Integration of metal nanowire networks on silicon-based solar cells

A thesis submitted for the degree of

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by

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Declaration

I, Shouyi Xie, declare that this thesis entitled:

"Integration of metal nanowire networks on silicon-based solar cells"

is my own work and has not been submitted previously, in whole or in part, in respect of any other academic award.

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Abstract

Photovoltaics (PV) is the effect of converting light into electricity. It can be used to harvest the “eternal” solar energy without producing greenhouse gases, and thus is believed to be one of the most promising solutions to the ever increasing demand for energy and exacerbating global climate change. Given the great potential, continuous efforts have been spent to improve the efficiency and decrease the costs of PV devices (i.e., solar cells) to make them readily affordable for the civil use.

The efficiency and cost of solar cells are fundamentally determined by the PV materials and the related manufacturing technologies. Silicon (Si)-based solar cells have been the dominant PV technology that takes over 90% of the market share ever since their commercialisation in 1960s due to the material abundance, comparatively high efficiency and low costs. Considering their overwhelming advantages to the other types of solar cells, Si-based solar cells are expected to continue leading the PV market share in the near future.

Crystalline wafers and hydrogenated amorphous silicon (a-Si:H) thin films are the two main types of the Si-based solar cells, each with distinguished fabrication methods and material properties. The former is designed for higher efficiency with better material qualities and thicker absorbing layers, while the latter aims at achieving lower costs with lower requirements on the material quality and less Si consumption.

Recent advancements in nanotechnology have inspired a variety of new concepts to improve the solar cell performances by more efficiently manipulating photons and
electrons. Extensive research has been carried out on the integration of plasmonic nanostructures on the surface of solar cells, nanotexturing on the active layers of solar cells and even solar cells with nanostructured Si materials. However, most of these technologies only aim for enhancing the light absorption, i.e., optical responses of the solar cells.

Metal nanowire (NW) networks, being both transparent and conductive, are becoming increasingly attractive for the application of nanotechnology on solar cells. As front electrodes, they can allow the light transmission into the active layers and meanwhile extract the light-generated current out. Thus they are able to link to both the optical and electrical aspects of the solar cells. Moreover, with rapidly improved fabrication techniques, they have shown outstanding optical and electrical performances that are comparable or even outperform the conventional transparent electrodes. Other attractive features of the metal NW networks on solar cells are their inherent advanced light trapping effects such as the plasmonic near-field enhancement, the plasmonic far-field scattering, and the waveguiding effect.

The application of metal NW networks as transparent electrodes has been demonstrated on a variety of solar cells, including the organic solar cells, the dye-sensitised solar cells, the copper indium gallium selenide (CIGS) solar cells, and the Si micro/nanowire solar cells. However, their potential applications on the crystalline Si wafer and the a-Si:H thin film solar cells have rarely been investigated. The advanced light trapping effects were mostly designed for ultrathin Si layers rather than functional solar cell devices.

One of the main aims of this thesis is to investigate the use of metal NW networks as transparent electrodes on the crystalline Si wafer solar cells. Silver NW (AgNW) networks were selected because of their high material conductivity, good ohmic contact with Si and well-developed fabrication methods. Before the AgNWs were practically integrated onto the solar cells, we performed numerical simulations to gain a thorough understanding on the optical behaviours of the AgNW networks.
The transmittance of the circular AgNWs that were produced by the solution-processed chemical methods and the rectangular AgNWs that were produced by the lithographical patterning methods were comparatively studied dependent on the NW densities, the incident light polarisations, the substrate materials and the dielectric embedding materials. We concluded that with the same electrical conductivity, the circular AgNWs can optically outperform the rectangular AgNWs due to less absorption and reflection by the AgNWs.

Based on the above conclusion, we selected the solution-processed circular AgNWs as a low-cost and high-performance candidate for the application on the crystalline Si wafer solar cells. The spin-coating method was utilised for fabricating large-size, high-uniformity AgNW networks on substrates. Due to their aggregation-free nature, the as-prepared AgNW networks had superior optical transmittance and electrical conductivity to the conventional transparent conductive oxide films. After integrating the AgNWs onto the solar cells, we developed an optimised two-step annealing process to form the ohmic contact between the AgNWs and the Si surface and effectively extracted the current. A significant efficiency enhancement of 19% was achieved due to the high conductivity of the AgNW network, while the optical loss due to the AgNWs was negligible.

Apart from the AgNWs, the application of other metal NWs is also a research interest of this thesis. We demonstrated the use of solution-processed ultrathin gold NWs (AuNWs) for the enhanced light trapping effects of the indium tin oxide (ITO) films on the crystalline Si wafer solar cells. Langmuir-Blodgett technique was applied as a facile and scalable method to fabricate highly uniform and aligned gold nanomembranes (AuNMs) and transfer them onto the solar cells. The roughened surface morphology was created for the ITO deposited on the top of the AuNMs. The enhanced anti-reflection effect on the AuNM/ITO integrated film on Si was confirmed by both experimental characterisation and numerical simulation. We obtained a photocurrent enhancement of 13% for the solar cell with the AuNM/ITO integrated film due to the enhanced light trapping, which is 5% higher than that of the reference solar cell with the ITO film only.
The outstanding optical and electrical performances of the metal NW networks are also very attractive for the application as transparent electrodes on the a-Si:H thin film solar cells. We theoretically investigated the optical properties of metal NW networks on the a-Si:H solar cells. The dependence on the shape, dimension, density, position and material of the NWs were systematically studied as guidance for designing the experiments.

