organic molecules into the device, which is a new approach for the preparation of MIS structures. However, there is no metal collector used in this device.
1. p-Si(1 0 0) wafers were chemically cleaned using RCA cleaning method.
2. The ultra-thin Al₂O₃ gate dielectric film was deposited using the RPALD system.
3. The SiN film was sputtered onto the surface as an anti-reflection coating.
4. Al was evaporated onto the rear surface and annealed at 400 °C using N₂ to complete the formation of MIS solar cells.

The lifetime increased more than three times compared to those without Al₂O₃ films as a result of passivated surface effects. The interface state density with SiN/Al₂O₃ structure was about one order higher in magnitude than that with only Al₂O₃ film because of the charge incorporated in the SiN film during the process. The efficiency increased from 0.9% to 8.2% because of the increase in the number of inversion carriers and the emergence of the anti-reflection coating effect as the SiN film was used.

The barrier heights increased in the range of 0.23-0.63 eV with the ideality factor decreased in the range of 5.92-1.66 with increasing temperature. The variation in electrical characteristics as a function of temperature for this MIS structure demonstrated it has the potential to be used in solar cells. TiO₂/n-GaAs MIS structure showed promising than other insulator materials currently being used in high-performance device technology.

The calculated values of the barrier height for MS and MIS Schottky diodes were found to be 0.79 eV (V), 0.87 eV (C-V) and 0.86 eV (I-V), respectively. The increase in barrier height is ascribed to the negative charge at the interface, while recombination in the oxide is presumed to be the cause of the latter. The dominant interface trap was found to be located at 0.76 eV below the conduction band.

The as-deposited MIS devices showed characteristic diode behaviour with a turn-on voltage at approximately 0.5 V but presented a breakdown field of only 0.2 MW/cm². After annealing, an increase in the dynamic impedance was observed. There was also a breakdown field of only 0.2 MW/cm² Si interface as well as in the bulk of the film. After annealing, an increase in the dynamic impedance was observed. There was also a breakdown field of only 0.2 MW/cm² Si interface as well as in the bulk of the film.

This device required the incorporation of SiN film for double insulator layers, making the structure more complicated. The fabricated cell efficiency without SiN was only approximately 0.9%. However, with SiN, of 91 nm, the efficiency reached approximately 2% because of the increase in the number of inversion carriers and the emergence of the anti-reflection coating effect as the SiN film was used.
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<thead>
<tr>
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<th>Figure</th>
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<th>Advantages</th>
<th>Disadvantages</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Evidence of trapped charges at the insulator-semiconductor interface</td>
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<td>PEC water oxidation was observed to occur below the reversible potential whereas dark electrochemical water oxidation was found to have low-to-moderate overpotential at all pH values, resulting in an inferred photovoltage of 550 mV. Water oxidation was sustained at these anodes for many hours under harsh pH and oxidative environments, whereas comparable Si anodes without the TiO$_2$ coating quickly failed</td>
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<td>2011</td>
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<td>11</td>
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<td>Thickness: Si was protected by ALD-TiO$_2$ of 2 nm thick and then coated with an optically transmitting layer of known Ir catalyst (3 nm)</td>
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<td>Efficiency: 16 mA at 0.6 V vs NHE in 1 M NaOH under 1 sun illumination Stability: It can last at least 8 h under 1 sun illumination during water splitting process</td>
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</table>

Carbon nanotube (CNT)/Si hybrid solar cells are a new class of photovoltaic devices which benefit from the superior opto-electronic properties of CNTs coupled with well-established Si photovoltaic technologies. SWNTs are more suitable than double- (or multi-) walled carbon nanotubes owing to their tunable direct band gap energies matching with a wide range of the solar spectrum and better charge carrier transport properties. By employing temperature-dependent electrical characterisations, it is known that diffusion-dominated p-n junction transport and dominant photocarrier generation in Si. This study suggests that the superior photovoltaic properties of single-crystalline Si could be realised by a simple, low-temperature process, thus implying a great potential for low-cost, high-efficiency solar cells.

Besides the limited PCEs, the underlying transport mechanism of SWNT/Si solar cells is not well-established and remains under debate. This is mainly because SWNTs are mixtures of both semiconducting and metallic nanotubes with inhomogeneous diameters and chiralities, which lead to the complexity in the nature of the electronic junction of SWNT/Si.

This MIS nanojunction structure remains a challenge when it is being used on other crystal structures or high profile photoelectrodes as earth abundant materials are usually preferred for large-scale production of solar fuels.
1. The Si wafer was immersed in HF solution to remove the native SiO,
and then cleaned.
2. GO was synthesized by a modified Hummers method. The GO thin film was deposited on Si by spin coating from GO solution.
3. Both the top Au bottom contacts Al were deposited by thermal evaporation.

1. HF solution was used to remove the native oxide formed on Si surface.
2. Nanoporous Si was fabricated by a modified metal-catalysed electrodeless etching (MCEE) method and then washed with deionised water.

For the thickness of ALD-TiO$_2$ films greater than $\sim$2.0 nm, the effective overpotential for water oxidation increased linearly when the TiO$_2$ thickness was increased in accordance with a bulk-limited conduction mechanism that required a characteristic E-field in the TiO$_2$ layer to maintain a given water oxidation current across the MIS anode. For ultrathin TiO$_2$ films in which direct tunnelling can dominate charge transport, the minimum overpotential and reaction rate were relatively independent of TiO$_2$ thickness and were apparently dominated by the kinetics of the water oxidation on the catalyst surface.

The solution-processable GO can be used as an effective insulating layer for MIS Si solar cells. The $V_{oc}$ of the GO-based MIS Si solar cells leads to a PCE enhancement of 88% as compared with that of reference device (Schottky solar cells). It is because the overall reduced carrier recombination arising from both the increase in built-in potential and the reduced interface defects. The fabricated r-GO based Si solar cells exhibited inferior performance than that of GO based MIS Si solar cells, mainly owing to the larger series resistance from the additional SiO$_x$ layer formed during the thermal reduction process.

The insulator GO is solution-processable and the work function is tunable. They can be worked as effective hole and/or electron transport layers in both organic solar cells (OPV) and organic light emitting diodes (OLEDs). It can be also used as an effective insulating layer for MIS Si solar cells.

1. The metal collector Au in this structure is not cost-effective.
2. The uniform GO insulator with thickness more than 4 nm was hard to obtain.

Prospects of metal insulator–semiconductor (MIS) nanjunction structures for enhanced hydrogen evolution...
photoelectrodes, more attention should be brought to the development of a new strategy for electrode protection. We speculate that a proper choice of protection materials, other than Al$_2$O$_3$, could further improve the PEC performance of Si photocathodes. Although thick GO flakes may prevent the tunnelling of carriers, GO sheets were deposited on Si electrodes via the ALD method and made hydrophilic by treatment with SCI solution (NH$_4$OH/H$_2$O$_2$/H$_2$O=1:2:8) for 15 min.

<table>
<thead>
<tr>
<th>Nos.</th>
<th>Figure</th>
<th>Synthesis method</th>
<th>MIS Devices Characterisation</th>
<th>Materials/thickness</th>
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<th>Stability</th>
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</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td><img src="image1.png" alt="image" /></td>
<td>Thin Al$_2$O$_3$ layer was deposited in a layer-by-layer fashion onto the Si electrode via the ALD method.</td>
<td>GO was deposited on Si to form an Al/GO/SiO$_2$/Si MIS tunneling diode.</td>
<td>Thickness: Substrate: p-type Si; Insulator: Al$_2$O$_3$ (50 Å); Semiconductor: PVA: n-CdS (30 μm)</td>
<td>1.34 × 10$^{-6}$ A, while the photocurrent of the control device was 1.94 × 10$^{-7}$ A. Thus, the GO-based device is a promising candidate for detector applications.</td>
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<td>356</td>
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<td>16</td>
<td><img src="image2.png" alt="image" /></td>
<td>Al substrate was washed with NaOH or KOH pellets to remove native alumina layer and other soluble salts.</td>
<td>The energy density distribution profile of the interface states was obtained from the forward bias $I$-$V$ data by taking into account the bias dependence ideality factor ($n(V)$) and effective barrier height ($\phi_e$) for MIS structure.</td>
<td>Thickness: Substrate: Al metal; Insulator: Al$_2$O$_3$ (50 Å); Semiconductor: PVA: n-CdS (30 μm)</td>
<td>Polyvinyl alcohol (PVA) as polymer matrix. PVA is a poor electrical conductor, and the conductivity of the polymer is of major importance in constructing a Schottky barrier. When a polymer is doped with semiconductor, especially II-VI semiconductor such as CdS and ZnS in various quantities and forms, their incorporation within a polymeric system may be expected to improve the conductivity.</td>
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Table 1 (continued)
1. Substrates were surface polished in a HF: HNO₃ solution and then cleaned. In both cases an increasing dielectric thickness leads to a reduction in surface recombination and is accompanied by an increase in contact resistivity. Optimum thicknesses of ALD Al₂O₃ and thermal SiO₂ were found to be ~22 Å and ~16 Å, respectively. This amounts to a maximum potential $V_{oc}$ gain of 15 mV. These gains are found to diminish significantly after annealing at 300 °C. The Al₂O₃-Si MIS type contacts exhibit a lower maximum $V_{oc}$ gain of 6 mV but greater thermal stability.

2. The substrates were then immersed in diluted solution of HF with AgNO₃ for galvanic displacement. Ag particles were removed by using HNO₃.

3. A thin Al layer was evaporated on top of the thin passivating layers. This study investigated the optimum dielectric thickness and potential benefit of applying MIS contacts to conventional diffused junction Si solar cells. The Al₂O₃ passivated contacts demonstrated could also be applied uniformly to the n+ rear side of a p + nn+ solar cell. In that case, the tolerable contact resistivity for a 100% metal contact fraction is far higher than a partial metal grid. An increasing dielectric thickness leads to a reduction in surface recombination and is accompanied by increase in contact resistivity. The use of anti-reflective Si nanostructures is essential to improve the performance of thin-crystalline Si solar cells. The field-effect passivation effect induced by ALD Al₂O₃ was resolved utilizing metal-assisted chemical etching, according to the evolution of surface roughness in the range of 1.7–11.7 nm. Significant nanostructuring of a Si surface resulted in an increase of positive fixed charges according to the formation of a SiO₂ 1 L.

4. About 10 nm thick Al₂O₃ films were deposited via ALD at 230 °C using trimethylaluminium as metal precursor and H₂O as the oxygen source. The use of forming gas (H₂/N₂), annealing was not sufficient to improve the passivation performance because, in the case of highly nanostructured surfaces, the positive $Q_f$ in the SiO₂ 1 L was hardly affected when compared to the improvement of $D_{it}$.
layer capacitance $C_{sc}$ coincides with theoretical $C_{sc}$ corresponding to the inversion and depletion region of the MIS structure. The constant phase elements CPE1 and CPE2 connect in series with resistors $R_1$ and $R_2$, which relate to electron processes with a broad distribution of time constants. These time constants characterise the exchange of electrons between the SiO$_2$-Si interface and semiconductor states. The constant phase element CPE2 in series with $R_2$ resistance describes the dispersion phenomena evoked by the SI states. The time constant $\tau_1$ is practically gate-voltage independent. This type of behaviour points to the presence of deep traps in the semiconductor space charge region. The CPE1 element with parameter $n_1=0.95$ for $U_g<-5$ V has “capacitive” character and, together with $R_1$ resistance, they characterise the time constant of monoenergetic electron traps in a lower part of the energy gap of the semiconductor. For $U_g>3$ V, which corresponds to the traps located in an upper part of the energy gap, the CPE1 element with parameter $n_1=0.46$ connected with $R_1$ resistance describes electron processes with a broad spectrum of time constants. Previous studies also estimated the basic parameters of MIS structure from the analysis of capacitance-voltage and conductance-voltage characteristics. Levin et al. [40] found that the photoemission currents in MIS structure, which was determined by the external field, were derived when the space charge was randomly distributed over the insulator layer.

**Generalised approaches for synthesising MIS nanojunctions**

Overall, the synthesis of a MIS nanojunction includes three parts, namely the semiconductor, insulator and metallic collector. In this section, we summarise the approaches for synthesising a MIS nanojunction. Table 1 shows the summary of the generalised approaches for synthesising MIS nanojunctions.

**Semiconductor pretreatment**

Silicon (Si) is the most widely used semiconductor substrate for the synthesis of MIS nanojunctions [41]. Prior to the synthesis of MIS nanojunctions, pretreatment of the semiconductor substrate usually based on the RCA standard is necessary. The standard RCA procedure consists of immersion steps in standard clean 1 (SC1) (5:1:1 water (H$_2$O):ammonium hydroxide (NH$_4$OH):hydrogen peroxide (H$_2$O$_2$)), 2% hydrogen fluoride (HF) and SC2 (5:1:H$_2$O$_2$:hydrochloric acid (HCl):H$_2$O$_2$) solutions [27]. In the pretreatment procedure, semiconductor Si is immersed in the 2% HF solution for 5 min to remove the native SiO$_2$ on the surface. It was also reported that the semiconductor substrates could be dipped in aqua regia for 10 min to remove the native oxides on the surface [42,43]. After that, the Si semiconductor wafer was rinsed thoroughly using deionised water and dried by a flow of nitrogen gas before use [44]. Apart from the Si semiconductor, other semiconductor substrates such as gallium arsenide (GaAs) [45], gallium nitride (GaN) [42] and cadmium sulphide (CdS) [46] were also reported useful for the synthesis of MIS nanojunctions. For instance, Sömmezöglü et al. [45] reported the MIS nanojunction structure based on copper (Cu)/TiO$_2$/n-GaAs fabricated using n-type liquid-phase epitaxial (LPE) tellurium (Te)-doped GaAs wafers. They found variation in electrical characteristics of the Cu/TiO$_2$/n-GaAs MIS structure as a function of temperature, which was of great help in improving the quality of TiO$_2$ grown on the GaAs semiconductor substrate. Reddy et al. [42] reported a 2 nm thick Si-doped GaN layer grown on a c-plane aluminium oxide (Al$_2$O$_3$) sapphire semiconductor substrate by using the metal organic chemical vapour deposition (MOCVD) method. They found the barrier heights for this MIS structure to be 0.86 eV (I-V) and 0.99 V (C-V). Lee et al. [43] reported the epitaxial structure of MIS hydrogen gas sensors consisting of a 750 nm thick GaN buffer layer and a 0.8 nm thick undoped GaN layer. The GaN layer was grown on a c-plane sapphire substrate using the MOCVD system. They found that when MIS hydrogen-gas sensors are exposed to dilute hydrogen ambience, hydrogen dipoles are formed at the platinum (Pt)/zinc oxide (ZnO) interface, with electrons released back to the ZnO layer. The hydrogen adsorption reaction leads to the reduction of barrier height and series resistance.