As a low-cost approach, solution-processed AgNW networks were experimentally demonstrated as transparent electrodes on the a-Si:H solar cells. We showed that the design of AgNWs on top of the ITO charge collection layers can lead to significantly improved solar cell performances due to the high electrical conductivity of the AgNWs. Finally, based on a few major findings from the simulations and the experiments, we proposed potential future work to further explore the applications of AgNW networks on a-Si:H solar cells.

This thesis for the first time presents the theoretical and experimental study on the use of metal NW networks as transparent electrodes and light trapping schemes on the crystalline Si wafer solar cells and the a-Si:H thin film solar cells. The well understood optical behaviours, outstanding electrical conductivity and well developed fabrication methods of the metal NW networks make them very promising functional parts that can improve both the optical and electrical performances of the Si-based solar cells.
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Chapter 1

Introduction

Photovoltaics (PV) is believed to be one of the most promising solutions to the energy challenge and global climate change we are facing since it can be used to harvest the “eternal” and abundant energy from the sun. The PV process in principle involves three major steps: (i) absorption of photons, (ii) energy transfer from photons to electrons and (iii) transport of the generated charges out of the devices by the electrodes.

In spite of the continuous efforts on the better designs for solar cells and refined fabrication processes, PV is still facing its biggest challenge in terms of the practical application: the energy conversion efficiency of the solar cells needs to be further improved and the costs to be further decreased so that this technology can become competitive to the conventional fossil fuels and readily affordable for the civil use.

The efficiency and cost of the PV devices (i.e., solar cells) are fundamentally determined by the PV materials and the related manufacturing technologies. Figure 1.1 shows the market share of a few major PV technologies in 2008 (data from [1]). Clearly, silicon (Si)-based solar cells have been the dominant PV technology ever since their commercialisation in 1960s due to the material abundance and high efficiency at relatively low fabrication costs. It is expected that Si-based solar cells
will continue to play a leading role in the PV market in the near future [2]. The copper indium gallium selenide (CIGS) and Cadmium Telluride (CdTe) solar cells that also have remarkable market shares suffer from material scarcity and toxicity. In this figure the solar cells made of other materials such as the organic materials and the III-V materials that have less than 1% shares are not included. The application of these solar cells is limited by either of ultralow efficiency, material instability or ultrahigh fabrication costs.

![FIG 1.1 Market shares of a few major PV technologies in 2008.](image)

The advancements in nanotechnology over the past few decades have made revolutionary progress in the fields of optics and electronics, enabling human beings to manipulate photons and electrons in more efficient ways. Numerous nanotechnology-based Si solar cells thus have been developed aiming at higher efficiencies. Specifically, the solar cells integrated with plasmonic nanostructures have attracted intensive research interest in the very recent years [3]. By utilising the metallic nanostructures, light can be confined into sub-wavelength scale via resonant interaction with the free electrons on the metal/dielectric interface. This causes highly localised electric field with enhancement by several orders of magnitude and strong scattering ability, both of which lead to enhanced light absorption within the solar cells. While the metallic nanostructures normally induce intrinsic loss within the metal, other low-loss light trapping schemes have been introduced including the dielectric nanoparticles [4-9], the nanotexturing on the
surface of solar cells [10-12] and the nanostructured Si as absorbing layers in solar cells [13, 14].

However, most of these nanostructures are designed to improve only the optical performances of the PV process. Metal nanowire (NW) networks, which are both transparent and conductive, can be used as front electrodes of the solar cells. This is of particular interest as the front electrodes fundamentally link to both the optical aspects (steps (i) and (ii)) and the electrical aspect (step (iii)) of the PV process. Therefore, any improved designs on front electrodes tend to result in improved solar cell performances. For an electrode on the front surface of a solar cell in general, the most important design principle is to achieve a high transmittance while keeping the conductance as high as possible, which are essentially two contradictory factors. Encouragingly, the metal NW networks have shown a great potential as front electrodes as they have been found to have superior optical and electrical performances compared to the conventional transparent conductive materials.

Si-based solar cells and metal NW networks are both very promising fields for the practical application of PV technology. In this chapter, we provide a basic introduction to these two fields in terms of their physical and engineering background. The objectives and outline of this thesis are then discussed at the end of this chapter.