**Insulator preparation**

The insulator layer plays an important role in the synthesis of efficient MIS nanojunctions. To date, the most widely used insulator layer is native SiO$_2$, which was reported in previous studies [38,42,47]. This is because the SiO$_2$/Si interface acts as recombination centres to facilitate tunneling, whereas the lower trap density decreases the reverse saturation current and, thus, increases the overall photovoltages in the MIS structure [27]. The native oxide layer of SiO$_2$ could be formed by exposing the cleaned n-Si surface to air for 10 consecutive days [48]. The most widely used method for artificial synthesis of an insulator layer is atomic layer deposition (ALD). Overall, ALD is mostly used for the fabrication of thin films through the reaction of two chemical precursors on a semiconductor surface in sequential and repeated exposure to the precursors over time. Therefore, it has a feature of angstrom-resolution due to the layer-by-layer growth of thin films. Although the nature of deposition speed in ALD is very slow, it unarguably produces good quality, uniform and ultrathin films over a wide range of materials [49]. In a study by Seo et al. [50], the researchers synthesised thin SiO$_2$ insulator films 1.2 μm thick by annealing at 500 °C for 150 s in an oxygen-rich environment. Additionally, the organic molecules of copper hexadecafluorophthalocyanine (F$_{16}$CuPc) and copper phthalocyanine (CuPc) were deposited as insulators on the SiO$_2$ surfaces from highly vacuum-conditioned Knudsen cells (i.e., $5 \times 10^{-7}$ Pa). They found that using ALD actually allows the organic molecules to be embedded in high-quality SiO$_2$ insulator thin films, as shown in Fig. 4. TiO$_2$ film is another alternative insulator for MIS structure. It is reported that different thicknesses of TiO$_2$ between 1 nm and 12 nm have been deposited through the ALD method on degenerately doped p-type Si semiconductor wafer substrate [38]. The researchers reported that the ALD-TiO$_2$ thin films yield water oxidation overpotential between 300 mV and 600 mV at 1 mA/cm$^2$ in aqueous solution. Apart from the commonly used native oxides of SiO$_2$ and TiO$_2$, another native oxide such as Al$_2$O$_3$ was also used as an insulator layer to provide efficient interfacial
tunnelling effects within the MIS nanojunction structure. For instance, Arquer et al. [51] employed the ALD method to assemble thin-film layers of TiO$_2$ and Al$_2$O$_3$ over the indium-doped tin oxide (ITO) photoelectrode substrate. The precursors used for Al$_2$O$_3$ thin films during the ALD method were H$_2$O and trimethylaluminium Al (CH$_3$)$_3$, whereas the titanium isopropoxide (C$_{12}$H$_{28}$O$_4$Ti) was the precursor used for TiO$_2$ thin films. They found that without the Al$_2$O$_3$ insulator layer, the built-in field vanished and that this directly resulted in the absence of open-circuit voltage. In another study, Kim et al. [24] synthesised the Al$_2$O$_3$ thin films on p-type Si semiconductor substrates by using the remote plasma atomic layer deposition (RPALD) method, as depicted in Fig. 4. The RPALD method is superior to typical types of ALD techniques because it incurs lower plasma damage and can used at a low process temperature. Therefore, this technique is expected to deposit high-quality insulating layers and improve the interface properties in MIS devices. The RPALD method utilises an alternative Al (CH$_3$)$_3$ precursor and oxygen radicals to obtain good interfacial properties for MIS-IL solar cell applications. Apart from the ALD-related synthesis methods, other methods for the structuration of efficient MIS nanojunction structure were also reported. For instance, Voitsekhovskii et al. [52] investigated the MIS nanojunction structure based on mercury cadmium telluride (HgCdTe) grown by using the molecular-beam epitaxy method. To match the crystal lattices of GaAs and HgCdTe on the semiconductor substrate, buffer layers of zinc telluride (ZnTe) and cadmium telluride (CdTe) are grown, respectively. In this instance, the respective CdTe and ZnTe layers match the lattice constants between the semiconductor substrate and bottom HgCdTe layer. The authors found that the upper HgCdTe thin film on the working layer is necessary to (i) produce a potential barrier for charge-carriers; (ii) reduce surface recombination velocity and (iii) influence hot electron lifetime in the bulk photocarrier.

Silicon-nitride (Si$_n$N$_m$H) films have been widely used as insulators in MIS structures due to their good mechanical strength, good dielectric properties, and good barrier capability against moisture and mobile ions [53,54]. There is a variety of deposition techniques that have been used to deposit Si$_n$N$_m$H films over a wide range of plasma pressures and temperatures [55,56]. However, the most general technique for the deposition of Si$_n$N$_m$H films is plasma-enhanced chemical vapour deposition (PECVD) using reactive gases of silane (SiH$_4$) and ammonia (NH$_3$) in the temperature range of 200–400 °C [57]. Lin et al. [58] developed a synthesis method to deposit graphene oxide (GO) thin films on Si semiconductor substrate, as depicted in Fig. 5. A 100 nm thick Al-gate with a circular area of $5 \times 10^{-4}$ cm$^2$ defined by a shadow mask was sputtered onto the GO-deposited side of Si semiconductor substrate. The Al was also sputtered onto the backside of the Si semiconductor substrate to form an ohmic contact. The researchers found that the accumulations of dark current and inversion photocurrent in the GO-device were superior to those in the control device. Apart from these materials, it was reported that the use of III–V nitrides thin films as insulating materials have been extensively studied for their potential applications in optoelectronics and microelectronics [59]. One of the promising insulating materials is aluminium nitride (AlN), which has a high dielectric constant, excellent thermal conductivity and wide band gap. The high dielectric constant in AlN is particularly suitable for application in MIS devices, where a thermal SiO$_2$ layer cannot be grown [60]. Because the thickness of the insulator layer is also a critical parameter in determining an efficient MIS nanojunction structure, it is thus important to understand how to control the thickness of the insulator layer. For instance, Esposito et al. [27] found that the thickness of SiO$_2$ tunnelling layers could be adjusted by varying the duration of rapid thermal oxidation (RTO) treatment. In another study, Liu et al. [44] fabricated MIS-based solar cells on an n-type c-Si(1 0 0) semiconductor wafer substrate and found that the thickness of insulator GO thin film varies with the spin-casting rate. The synthesis temperature can also affect the physical characteristics of the MIS nanojunction structure. Previous studies have shown that the SiO$_2$/Si interfaces formed at high temperature contain lower trap densities than do the interfaces formed at low temperature [27].

During the water-splitting process in a PEC cell, the insertion of an ultrathin insulator layer between the metal and semiconductor layers can substantially reduce the Fermi level pinning, which has a deep effect on the separation of electron-hole pairs. According to the MIS mechanism illustrated earlier, to obtain high performance on the MIS structure application in water splitting, the design of the insulator is quite important. Recently, some research has focussed on the application of SiO$_2$ and TiO$_2$ MIS structure.
for water splitting, but there have been few reports concerning the Al₂O₃ and AlN for example. In this part, we summarised most types of insulators, such as SiO₂, Al₂O₃, and TiO₂, and the synthesised methods including RPALD, PECVD, etc. Some characterisations can be applied to the PEC water splitting. For example, various thicknesses of the insulator will lead to different results during the water-splitting process. Moreover, the synthesis temperature, spin-casting rate, etc. can also affect the trap densities; currently no result is reported in the PEC water-splitting research.

**Metal deposition**

As for the metal layer synthesis in MIS nanojunction structures, thermal evaporation deposition (TED) is suitable for metals due to their relatively low melting points compared with those of metal oxides. In addition, a very high vacuum condition in the thermal evaporation chamber enables the evaporated atoms or molecules from the targeted metals to be kept in line-of-sight deposition on the semiconductor substrates due to almost no other gas molecules colliding with them. For instance, metals with low melting points that can be deposited by TED are gold (Au) [61–63], silver (Ag) [64,65], copper (Cu) [66–69], nickel (Ni) [70–72], iron (Fe) [73–76] and cobalt (Co) [77,78]. Through the deposition method, different-ordered nanostructured arrays including nanoparticle, nanochain, nanogap, and nanoring arrays can be achieved based on colloidal monolayer masks by controlling the synthesis parameters, i.e., angle (θ) between the normal direction of the semiconductor substrate with the colloidal monolayer, deposition direction and rotation of semiconductor substrate [49]. For instance, Liu et al. [44] deposited both Au and Al films as top and bottom layers by using the TED method, respectively. They found that the thicknesses of Au and Al metal layers were approximately 12 nm and 150 nm, respectively, and the area of each device was 0.09 cm², as determined by the area of a gold electrode [44]. Similarly, in another study by Yoo et al. [57], researchers reported on the use of the TED method to evaporate the Al metal followed by annealing on the back surface of a Si semiconductor wafer to provide ohmic contact for the bulk. Meanwhile, the front Al dots with diameters ranging between 450 μm and 850 μm and with thickness of 0.4 μm were evaporated onto the annealed SiN:H film by using a metal mask [57]. Apart from the TED method, the electron beam evaporation (EBE) method is also widely used for the preparation of metal layers in efficient MIS nanojunction structures. During the EBE synthesis process, the targeted metal is usually bombarded with an electron beam of high energy that results in the formation of an atomic gaseous phase. These gaseous atoms are then deposited onto the desired substrates within line-of-sight under a high-vacuum condition in the chamber. This EBE method can be used to deposit most metals such as Au [79–81], Ag [82–84] and palladium (Pd) [85–87], as well as semiconductors or ceramics such as ZnO [85–87], ZnS [88–90], TiO₂ [84,91] and Al₂O₃ [88–90] at a relatively high deposition rate and low substrate temperature. Due to the potential sight-line movement of evaporated metal or semiconductor atoms, the colloidal monolayer can be used as a marker to fabricate the periodic array via the EBE deposition method [49]. Of late, the EBE is an emerging deposition method used for the fabrication of Si thin-film devices in microelectronics and photovoltaics at high growth rates of up to a few micrometres per minute. This is by far the highest growth rates for Si thin films and has even exceeded rates achievable by using the conventional plasma enhanced chemical vapour deposition (PECVD) method by more than a factor of 20. With the EBE method, PECVD will further contribute to substantial cost reduction potential by enabling industrial-scale production [92]. The schematic of the EBE system is shown in Fig. 6. A number of previous studies reported the application of EBE in the synthesis of thin metal layers [93–95]. For instance, Kenney et al. [96] reported the fabrication of MIS-based electrodes, wherein the Ni thin films were initially deposited on raw P-doped (1 0 0) n-type Si semiconductor wafers using the EBE method at a deposition rate of 0.2 Å/s. This was followed by the formation of ohmic contact on the backside of the Si semiconductor wafers via the EBE deposition of Ti metals. The researchers measured the thicknesses of Ni and Ti films at approximately 2–20 nm and 20 nm, respectively. Similarly, Seo et al. [50] reported the EBE deposition of Au thin films with an effective area of 3.1 mm² on top of an Al₂O₃ layer through a metal shadow mask. With reference to the MIS nanojunction structure, generally the Au and Si layers are functionalised as the top metal and bottom semiconductor layers, respectively [50]. More interestingly, it was reported that ordered

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**Fig. 5** Schematic illustration of Al₂O₃ thin films fabricated via the RPALD method. Reproduced from Ref. [24].
Arrays of metallic collectors such as Pt and Ti could be sequentially evaporated through shadow masks onto oxide-covered semiconductor wafers via the EBE method [27]. Reddy et al. [42] also reported on the EBE of a Au Schottky contact of 50 nm thickness and 0.7 mm diameter on GaN thin film through a stainless steel mask. This was followed by a sequential deposition of a 20 nm-thick SiO2 layer and a 50 nm-thick Au layer on the GaN film using the same EBE system. It was reported that the Au evaporation process was carried out in a vacuum coating unit at a pressure of approximately $5 \times 10^{-6}$ mbar [42].

**Key challenges in the development of MIS nanojunctions**

**Semiconductor substrate**

For the synthesis of MIS nanojunctions, Si is the most widely used semiconductor substrate, as it is an earth-abundant element and a suitably efficient photovoltaic material. However, the major disadvantage of the use of Si as a semiconductor substrate is that it can be easily corroded in electrolyte. The corrosion in electrolyte issue can be resolved by depositing an insulator layer such as TiO2 or Al2O3 to improve its long-term stability. Previously, Chen et al. [41] synthesised an ultrathin TiO2 layer of 2 nm thickness via the ALD method to protect the Si semiconductor wafers from corrosion. This was followed by the coating of an optically transmitting layer of Iridium (Ir) catalyst of approximately 50 nm thickness to catalyse the oxygen evolution reaction (OER) (Fig. 7). In general, PEC water oxidation occurs below the reversible potential, whereas dark electrochemical water oxidation exhibits low-to-moderate overpotentials (OER) (Fig. 7). In this instance, the ultrathin Ni film acts as a surface-protection layer against corrosion in addition to functioning as a non-precious metal electrocatalyst for the water-splitting application [5]. Kenney et al. [96] found that the deposition of an ultrathin Ni film of 2 nm thickness on n-type Si/SiO2 surfaces resulted in a high-performance MIS-based photocathode for PEC water oxidation even under extreme aqueous borate buffer and KOH solutions of pH 9.5 and pH 14, respectively (Fig. 8). In this instance, the ultrathin Ni film acts as a surface-protection layer against corrosion in addition to functioning as a non-precious metal electrocatalyst for enhanced oxygen evolution. From the study, the resultant Ni/n-Si photoanodes exhibited high PEC water oxidation activity with low onset potential ($\sim 1.07$ V vs RHE), high photocurrent density and durability in 1 M aqueous KOH solution. In addition, the Ni/n-Si photoanodes showed no sign of decay even after 80 h of continuous PEC water oxidation in a mixed lithium borate-potassium borate electrolyte solution. The measured high photovoltage was attributed to the high built-in potential in the MIS-based device with an ultrathin and incomplete screening Ni/NiOx layer from the electrolyte. According to the discussion by Turner [5], however, the current finding by Kenney...
Ultrathin insulator layer

In accordance with the basic principles of MIS nanojunctions, the ultrathin insulator layer plays an important role in ensuring high performance of solar conversion efficiency. A previous study showed that the insertion of an ultrathin insulator layer between the metal and semiconductor layers in a Schottky junction can substantially reduce Fermi level pinning [99]. A similar trend in the reduction of Fermi level pinning was also reported in other studies [38,100]. Esposito et al. [27] proposed a novel MIS-based photoelectrode architecture (Fig. 9) that allows for stable and efficient water-splitting activity using narrow-band gap semiconductors. In the study, the performance of Si-based MIS photocathodes was substantially improved through the combination of a high-quality thermal SiO₂ layer and bilayer metal catalysts of Ti and Pt layers, respectively. Under light illumination, the thin and negatively charged inversion layer induced by the electrolyte would significantly reduce photogenerated charged carriers recombination, allowing electrons to be transported over a very long distance \( \sim (L_e + D) \). The benefits of reduced recombination have been fully established in previous studies [101,102] for MIS-type photovoltaic cells based on inversion layers (Fig. 10). The lateral transport of electrons within the inversion layer can be ascribed to the differences in the band alignment of MIS and liquid junctions, as well as the lateral gradients in electron concentration bolstered by non-uniform illustration from shading. These findings have important implications for the further development of MIS-based photoelectrodes and offer the possibility of achieving a highly efficient PEC water-splitting reaction.

Arquer et al. [51] also investigated the effects of an insulator layer on MIS nanojunction structures. They developed a MIS nanojunction heterostructure for plasmo-electric energy conversion, which is a novel architecture to harvest hot electrons derived from plasmonic excitations. In the study, the insulator interfacial layer was found to play a crucial role in the interface passivation. This is a requisite in photovoltaic applications to achieve higher open circuit voltages of up to 0.5 V and fill factors of 0.5 (i.e., the coefficient parameter). The introduction of an insulator layer is observed to modify simultaneously the hot-electron injection and transport, respectively. In addition, they also investigated the influences of passivation on different material configurations and characterised different types of electron transport depending on the initial plasmon energy band. It was found that the PCE of nanopatterned silver electrodes was 0.03%. This design of nanostructures can increase the poor efficiency of electron-hole generation of photon radiation, which surmounts the limited applications of complex metallic nanostructures in the past.