1.1 Silicon-based solar cells

According to the fabrication methods and the intrinsic material properties, the Si-based solar cells can be categorised into two major types: crystalline wafer solar cells and amorphous thin film solar cells. This section briefly introduces their distinctive structures, operational mechanisms and current challenges.
1.1.1 Crystalline silicon wafer solar cells

The Si materials used for the crystalline wafer solar cells are cut from the Czochralski or float zone grown high-purity Si ingots [15]. The schematic structure of a typical crystalline Si wafer solar cell is shown in Fig. 1.2(a). The active layer for light absorption is essentially a $p$-$n$ junction diode. A patterned gridline front electrode and a full-area rear contact are fabricated for charge collection and power output. Additional light trapping schemes such as the micro-structured texturing on the Si surface and the front dielectric anti-reflective layer (also acts as the passivation layer) are normally designed to further enhance the light absorption within the Si layer.

![Schematic structure of a typical Si wafer solar cell](image)

The operational mechanism of a Si wafer solar cell is illustrated by the band diagram in Fig. 1.2(b). Under light illumination, electron-hole pairs are generated...
within the \( p \)-type Si excited by the incident photon energy. The increase in the number of the minority carriers (i.e., electrons) in the \( p \)-type Si causes a gradient in the quasi-Fermi level (\( E_{Fn} \)), forcing the electrons to flow across the junction region into the \( n \)-type Si. The drifted electrons then diffuse towards the \( n \)-type Si surface driven by the carrier concentration gradient. When the diode is short-circuited, the electrons flow through the external circuit and recombine with the holes in the \( p \)-type Si, forming a light-generated current \( I_L \) (also called photocurrent) that is in the reverse direction of the dark current of the diode.

When an external load is added to the diode under light illumination, the current-voltage (I-V) characteristic of the diode can be simply considered as shifting down the dark I-V curve of the diode by the constant \( I_L \) as illustrated in Fig. 1.2(c). However, in practice, the solar cells generally have parasitic series and shunt resistance (\( R_S \) and \( R_{SH} \)) induced during the device fabrication, which could affect the final shape of the illuminated I-V curve. There are a few important parameters to characterise the overall performance of the solar cell including:

- **Short-circuit current (\( I_{SC} \))**: The current at \( V = 0 \). For an ideal solar cell without the parasitic resistances, this equals to \( I_L \). Practically, the value of \( I_{SC} \) is determined by how many light-generated charges can be exported out of the device. It can be affected by the light trapping schemes, the surface passivation conditions, the electrode design and fabrication, and many other factors.

- **Open-circuit voltage (\( V_{oc} \))**: The voltage at \( I = 0 \). This parameter is strongly dependent on the saturation dark current of the diode and thus the properties of the semiconductor.

- **Maximum power point voltage and current (\( V_{MP} \) and \( I_{MP} \))**: This is the operating point of a solar cell where the output power (\( V \cdot I \)) reaches the maximum value. The efficiency (\( \eta \)) of the solar cell is determined from this point under the standard one-sun air mass 1.5 global (AM1.5G) testing conditions where the power density of the incident light is 1000 W/m\(^2\).
• **Fill factor \((FF)\):** It is defined by \(V_{MP}I_{MP}/V_{OC}I_{SC}\). The fill factor characterises the squareness of the \(I-V\) curve. It is an important parameter to measure the effect of the parasitic resistances on the overall quality of the device.

Specifically, \(I_{SC}\), \(FF\) and \(\eta\) are all strongly related to the design and fabrication of the front electrodes. An important design criterion for the front electrodes on crystalline Si wafer solar cells is to minimise the shadowing and resistive power loss by reducing the width and spacing of the gridlines. However, in practice, the resolution of the gridlines is limited to the order of micrometre scale by the state-of-the-art manufacturing technologies. The application of metal NW networks has opened up the possibility of nanometre-scale front electrodes on crystalline Si wafer solar cells.

The crystalline Si wafer solar cells have a relatively high energy conversion efficiency due to the better intrinsic material properties such as longer carrier lifetime and larger carrier diffusion lengths. The wafer thicknesses are generally more than 100 \(\mu m\) for sufficient light absorption and thus a higher \(I_L\). However, large consumption of high-quality materials contributes greatly to the total costs of the wafer solar cells. Further reducing the wafer thickness is challenging for the state-of-the-art wafer cutting technologies since more materials are wasted during sawing. In addition, thinner wafers are more likely to break during handling. Furthermore, thinner wafers also suffer from reduced light absorption because creating textured structures for light trapping by conventional alkaline or acid etching would be not realistic for the wafers with thicknesses on the order of the texturing size.
1.1.2 Amorphous silicon thin film solar cells

The demand for low material costs of the Si solar cells has driven the development of hydrogenated amorphous Si (a-Si:H)\(^1\) thin film solar cells since their first discovery in the 1970s [19]. Instead of the ingot cutting technologies for the wafer solar cells, the a-Si:H thin films are deposited on substrates. A variety of deposition methods have been reported. So far the most popular method is plasma-enhanced chemical vapour deposition (PECVD).

The working principles of the a-Si:H thin film solar cells are similar to that of the crystalline wafer solar cells in terms of the energy band theory (Fig. 1.2(b)). However, due to the high defect density in the doped amorphous Si materials, the \(p\)-layer and \(n\)-layer of the solar cells have to be very thin (less than 20 nm) since the carriers would otherwise recombine before they can travel to the solar cell surfaces to be collected. An intrinsic amorphous Si layer (\(i\)-layer) in between the doped regions is deposited for light absorption and carrier generation. In such a case, the doped regions are only for setting up the internal electric field that drives the electrons and holes towards opposing surfaces.

There are two types of a-Si:H solar cells: \(p-i-n\) (or superstrate) and \(n-i-p\) (or substrate) structures as shown in Figs. 1.3(a) and 1.3(b), respectively. The cell types are named after the deposition sequence of the individual layers. The front transparent conductive oxide (TCO) film is applied for light transmission and charge collection while the back TCO film as a diffusion barrier between the \(n\)-layer and the metal electrode. For both types, the incident light comes from the \(p\)-layer side. Since the diffusion lengths of the carriers within the \(i\)-layer are generally less than 2 \(\mu\)m [20], the thickness of an \(i\)-layer is on the order of hundred nanometres for efficient carrier collections. However, this can incur insufficient light absorption. Textured surfaces on TCO films are usually introduced prior to

\(^1\) There are other types of Si thin film solar cells such as the hydrogenated micro-crystalline Si and the micromorph Si tandem solar cells, both of which have similar cell structures and fabrication methods to that of the a-Si:H solar cells. In this thesis we select a-Si:H solar cells as an representative of the Si thin film solar cells.
the deposition of the active layers for improved light trapping via increased light path lengths within the absorber layer.

![Diagram of solar cell structures](image)

**FIG. 1.3** Schematic structures of (a) p-i-n and (b) n-i-p type amorphous Si thin film solar cells with textured interfaces. Images from [21].

In spite of the long-term developed fabrication technologies, there are some intrinsic limitations for the state-of-the-art TCO films. On one hand, the TCO films need to be thick enough to ensure high electrical conductivity and thus low resistive power loss on the front electrodes. On the other hand, the thick films can have compromised optical transmittance and thus reduce the light absorption within the active layers. Moreover, high-vacuum deposition processes are normally required for high-quality TCO films. Some of the high-performance TCO materials such as indium tin oxide (ITO) contain toxic and scarce materials. Therefore, in order to improve the overall performances of the a-Si:H solar cells, one needs to seek for alternative transparent conductive materials that have better optical and electrical properties as well as low fabrication and material costs.
1.2 Metal nanowire networks

After less than one decade’s development, metal NW networks have rapidly emerged as one of the most attractive transparent conductive materials amongst all the nanomaterial-based networks due to their high optical and electrical performances [22]. The NWs, with the diameters from sub-tens to a few hundred of nanometres, are not visible to human eyes. They should have high aspect ratios (length/diameter) of more than 100 so that they can easily form conductive networks. Depending on the state-of-the-art fabrication methods, the formation of the metal NW networks could be either random or aligned on substrates, as shown in Figs. 1.4(a) and 1.4(b), respectively.

The random metal NW networks have less controllable network formation and NW dimensions. But they can be fabricated by a variety of simple and low-cost solution-processed methods that are readily scalable in industry integration such as spin-coating, spray-coating and roll-to-roll processing [23]. Furthermore, no high temperature or high vacuum deposition systems are required as for the TCO films, which means less potential damages will be introduced to the devices and the manufacturing costs can also be significantly reduced.

On the other hand, the aligned metal NW networks can have flexibly designed network formation and NW dimensions, but their applications are normally limited
to small scale due to high equipment costs and time-consuming fabrication processes. Encouragingly, the recent development on nanoimprint lithography has enabled the fabrication of large-scale and highly controllable nanostructures [24].

The transmission of the metal NW networks is governed by the direct light propagation through the open regions among the NWs as well as the plasmonic and optical interactions between the incident light and the NWs. Electrical conductivity of the networks is determined by a wide range of parameters including the material, quality, dimensions and density of the NWs, the junction resistance among the NWs and the formation and uniformity of the networks. Typically, the transmittance of the metal NW networks is in the range of 80 – 96% (at the wavelength of 550 nm) and the sheet resistance \( (R_{sh}) \) in the range of 1 – 50 \( \Omega/\square \) [23], which are comparable to or even outperform some of the conventional TCO films.

Due to their superb optical transmittance and electrical conductivity, metal NW networks have been applied as alternative transparent electrodes on a variety of PV solar cells, including the organic solar cells [25, 26], the dye-sensitised solar cells [27], the CIS [28] or CIGS solar cells [29], and the Si micro/nanowire solar cells [30]. Nevertheless, their potential applications and the optical and electrical performances as transparent electrodes on the two major types of Si-based solar cells have rarely been investigated.

Like other metallic nanostructures, the plasmonic effect of the metal NWs is another attractive feature on solar cells for the advanced light trapping such as near-field enhancement at the surface plasmon resonance and increased light path lengths within the solar cells by the scattering of the NWs [31-34]. The waveguide modes excited by the periodic metal NWs have also been reported to be able to enhance the light absorption within the active layers. However, the reported work was mostly for fundamental study on the physical mechanisms of the light trapping effects. The designs of the metal NWs were based on the simulation for ultrathin
(less than 50 nm) Si layers [31, 32], which are not realistic for the fabrication of functional solar cell devices.