However, the key challenge to achieving a higher performance MIS nanojunction structure is the low quantum efficiency of this novel architecture. The low quantum efficiency of the novel MIS nanojunction structure, which is far from the theoretical efficiency, can be attributed to the following limitations: (i) poor efficiency of electron-hole generation over photon reradiation for localised surface plasmon resonance (LSPR); (ii) small tunnelling probability; and (iii) cooling and recombination rates of electrons in the metal are faster than the tunnelling rate into the semiconductor. These limitations can be surmounted with the use of more-complex metallic structures with tailored photonic density of states [51]. This enables an increase in plasmon-to-hot electron conversion efficiency by manipulating the interfacial electronic properties. A proper tuning in the...
Interfacial electronic properties of the resultant plasmonic MIS nanojunction structure is crucial to vary the rates of radiative and Landau damping mechanisms, which can result in favourable hot-electron generation. In addition, the use of plasmonic nanostructures supporting Fano resonances also can reduce re-radiation channels to increase hot electron generation. Overall, the engineered MIS nanojunction structures are employed to improve hot electron collection. Additionally, the research on novel passivating layers will open up exciting opportunities for precise control of the transport and electronic properties of these MIS-based devices. This will drive future developments towards achieving high quantum efficiency, open circuit voltage and fill-factor.

Scheuermann et al. [38] discussed the potential effects on water oxidation performance by varying (1) the nanoscale TiO$_2$ thickness and (2) different catalysts in the catalyst/TiO$_2$/SiO$_2$/Si MIS-based anodes, as shown in Fig. 11(a). Their study found that uniform ALD-TiO$_2$ films with 1-12 nm thickness on degenerately doped p$^+$-Si semiconductor substrate are capable of yielding water oxidation overpotentials of 300-600 mV at 1 mA/cm$^2$ in aqueous solution (pH0-14). In addition, they investigated the electron-hole transport through the Schottky tunnel junction structures of varying TiO$_2$ thickness using the reversible redox couple of ferri/ferrocyanide. Through their study, it was found that the dependence of water oxidation overpotential on ALD-TiO$_2$ thickness exhibits a linear trend that corresponds to approximately 21 mV of added overpotential at 1 mA/cm$^2$ for every nanometre of TiO$_2$ thickness ($\approx 20 \text{nm}$). For thinner ALD-TiO$_2$ films ($<2 \text{nm}$), an approximate thickness-independent water oxidation overpotential was observed. The linear behaviour for photoanodes with thicker TiO$_2$ films ($>2 \text{nm}$) is consistent with the predicted effect of bulk TiO$_2$-limited electronic conduction on the voltage required to sustain the current density across the TiO$_2$/SiO$_2$ insulator stack (Fig. 11b).

In a similar study, eight different metal catalysts of 1–3 nm thickness were studied: iridium (Ir), ruthenium (Ru), platinum (Pt), aluminium (Al), nickel (Ni), gold (Au), and cobalt (Co). The study concluded that both the ultrathin Ir and Ru films (3 nm) thickness were studied: iridium (Ir), ruthenium (Ru), platinum (Pt), aluminium (Al), nickel (Ni), gold (Au), and cobalt (Co). The study concluded that both the ultrathin Ir and Ru films (3 nm) resulted in the highest water oxidation performance.

**Metallic collector**

Based on the MIS structure mechanism, the metal layer plays an important role in ensuring high performance on solar conversion efficiency. Under light exposure at the...
inversion bias, excess electron-hole pairs are generated in semiconductors and contribute to the photocurrent. For the MIS structure with a non-transparent metal gate, the incident light is incorporated into the semiconductor from the edge of the metal gate. To increase the photocurrent, in general, a transparent gate could be utilised and the incident light would be incorporated into the semiconductor directly from the gate. Transparent gates can be roughly classified into two categories. In the first category are the transparent conducting oxides (TCOs) such as indium tin oxide (ITO) or zinc oxide (ZnO). However, the traditional n-type TCO has a large-hole effective mass and a low-hole conductivity. In the second category are the metal films with thicknesses of approximately 10 nm. Because the metal film is so thin, absorption of incident light in the metal is suppressed. A suitable selection of the metal in the MIS structure may reduce the dark current. If high work-function metal were used, the dark current could be decreased with the suppression of electron tunnelling from the metal to n-Ge. Dark inversion current reduction has been achieved with the high work-function metal, Pt (5.65 eV), instead of the typical low work-function metal, Al (4.1 eV), for Ge MIS structure. On the other hand, using a high work-function metal contact would cause significant light attenuation from the thick protection coatings, which would lead to decoupling of light absorption and an electrochemical reaction. It would be interesting to examine the earth-abundant transition metals with a high work function (such as Cu, Ni, Mo, etc.).

The suitable gate electrode selected here is Al instead of Pt, which has been suggested. If the semiconductor is n-type, then the selection of the high work-function metal, Pt, can suppress the electron-tunnelling current from the metal to the semiconductor at the inversion (negative) bias. However, for this SiGe/Si QDIP structure, the semiconductor is p-type. Pt will lead to a hole-tunnelling current at the inversion bias, which should be avoided. It is well known that Ni-based catalysts exhibit the highest OER activity in basic conditions among first-row transition metals. For example, in Kenney’s report on the Ti/n-Si/SiO₂/Ni MIS structure, the thin Ni film on Si played multiple roles during PEC water oxidation. First, the metallic Ni at the n-Si interface formed a junction to afford band bending, thereby favouring charge separation and motion of photoexcited holes towards the OER catalyst-electrolyte interface. The Ni film thickness provides a degree of tuning of the built-in potential and photovoltage. Second, surface Ni species served as the active electrocatalyst for OER. At high potentials, oxidised Ni species are formed in situ and act as OER active sites, and the OER activity is only slightly inferior to that of precious metal catalysts. Finally, the Ni/NiO film provides excellent protection to Si. In particular, remarkable stability was conferred by a 2-nm Ni coating on the Si photoanode in a mixed aqueous K-borate/Li-borate (pH = 9.5) electrolyte.

Ir film is also suitably employed as a metal collector; for example, Chen et al. [97] used a high-quality ultrathin TiO₂ within the tunnelling range to protect a n-Si photoanode and a thin Ir film for catalysing an OER reaction. This structure showed the champion solar-to-oxygen conversion efficiency (SOCE) of 0.37% due to the high barrier height defined by the MIS junction and the high activity of Ir noble metal. This technique remains a challenge when used on other crystal structures or high-profile photoelectrodes.

Earth-abundant materials are preferred for large-scale production of solar fuels. A few other recent studies have demonstrated the capability of using transition metal oxides or a single layer of graphene to protect and catalyse n-Si photoanodes for water oxidation. The uniform coating of metal oxide does not provide a large surface area, which is important for non-noble metal catalysts with inferior catalytic activity. Due to the pinholes developed during fabrication or operation, long-term stability of the thin oxide is also a concern. An insulating layer can almost fully passivate the semiconductor surface. In this case, the semiconductor’s equilibrium band bending is dominated primarily by the difference between the (n-type) semiconductor electron affinity and the metal work-function, following the Schottky-Mott model. Then, with the appropriate semiconductor-metal combination (n-semiconductor/high work-function metal; p-semiconductor/low work-function metal) the semiconductor interface will be strongly depleted or even inverted. In the latter case, a p-n homojunction forms underneath the insulating layer.
**MIS design**

To be utilised in a commercial process, a photoelectrochemical water-splitting device should have an affordable catalyst that minimises the overpotential and increases the efficiency of the water oxidation half-reaction, and the MIS device must be capable of absorbing a large fraction of the solar spectrum. In comparison with Schottky barrier solar cells, MIS Si solar cells with an insulator layer (typically SiO$_2$) between the metal and the Si show higher open circuit voltage ($V_{oc}$) and superior device performance. The purpose of the insulator layer in the MIS solar cells is to block the majority carriers injected into the metal at forward bias to reduce surface recombination. However, as for the conventional MIS Si solar cells, elevated temperature is necessary to passivate the surfaces, which is critical for surface passivation and carrier transportation. A possible improvement is to passivate the semiconductor with an ultra-thin dielectric, allowing a lighter (either local or global) dopant diffusion with a capping layer applied in the non-metallised regions. A possible improvement is to passivate the metallised surface regions with an ultra-thin dielectric, allowing a lighter (either local or global) dopant diffusion with an insulator layer (typically SiO$_2$) between the metal and the Si, which not only complicates the fabrication process but also increases the energy consumption and cost to a certain extent.

Therefore, investigation of high quality but low-cost insulating layers is of great importance for future MIS Si solar cells. Graphene oxide (GO), a derivative of graphene, attracts much attention in optoelectronic devices due to its solution processability as well as its tunable work function. These studies experimentally demonstrated that solution-processed GO can be used as an effective insulating layer for MIS Si solar cells. Compared with the conventional insulating SiO$_2$ layer, the preparation of GO via solution processing has a far lower temperature, which can minimise the grain boundary diffusion in doped crystalline Si, preserve minority carrier lifetime and reduce energy consumption. In addition, the highly water-soluble GO nanosheets can produce a good contact with the hydrophilic silicon surfaces, which is critical for surface passivation and carrier transportation. A possible improvement is to passivate the metallised surface regions with an ultra-thin dielectric, allowing a lighter (either local or global) dopant diffusion to be used. This dielectric must be sufficiently thin to present negligible resistance to current flow (possibly via quantum mechanical tunnelling) whilst being sufficiently thick to provide appreciable surface passivation. The same ultra-thin layer can be applied to the entire wafer surface with a capping layer applied in the non-metallised regions.

The metal layer is vital, however, as very little charge will pass without this layer acting as a tunnel current mediator between the silicon substrate and redox species in solution; a several order-of-magnitude decrease in current was previously observed when the oxygen-evolution-reaction metal was omitted. Without a sufficient density of states, tunnelling will likely be dramatically reduced, thus limiting the overall device efficiency. Changing the metal is anticipated to have two primary effects on the performance of a Schottky junction photoanode device: (1) altering the built-in potential essential for separating the photo-generated excitons by changing the catalyst work function, and (2) altering the water oxidation kinetics by changing the nature of the catalytic site. If the Fermi level in the MIS device was pinned, the photovoltage could no longer be manipulated to improve device performance. The thickness of the metal was also varied to determine how this affected water oxidation and charge transfer efficiency. However, even-thinner metal layers could be employed in photoelectrochemical water splitting devices, as efficiency may not suffer in basic and neutral solutions and should decrease only slightly in acid, whereas the amount of precious metal catalyst, and thus the cost, could be reduced.

In addition to varying the thickness of the metal layer, the identity of the catalyst should be varied. Water-oxidation catalysts that are more earth-abundant are desirable. Moreover, different catalysts may be optimal for different electrochemical reactions. It is reported that Pt is not as good a water oxidation catalyst as Ir or Ru. Despite its lower efficiency for catalysing water oxidation, the Pt layer still demonstrates a comparable ability to mediate charge transfer to and from the silicon substrate as evidenced by the ferri/ferrocyanide half peak-to-peak splitting result. Gold is not a good water oxidation catalyst unless extensively nanostructured and combined with other materials. The search for a cheap, efficient and robust water oxidation catalyst made from earth-abundant elements has led to the discovery of a cobalt-phosphate (Co-Pi) catalyst found to oxidise water in neutral pH.

**Other photovoltaic structures based on MIS nanojunctions**

The defining similarity between PEC and PV devices is that both are designed to harness the energy of hole-electron pairs created by light absorption (usually in a semiconductor or a molecule), by separating them and causing them to recombine through a work-producing route. The defining difference is that a PEC device contains an electrolyte phase, in which ions carry the moving charge, and electrode/electrolyte interfaces at which electrochemical reactions occur. PEC cells can also be configured as ‘wet PV devices’. A number of different approaches are possible with semiconductors as the photo converter. The most direct, brute force approach employs a solid-state photovoltaic solar cell to generate electricity. The electrolysis of water at a reasonable rate in a practical cell requires applied voltages significantly larger than the theoretical value (1.23 V at 25 °C), and electrolysis energy efficiencies of approximately 60% are typical. Thus, the efficiency of the combined solar/electrolyser system using commercially available components is close to the desired 10% defined for solar hydrogen generation. Moreover, the components are rugged and should be long-lived. The problem with such a system is its cost. Solar photovoltaics cannot currently produce electricity at competitive prices, and hydrogen from water electrolysers is significantly more expensive than that produced chemically from coal or natural gas. Another alternative system involves the semiconductor photovoltaic cell immersed directly in the aqueous system. At the least, this eliminates the costs and mechanical difficulties associated with separate construction and interconnection of solar and electrochemical cells. In one such system, the electrodes are composed of single or multiple junctions based on semiconductors that are irradiated while they are within the cell. This simpler apparatus is attained at the cost of encapsulating and coating the semiconductors to protect them from the liquid environment and most likely with a more limited choice of electrocatalyst for O$_2$ or H$_2$ evolution as shown in Fig. 13.
In principle, the direct PEC water-splitting device for molecular cleavage of water molecules into hydrogen and oxygen [5] combines a photovoltaic cell and an electrolyser into a single device. Because MIS-based structures are widely used in the fabrication of photovoltaic cells, recent developments in photovoltaic cells are also reviewed, as they can be potentially applicable in the development of photoanodes for water-splitting applications.

As previously discussed, the ultrathin insulator layer plays an important role in the MIS nanojunction structure. In this study, we focused on the different insulator layers used in the MIS-based photovoltaic cells that are replicable for PEC water-splitting devices. This finding is observed because the characteristics of an MIS Schottky junction and a p-n junction are similar, as they are based on similar minority carriers transport and activation energies [103,104]. In the previous section, the significance of a native oxide layer of SiOx in the Si-based MIS solar cells on efficient charge carriers’ separation and minority carriers’ transport through tunnelling was elaborated and discussed in detail. The transport mechanism was proven on the carbon nanotube (CNT)/silicon (Si) solar cells, where improved device characteristics were observed after the insertion of a thin SiOx layer on the Si surface [105]. In contrast, Jung et al. [32] found that single-walled carbon nanotube (SWCNT)/Si solar cells showed that enhanced power conversion efficiency (PCE) was achieved when the ultrathin insulator layer of SiOx was removed by using HF. In this instance, it was reported that the presence of an insulator SiOx layer in the SWCNT/Si solar cells could significantly degrade the short circuit current density (Jsc), which is inconsistent with the MIS Schottky nanojunction model.

Kim et al. [24] fabricated Si-based MIS solar cells with ultrathin Al2O3 films of 1-6 nm gate dielectric and SiN4 films by using RPALD at 300 °C and room temperature, respectively. The resultant Si-based MIS solar cells were fabricated with a resistivity of 1 Ω cm on p-Si semiconductor wafers passivated with ultrathin Al2O3 and SiN4 films and were able to achieve a relatively high energy conversion efficiency of 8.21%. As Al2O3 films formed by RPALD indicate a self-limiting surface reaction, they were able to offer excellent atomic-level control of the deposited film thickness. Smooth interface and uniformity of the Al2O3/silicon interfaces were observed. After the RPALD deposition of Al2O3 films on Si surfaces, the lifetime increased more than three times compared with those without Al2O3 films due to passivated surface effects. The interface state density in the SiN4/Al2O3 structure was approximately one order higher in magnitude than that with only the Al2O3 film because of the charges incorporated in the SiN4 film during the process. Song et al. [25] postulated that the ultrathin Al2O3 film forms a built-in potential on the bare p-Si surface due to the presence of negative fixed charges within the Al2O3 film. These negative fixed charges will attract the majority carriers (holes for p-Si) to form an accumulation layer of holes close to the surface of p-Si, leading to an upward band bending. In this instance, the height of the band bending is defined as the surface potential (i.e., barrier) of the bare p-Si. When the minority carriers (i.e., electrons for p-Si) are repelled from the p-Si surface, an improvement in the lifetime of minority carriers that is called the field-effect passivation can be realised (Fig. 12).