1.3 Thesis objective

The objective of this thesis is to investigate and demonstrate the use of metal NW networks as transparent electrodes and light trapping schemes on Si-based solar cells. To achieve this objective, we identify a few major milestones to be accomplished in this thesis as follows:

• **Thoroughly and comprehensively understand the physical mechanisms that govern the optical behaviours of the silver NW (AgNW) networks before they are practically integrated onto solar cells (Chapter 3).** This includes the effect of the NW shapes that can be produced by the state-of-the-art fabrication methods, the substrate materials that can vary during the experiments, and the dielectric materials that can embed the NWs for improved solar cell performances.

• **Demonstrate the use of AgNW networks as transparent electrodes on crystalline Si wafer solar cells (Chapter 4).** This includes the fabrication of low-cost, large-size and high-uniformity metal NW networks to satisfy the requirements of application on the Si wafer solar cells. The optical transmittance and electrical conductivity of the as-fabricated NW networks are expected to be superior to the conventional TCO films. Furthermore, an optimised integration process is required to be specifically developed to realise the function of the NW networks on Si wafer solar cells.

• **Investigate the use of ultrathin gold NWs (AuNWs) as light trapping schemes on crystalline Si wafer solar cells (Chapter 5).** Apart from the AgNWs, the application of other metal NW networks on solar cells is yet to be discovered. The ultrathin AuNWs are especially attractive in this thesis due to
their facile, scalable and low-cost fabrication and integration methods. These features enable them to be utilised in combination with the ITO films, whose light trapping effects on solar cells are usually enhanced in costly and complex ways. The improved optical performances of the AuNWs/ITO hybrid electrode need to be demonstrated and understood.

- **Investigate the use of metal NW networks as transparent electrodes on amorphous Si thin film solar cells (Chapter 6).** The design of the metal NW networks should be based on the structure of a practical device. As a guidance for the experiments, the effects of a wide range of NW parameters (including the shape, dimensions, density, position and material of the NWs) on the optical performance of the solar cell are to be investigated via the numerical simulations. The electrical performances of the AgNW networks on the solar cells need to be experimentally demonstrated.

### 1.4 Thesis preview

This thesis has the following structure:

Chapter 2 begins with a review of the state-of-the-art front electrodes for Si solar cells. This is followed by an introduction and comparison of a few emerging alternative electrodes, which explains why metal NW networks are of special interest in this thesis. We then review the fabrication methods for different types of metal NW networks and compare their advantages and drawbacks. The optical and electrical properties of the as-fabricated metal NW networks are briefly summarised. The applications of metal NW networks on solar cells are then reviewed. A few important topics are covered, including the functions of the NWs, the types of the solar cells that have been demonstrated and the existing challenges.

Chapter 3 presents a thorough understanding on the optical and electrical properties of the AgNW networks through numerical simulations as a guideline for the design
of the experiments. We first introduce the setup of the numerical models employed throughout this chapter. The circular and rectangular AgNWs that can be produced by the state-of-the-art fabrication methods are comparatively studied. Three types of dielectric environment are investigated to represent the cases where the AgNW networks can be practically applied: on glass substrate, on Si substrate and on Si substrate covered with a SiN_x anti-reflection coating. Finally, we discuss the figure of merit (FoM, defined as the transmittance versus $R_{sh}$) of the optical and electrical properties of the AgNW networks for each case.

Chapter 4 demonstrates the use of solution-processed AgNW networks as transparent electrodes on crystalline Si wafer solar cells. The spin-coating deposition method is used to fabricate large-size (up to 5.6 cm × 7.1 cm) AgNW networks, whose high uniformity is confirmed by both the scanning electron microscopic (SEM) image analysis and $R_{sh}$ measurements. We show that the aggregation-free AgNW networks can have a higher FoM compared to the ITO films. An optimised two-step annealing process is then developed for the AgNW network on the Si wafer solar cells, achieving a significant efficiency enhancement of 19% due to the high conductivity of the AgNW network, while the optical loss due to the AgNWs is negligible. Through the loss mechanism analysis for solar cells, we expect an even larger efficiency enhancement if the physical contact between the AgNWs and the Si are further improved.

Chapter 5 explores the use of ultrathin AuNWs for the enhanced light trapping of ITO films on crystalline Si wafer solar cells. The Langmuir-Blodgett (LB) technique is applied as a facile and scalable method to fabricate and transfer the AuNWs onto the solar cells. We show that by using the AuNWs, roughened surface morphology and enhanced anti-reflection effect of the ITO film can be realised. We then further investigate the mechanisms of the optical and plasmonic behaviours of the AuNWs/ITO integrated film through the numerical simulations. Finally, the enhanced light trapping effect for the solar cell with the AuNWs/ITO integrated film is confirmed via the external quantum efficiency (EQE) and $I-V$ characterisations.
Chapter 6 provides a comprehensive investigation on the use of metal NW networks as transparent electrodes on a-Si:H solar cells. The optical performances of the metal NW networks on a-Si:H solar cells are systematically studied through the numerical simulations. A wide range of parameters are optimised including the shape, dimensions, density, position and material of the NWs. We then experimentally demonstrate the electrical performances of the solution-processed AgNW networks on the solar cells. Through a series of experiments of solar cells with different designs of the front electrodes, we discover that the AgNWs on top of the ITO films as a charge collection layer can lead to significant solar cell efficiency enhancements due to the high conductivity of the AgNW networks.