Bullock et al. [47] investigated the contact properties of Al2O3 and SiO2 passivating dielectrics in MIS-typed contacts on the phosphorus-diffused regions. In both cases, the increase in dielectric thickness leads to a reduction in surface recombination but an increase in the contact resistivity. The optimum thickness of ALD-Al2O3 and thermal SiO2 layers were found to be 22 Å and 16 Å, respectively. The SiO2 MIS contact was found to have a greater thermal stability than that of the Al2O3. However, it is worth noting that the Al2O3 and SiO2 passivated contacts also could be applied uniformly to the n+p rear side of a p+nnn+ MIS structure. In that case, the tolerable contact resistivity for a 100% metal contact fraction is far higher than a partial metal grid. Liu et al. [44] reported that the solution-processable GO thin film was initially utilised as an insulator layer in the construction of Si-based MIS solar cells as shown in Fig. 13. It was found that the efficient water-soluble GO nanosheets with controlled thicknesses produced a good contact with the hydrophilic Si surfaces. The average open circuit voltage (Voc) of the GO-incorporated Si-based MIS solar cell was increased by 0.2 V, whereas the PCE was found to be 88% higher than that of the corresponding Schottky solar cells. These improvements via the incorporation of GO nanosheets in the Si-based MIS solar cell are attributed to the increased built-in potential, as well as the reduced interface defects that result in reduced carrier recombination. The ability to establish a low-cost and solution-processable thin insulating layer will open the door for wide application in photovoltaic and other optoelectronic devices. This GO insulator can also be applied as an effective insulating layer for MIS structure in water-splitting PEC cells. These results open up a new approach to increasing built-in potential and reducing interface defects, which is useful in the MIS water-splitting application.

In recent years, many studies have focused on utilising graphene [6,44,58,106], particularly the GO because it is a good insulator material and an intermediate product to form graphene. Thus, it has been significantly used to form a graphene insulator layer for applications in MIS nanojunction structures [58]. The insulator thickness decreases as the dimension of a transistor becomes smaller, resulting in a significant gate tunnelling current. Such a tunnelling current in the vertical direction (from metal to semiconductor or from semiconductor to metal) of a MIS structure has been employed in a number of applications, such as solar cells. For solar cells, the thickness of the insulator layer in the MIS tunnelling diode is critical. For example, if the insulator is too thick, only limited tunnelling can occur, leading to a small responsivity. In contrast, if the insulator layer is too thin, Fermi level pinning may degrade the device current-voltage characteristics. In addition to the thickness dependence, insulator composition also affects the IV characteristics of MIS devices. The GO layers were deposited onto Si substrates to form a MIS tunnelling structure and the optoelectronic properties were studied. The accumulation of dark current and inversion photocurrent from the GO-incorporated MIS-based device were found to be superior to the control MIS-based device. The incorporation of GO also improved the rectifying characteristic of the diode and enhanced its responsiveness as a photodetector. At the gate voltage of 2 V, the photo-to-dark current ratio for the GO-incorporated MIS-based device was 24, which was higher than the measured ratio in the control MIS-based device, as shown in Fig. 14. GO
was deposited onto the Si substrate to form a Al/GO/native oxide/Si MIS tunnelling diode. Yoo et al. [57] fabricated the MIS-based devices using SiN\textsubscript{x}:H thin films as insulator layers by PECVD, where the insulator layers were analysed in the temperature range of 100–400 K by using capacitance–voltage (C–V) and current–voltage (I–V) measurements. In addition, the annealed SiN\textsubscript{x}:H thin films were evaluated by using the electrical properties at different temperatures to determine the effect of surface passivation. From the study, they reported that the energy conversion efficiency of 18.1% was achieved under one-sun standard testing conditions for large-area (156 mm × 156 mm) Si-crystalline MIS-based solar cells. SiN\textsubscript{x}:H films function well as gate insulators in MIS devices due to their good dielectric properties, being excellent barriers against moisture and mobile ions. Moreover, the deposition method PECVD in this report is a quite cost-effective, performance-enhancing technique that can provide an anti-reflection coating, as well as a surface passivating layer, for crystalline-silicon solar cells. Wadhwa et al. [102] proposed a new type of Si-crystalline MIS-based solar cell as shown in Fig. 15. In comparison, the newly proposed Si-crystalline MIS-based solar cell is similar to the MIS-based PEC water-splitting cell. Within the Si-crystalline MIS-based solar cell, the liquid electrolyte creates a depletion (inversion) layer in the n-type Si wafer substrate. However, no regenerative redox couple is present to facilitate the charge transfer between the Si and the counter electrode. Instead, the holes trapped within the electrolyte-induced inversion layer will diffuse along the layer until they come to widely spaced gridlines for extraction. The gridlines consist of a SWCNT film etched to cover only a fraction of the n-Si surface. Further modelling and simulation studies showed that the inversion layer is a natural consequence of the device electrostatics. The electronic gating was demonstrated to boost the efficiency whereby the cell achieved a PCE of 12%, exceeding that of dye-sensitised solar cells. Such cells can be applied to trap more of the light reflected from a surface by the texturing of the Si. Additionally, this MIS junction cell with SiO\textsubscript{x} layer replaced by the ionic liquid electrolyte may provide the solution to the previous degradation problem even without the need for active gating (although gating incurs little energetic penalty, it does add to the device complexity).
large spacing permitted between the grid lines in this electrolyte-coated device indicates that by filling the nanoholes with electrolyte, we would obtain the benefit of both the inversion layer and the additional light trapping.

Previously, it was known that the annealing temperature also has an important effect on the characterisation of MIS nanojunction structures. For instance, Ortiz et al. [60] investigated the electrical properties of Au/AlN/n-Si/Ga MIS-based diodes by capacitance-voltage (CV) and current-voltage (IV) techniques. In the study, the MIS-based diodes synthesised via the molecular beam epitaxy approach showed improved electrical properties after annealing treatment at 200 °C under nitrogen ambient, which were attributed to partial out-diffusion of mobile ions from the thin films. The

![Fig. 14](image_url) Band diagrams of (a) Al₂O₃/p-Si and (b) Al₂O₃/SiO₂ 1L/p-Si structures. (c) Band diagram of Al₂O₃/SiO₂ 1L/p-Si structure including interface states; red open and filled rectangles denote acceptor-like states near the conduction band and donor-like states near the valence band, respectively. (d) Calculated surface potentials of Si as a function of the applied voltage to an MIS capacitor for a σ rms value of approximately 11.7 nm; solid black, red, and blue lines represent the surface potential in panels a–c, respectively, while the blue dashed line denotes the applied voltage of −0.65 V for a flat-band condition. Reproduced from Ref. [25].

![Fig. 15](image_url) (a) Device architecture of GO-based MIS Si solar cells, with the inset: a schematic of GO structure; (b) dark and photocurrents versus voltage characteristics of GO and control devices. The inset shows the structures of GO and control devices. The accumulation (negative bias) dark current and inversion (positive bias) photocurrent of the GO device are superior to the device. Reproduced from Refs. [44, 58].
use of II–V nitrides thin films as insulating materials has been extensively studied for its potential applications in optoelectronics and microelectronics. One of these promising materials is AlN, which has a high dielectric constant, excellent thermal conductivity, wide bandgap and high velocity of sound amongst others. Insulators with high dielectric constant such as AlN are particularly suitable for applications in MIS devices where thermal SiO$_2$ cannot be grown. The performance of these devices will strongly depend on the insulator-semiconductor interface quality. In another study, Sönmezoglu et al. [45] reported on the fabrication of a Cu/ TiO$_2$/n-GaAs MIS nanojunction structure. The variation in electrical characteristics of this MIS nanojunction structure was analysed as a function of temperature using current-voltage ($I$-$V$) measurements in the temperature range of 50-290 K with a step increase of 40 K. It was shown that the ideality factor ($n$) decreases with increasing temperature, whereas the zero-bias barrier height ($\phi_{B0}$) increases with increasing temperature. In this instance, the Gaussian potential model was used to explain the barrier height inhomogeneity observed in the MIS nanojunction structure. This discrepancy can be explained by the local inhomogeneity at the metal-semiconductor interface by considering the fluctuation in the local surface potential. According to the Gaussian distribution, the value of the Richardson constant that was obtained from fitting the modified Richardson plot in the first 290-170 K region is in very good agreement with the theoretical value for n-type GaAs. The result showed that understanding the temperature dependence of electrical characteristics on this MIS nanojunction structure may be of great help in improving the quality of TiO$_2$ grown on GaAs substrates to aid the future development of device technology.