Chapter 7 summarises the research outcomes for this thesis and proposes some future work based on the findings in this thesis.
Chapter 2

Literature review

2.1 Introduction

Front electrodes are one of the most important functional parts of photovoltaic solar cells as they link to both the optical and electrical performances. Whilst a variety of front electrodes have been well developed for different types of solar cells, intensive research has recently been focused on the development of nanomaterial-based alternative electrodes with the aim of reducing the material and fabrication equipment cost, improving the optical and electrical performance, and enhancing the mechanical flexibility [22]. The application of these alternative electrodes has also been demonstrated on various types of solar cells [27-30, 35-38].

In this chapter, we first review the state-of-the-art front electrodes for the silicon (Si) solar cells in Section 2.2. This is followed by an introduction of emerging alternative electrodes in Section 2.3. As a promising substitute for the conventional electrodes, metal nanowire (NW) networks are of special interest in this thesis. In Section 2.4, we then review the types of the metal MW networks that can be experimentally fabricated. Their optical and electrical properties are introduced in Section 2.5. This is followed by the review of the applications of metal NW
networks on solar cells in Section 2.6. Finally we conclude this chapter in Section 2.7.

2.2 Front electrodes for silicon solar cells

2.2.1 Micro-sized metal gridlines

Micro-sized metal gridlines have been used as the front electrodes for the crystalline Si wafer solar cells over the past few decades and the fabrication technologies is now well-established for the commercial production line [16]. A typical configuration of the grid electrode on Si wafer solar cells is shown in Fig. 2.1(a). Fine gridlines (fingers) with a width of hundreds of micrometres and a periodicity of a few millimetres are designed for collecting the current flowing laterally from the neighbouring emitter regions\(^2\). The total current is then collected by the major gridlines (busbars) for output. The gridlines should have a thickness of tens of micrometres for high electrical conductivity and thus low resistive power loss.

Up to date, the gridline electrodes are mainly made of silver for high electrical conductivity and efficient contact with Si [39]. Alternative metals (nickel and copper) are becoming attractive for material cost reduction [40] but the long-term stability of these metals has yet to be proved. In the early stage, the gridline electrodes were formed by photolithography [41], which was too expensive for mass production and only used for space solar cells. Later on, the invention of the screen-printing technology rapidly drove the commercialisation of the Si wafer solar cells, and now it is the most commonly used technology in the solar industry. The main principle is printing the Ag paste through a screening mesh onto the Si wafer, followed by a firing process at a high temperature (~ 800 °C) to open the contact between the gridline and the wafer.

\(^2\) The emitter of the Si wafer solar cell is usually heavily doped, leading to a low sheet resistance down to ~ 40 Ω/□. Therefore, it can be considered as a resistance that can efficiently transport the current in the lateral direction.
pre-deposited dielectric film and form the ohmic contact and mechanical adhesion to the Si.

![Photograph of a screen-printed Si wafer solar cell with a typical configuration of the grid electrode. The top right scanning electron microscopic (SEM) image shows the cross-sectional view of the fine gridline. The bottom right schematic diagram shows the current flow (red arrows) on the emitter and the grid electrode. SEM image from [42].](image)

The design of the gridline pattern is of particular importance to the solar cell performance. Special considerations need to be taken from both the optical and electrical aspects. Optically, the width of the fingers should be small and the periodicity should be large so that more light can be transmitted into the Si. While the width of the fingers fabricated by the screen-printing method has decreased from ~ 200 µm in the early stage [15] to ~ 80 µm [43] in the recent years, further reducing the width is challenging due to the limitation of the mesh resolution and Ag pastes. Another challenge is to increase the aspect ratio (height/width) of the fingers so that the cross section is adequate for low resistive losses. Advanced alternative technologies are under intensive research to overcome these bottlenecks including the metal plating [40] and the buried contact [44], etc., by which the finger width can be further reduced to ~ 25 µm [45, 46].

On the other hand, a large finger periodicity can lead to increased electrical loss on the emitter due to the lateral current flow (current flowing parallel to the plane of the emitter as indicated in Fig. 2.1). For a given finger width, a trade-off periodicity has to be found to minimise the total electrical and optical loss. This design strategy is especially important for the solar cells with lightly-doped emitters,
which aim for higher efficiency by enhancing the spectral response in the short wavelength range [47], but is more vulnerable to the resistive loss. For this type of cell, the finger periodicity is normally reduced to ~ 1 mm [47]. The semiconductor finger technology [48, 49] can effectively mitigate the requirement on the periodicity of the screen-printed metal fingers but is yet to be proved for commercialisation.

Other advanced technologies such as interdigitated back contact [50] and emitter wrap through [51] can completely remove the shadowing loss on the front surface of the solar cells by placing both the anode and cathode on the rear surface. However, a common critical issue for these technologies is the development of low cost processes to isolate the anodic and cathodic grids for full scale production.

### 2.2.2 Transparent conductive oxide films

For Si thin film based solar cells, the active layer would not be able to transport current laterally by itself due to the ultralow electrical conductivity and short carrier diffusion length. Transparent conductive oxide (TCO) films have been playing an important role as transparent electrodes on Si thin film solar cells. To ensure the overall performance of the solar cells, the TCO films must have high electrical conductivity on the order of $10^3 \, \Omega^{-1} \text{cm}^{-1}$ or more for efficient lateral current flow and high optical transmittance above 80% in the visible wavelength range with bandgaps exceeding 3 eV [52-54]. For the commercial solar cell products, the TCO films are used in conjunction with the micro-sized metal grids on the front side of the solar cells for current output.

A vast type of TCO materials have been developed ever since the first report on the CdO film in 1907 [52, 55, 56]. Most of the TCO materials are degenerately doped $n$-type semiconductors. Up to date, three TCO materials have emerged commercially available for the Si thin film solar cells: indium-doped tin oxide
(ITO), fluorine-doped tin oxide (FTO), and aluminium-doped zinc oxide (AZO), each with their advantages and limitations in terms of the practical applications.

ITO is commonly used for $n$-$i$-$p$ amorphous Si solar cells or the HIT (heterojunction with intrinsic thin layer) cells [57]. A main reason of employing ITO films on these cells is that highly conductive and transparent films can be deposited at relatively low temperature (less than 200 °C) [52] by magnetron sputtering [58, 59] or evaporation [60-62], which cannot be achieved with other types of TCO films. This requirement is critical since at elevated temperatures, the stability of the pre-deposited amorphous active layers becomes uncertain. The as-deposited ITO films have very low surface roughness. Creating textured structures on the ITO films is not as easy as other types of TCO films [63, 64]. Light trapping for the solar cells is usually achieved by anti-reflection effect of the ITO films or depositing the active layers on textured substrates [65, 66]. The main drawback of the ITO films is that the scarcity of the indium material is threatening the ever-increasing demand on the transparent electrodes and cost reduction of the solar cells. Moreover, the ITO films are easy to crack and fracture after repeated bending at relatively low strains [67], which can degrade the electrical performance and limit their application on flexible solar cells.

For $p$-$i$-$n$ amorphous Si solar cells, the TCO films are deposited prior to the active layers. Hence, there is no limitation on the deposition conditions of the TCO films. AZO or FTO is commonly utilised. On the one hand, the electrical conductivity of AZO/FTO is not as high as ITO. The thickness of the films needs to be increased up to a few micrometres for a low sheet resistance which in turn increases the optical absorption within the films. On the other hand, with the thick films, texturing with the sizes from hundreds of nanometres to micrometres can be formed either by controlling the deposition conditions via atmospheric pressure chemical vapour deposition (APCVD) [68, 69] or sputtering [70], or etching the as-deposited film by diluted HCl solutions [71, 72]. The texturing can significantly enhance the light trapping for the solar cells in a broadband wavelength range. Compared to ITO, the material costs of AZO and FTO can be dramatically reduced.
However, since the AZO or FTO films are highly fragile and the deposition is normally carried out at high temperatures, they can only be applied on rigid substrates.

### 2.3 Emerging alternative transparent electrodes

Due to the high material and equipment costs of the TCO films, nanomaterial networks are emerging as alternative transparent electrodes for the application on a wide range of photovoltaic devices. Three dominant nanomaterials so far are carbon nanotubes (CNTs), graphene, and metal nanowire (NW) networks.

Since the first experimental observation in 1993 [73], CNTs have been the most mature nanomaterials for the transparent electrodes. The solution-processed synthesis method, low-cost material and scalable deposition techniques of the CNT networks made them very promising as the substitute for conventional TCO films. Despite of the long-term development, a few critical issues are prohibiting CNTs from being commercialised such as the inability to fabricate large quantities of CNTs with a suitable purity and relatively poor optical and electrical performances compared to the TCO films [22]. The latter issue is especially disadvantageous for high-performance solar cells as it can lead to significant power losses.

Graphene has attracted intensive attentions in the past decade for both fundamental research and potential applications due to its unique optical and electrical properties. Typical graphene sheets are single or multiple-layers of two-dimensional networks composed of carbon atoms or in some cases with doped atoms. The sheet resistance of ideal graphene can be as low as $62.4/N \, \Omega/\Box$ (for highly doped graphene) [74] and the transmittance as high as $(100 - 2.3N)\%$ [75], where $N$ is the number of layers. In practice, the optical and electrical performances of graphene is limited by the boundaries and defects induced during fabrication. The solution-processed graphene networks are typically ~2000 $\Omega/\Box$ and ~85% in transmittance [22], while that of the best performing graphene with 30 $\Omega/\Box$ and 90%
has been fabricated by chemical vapour deposition followed by etching [76]. So far, graphene sheets with high quality and high throughput suitable for low-cost and full scale manufacturing have not been demonstrated yet.