In a separate study, Voitsekhovskii et al. [52] found that the resistance in epitaxial film can significantly affect the measured electrical characteristics of MIS nanojunction structures based on HgCdTe by molecular beam epitaxy (MBE) at a high-frequency test signal. The formation of a near-surface graded-gap layer with high CdTe content in the epitaxial HgCdTe film leads to changes in both the low- and high-frequency capacitance-voltage (C-V) characteristics in the inversion mode. In addition, the formation of a near-surface graded-gap layer also leads to an increase in the density of mobile charges for the MIS nanojunction structures with anodic oxide film (AOF) and SiO$_2$/Si$_3$N$_4$ insulators.

Liu et al. [107] reported a novel MIS nanojunction structure configuration that can be used to measure the surface photo-voltage (LS) spectroscopy of p-GaAs and p-Al$_{0.37}$Ga$_{0.63}$As/p-GaAs structures, respectively. In the study, the p-AlGaAs layer was assembled on a p-type GaAs substrate grown by the MOCVD method. The SPV was found to be dependent on the incident photo-intensity, whereas the band-to-band excitation was adopted for the calculation of ideality factor. The ideality factor of this MIS nanojunction structure configuration was found to be 0.008 for samples with both sides polished under ambient air. As for the p-Al$_{0.37}$Ga$_{0.63}$As/p-GaAs MIS nanojunction structure, the minority carrier diffusion length in the GaAs substrate was determined from a linear plot of inverse SPV against the inverse absorption coefficient by intercepting the line with the x-axis. The SPV spectrum of the p-Al$_{0.63}$Ga$_{0.37}$/p-GaAs MIS nanojunction structure showed that the incident light is absorbed in the AlGaAs layer when the wavelength is $\lambda < 580$ nm but is absorbed in the GaAs substrate when the wavelength is between 580 nm < $\lambda$ < 870 nm.

Furthermore, Armin et al. [108] adopted a novel method of injection-charge extraction by linearly increasing the voltage in an MIS structure (MIS-CELIV) to measure both the electron and hole mobilities of organic semiconductors in a diode structure of relevance to organic solar cells and other organic optoelectronic applications (Fig. 16). The method is based upon the total blocking of one carrier type using a suitably placed wide-gap insulator. The standard CELIV protocol (i.e., reverse bias voltage ramp) is used to generate extraction transients of the forward-bias injected carriers, from which the transit time and mobility are measured. They concluded that other effects such as the photo-carrier generation efficiency or charge trapping outweigh any issues associated with charge carrier mobility in the operational organic solar cells. Seo et al. [50] achieved multilevel manipulation of resonant tunnelling in a MIS nanojunction structure in which the heterogeneous molecules of F$_16$CuPc and CuPc were embedded in the insulator layer to form a double-tunnelling junction (Fig. 17). In the study, the carriers were injected into the respective molecules at corresponding threshold voltages. This finding demonstrated a new multilevel operation of resonant tunnelling through organic molecules in a practical MIS-based device structure. Recently, Sun et al. [109] proposed a theoretical model on the electrical characteristics of metal-ferroelectric-insulator-semiconductor field-effect transistors (MFIS-FET) by considering the history-dependent electric field-effect and the mobility model. It was concluded that the improved theoretical model is suitable for simulating the electrical characteristics of MFIS-FET. This improved theoretical model is expected to provide some guidance to the design and performance improvement of MFIS structure devices in the near future. Arquer et al. [51] introduced a MIS heterostructure of ITO/ TiO$_2$/Al$_2$O$_3$/Ag for plasma-electric energy conversion, which is a novel architecture to harvest hot-electrons derived from plasmonic excitations. A hot-carrier photocurrent could be obtained when energetic electrons derived from LSPR damping are emitted over or tunnel to the semiconductor (Fig. 18). In this instance, the LSPR excited by an incoming photon can result in the creation of an electron-hole pair, which can be split by the built-in field in the interface. Unpassivated interfaces contain traps that can result in Fermi level pinning, deteriorating the junction from the ideal case. This has resulted in a suppression of open-circuit voltage ($V_{oc}$) and no PCE, as shown in Fig. 18a. Depending on their energy level, the excited electron can either tunnel to the TiO$_2$ layer or undergo Schottky emission over the barrier. The height of the barrier determines the difference of metal work-function ($W_m$) and insulator electron affinity, as shown in (Fig. 18b).

**Summary and future outlooks**

Because current mass production methods for hydrogen are unable to enhance its cost-competitiveness over conventional fossil fuels, new and novel concepts must be introduced that combine very high PEC cell efficiency with cost-effective materials. In this instance, the integration of MIS nanojunction structure into a PEC water-splitting cell is a good approach that
has achieved some successes in recent years. In this review paper, we have discussed recent developments and prospects of MIS nanojunctions for hydrogen evolution from water splitting in PEC cells in the hope that readers could find new views in this niche area. Other important aspects such as the basic principles of MIS, generalised approaches for synthesising MIS nanojunctions and the key application challenges of PEC water-splitting cells are also addressed to close the knowledge loop and present holistic interconnections among the various aspects. Furthermore, recent developments of photovoltaic

Fig. 16  Effect of interface on the junction properties and resultant $I$-$V$ characteristics. LSPR excited by an incoming photon can result in the creation of an electron-hole pair, which can be split by the built-in field in the interface. Un-passivated interfaces (a) contain traps that can result in Fermi level pinning deterioration the junction from the ideal case (solid versus dashed lines, respectively). This results in a suppression of open-circuit voltage ($V_{oc}$) and no power conversion efficiency (PCE). (b) Depending on their energy, the excited electron can either tunnel to the TiO$_2$ or undergo Schottky emission over the barrier. The height of the barrier determines the difference of metal work-function ($W_f$) and insulator electron affinity. Reproduced from Ref. [51].

Fig. 17  (a) Schematic of device. Not shown is the EMI-BTI ionic liquid electrolyte that extends across both the gate electrodes SWCNT film and the n-Si junction. (b) Photograph of a SWCNT film across the exposed n-Si within the gold electrode window in which the SWCNT film was etched to form the grid pattern shown. The seeming break in the gridlines at the bottom edge of the window is an illustration. The lines run continuously up onto the gold electrode. Reproduced from Ref. [103].

Fig. 18  Schematic of MIS-based diodes in the case of (a) electron-only and (b) hole-only configurations. Electron (hole) mobilities can be measured from electron only (hole only) MIS-based diodes. The injected or induced charge carriers are distributed near the interface of the insulator/semiconductor. Reproduced from Ref. [108].
cell structures based on MIS principles have also been reviewed because the PEC cells are usually coupled with photovoltaic cells and electrolyzers for enhanced efficiency in water splitting. Previously, it was also reported that the MIS-based electrode could be a promising candidate to improve significantly the cost-competitiveness of hydrogen energy produced via the PEC water-splitting route due to the potential mass production of low-cost Si MIS-based electrodes. Moreover, the ALD method is widely used in the semiconductor device industry, indicating the method’s potential to be employed on a large-scale basis in energy applications such as solar fuel synthesis [29].

The MIS structures open up some additional possibilities for a solar water-splitting system with high efficiencies of 15% or greater. However, this is still a long distance from being integrated into a viable water-splitting device. For instance, the low cost of Si and its instability under anodic conditions make it an ideal material to demonstrate the effectiveness of a protection scheme. However, its band gap (1.1 eV) limits the amount of photovoltage that can be generated for water splitting. The use of semiconductors with larger band gaps than Si under similar surface protection/electrolyte conditions should result in a shift of the OER photocurrent onset to more-negative potentials. Other criteria also need to be considered in the successful large-scale synthesis of hydrogen from PEC water splitting, such as the stability and durability of photoactive materials against photocorrosion, regenerability of the surface activity of spent photoactive materials and others. In the long term, there are also many challenges in the commercialisation and upscaling of the PEC technology, such as separation, purification, transportation and utilisation of solar hydrogen energy.

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References

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