Metal NW networks are the most attractive nanomaterials for transparent electrodes due to their superior optical and electrical performance and ease of fabrication. This is the main initiative of employing metal NW networks on Si solar cells in this thesis. The development of metal NW networks has been fast-growing in the past decade, some of which are readily scalable in industry [77]. Figure 2.2 compares the transmittance ($T$) versus sheet resistance ($R_{sh}$) for the typical nanomaterial-based networks. Obviously, the metal NWs (CuNWs and AgNWs in the figure) can far outperform the CNTs and graphene. In the following sections, we will discuss the fabrication and properties of the metal NW networks and their application on solar cells in details.

![FIG. 2.2 Transmittance ($T$) versus sheet resistance ($R_{sh}$) for transparent conductive networks composed of carbon nanotubes (CNTs), graphene, copper nanowires (CuNWs) and silver nanowires (AgNWs). The dots represent the experimental data and the lines represent the fitted data. Image from [78].](image)

In addition, hybrid electrodes combining the metal NWs with other types of transparent electrodes are found to have fascinating performance compared to the individual ones. A variety of combinations have been reported including metal
NWs with graphene [79, 80], TCO films [29, 81], TCO nanoparticles [28, 82-89] and graphene oxide [90].

2.4 Fabrication of metal nanowire networks

2.4.1 Chemical synthesis

The chemical synthesis method can produce metal NWs with high yield and relatively low costs. The materials, shapes and dimensions of the metal NWs are highly dependent on the chemistry amongst the reactants and the experimental conditions. Synthesising NWs with a higher aspect ratio (length/diameter) is becoming a trend in the recent years for higher optical and electrical performance of the networks [91-93]. Herein we will only review the synthesis methods of the NWs that are already proved or potentially applicable for solar cells, mainly silver (Ag), gold (Au), and copper (Cu) NWs.

The most well-known synthesis method for AgNWs is the so-called “polyol process” first reported by Y. Sun et al. [94]. It is now a well-developed method for both laboratory and commercial use. In brief, the Pt seeds are first created by heating the PtCl₂ in ethylene glycol (EG) at ~ 160 °C. With the presence of the poly(vinyl pyrrolidone) (PVP) acting as surfactant, the AgNWs can grow from the Pt seeds with the reduction of the AgNO₃ by the EG in the solution. The experimental conditions need to be well-controlled to minimise the number of the particle byproducts. The as-grown AgNWs have crystalline structures and circular cross-section. The diameters of the AgNWs can range from 30 nm to 60 nm and lengths up to 50 µm by varying the concentration ratio of the reactants, the seeding condition, and the reaction temperature. Figures 2.3(a) and 2.3(e) show the Transmission electron microscopic (TEM) and scanning electron microscopic (SEM) images of typical AgNWs, respectively. Modified processes have been reported to increase the diameter up to 150 nm [95] or length up to 300 µm [96].
Other seedless or surfactantless methods have also been reported [100, 101]. However, the as-produced AgNWs are typically short (less than 10 µm), in low yield and can easily aggregate without surfactant separating each other, which are not comparable to the ones synthesised by the “polyol process”.

The synthesis of AuNWs for transparent electrodes has been reported by A. Morag et al. [97]. Water solution Au(SCN)₄⁻ precipitate is dissolved in dimethylsulfoxide (DMSO) and water. The mixture is then incubated for 24 hours, resulting in crystalline AuNWs with a diameter of around 300 nm and length of hundreds of micrometres (Figs. 2.3(b) and 2.3(f)). A different type of ultrathin AuNWs has been prepared by X. Lu et al. [102]. Gold precursor (HAuCl₄) was gradually reduced by triisopropylsilane (TIPS) in the presence of oleylamine (OA). The complete reduction is finished in two days. The resulting AuNWs are capped by the OA with a diameter of ~ 2.5 nm and a length up to tens of micrometres (Figs. 2.3(c) and 2.3(g)). In spite of the simplicity of the process, the AuNWs have not yet
been proved applicable as transparent electrode due to the ultralow electrical conductivity [98, 103].

A variety of synthesis methods have been developed for the CuNWs, each resulting in different diameters and lengths. The finest CuNWs so far have a diameter of ~16 nm and a length up to 40 µm (Figs. 2.3(d) and 2.3(h)) synthesised from the mixture of CuCl₂·H₂O, Ni(acac)₂, and oleylamine [99]. The CuNWs with the largest diameter of 120 nm and length of 50 µm has been synthesised via reducing Cu(NO₃)₂ with hydrazine in an aqueous solution containing NaOH and ethylenediamine [104]. The CuNWs with intermediate diameters of ~24 nm [105], ~50 nm [106], ~79 nm [107] have also been prepared.

Following the synthesis of the NWs, the techniques of integrating the solution-based NWs onto the substrates are vital for fabricating networks with high optical and electrical performance. The methods should be facile, repeatable and cost-efficient for potential commercialisation. Various deposition techniques have been developed including drop-casting [25, 108], Meyer rod coating [92], spray-coating [109-112], dip-coating [113] dry-transferring [114-116], brush-painting [81, 117] and spin-coating [26, 35, 118]. Random NW networks can be formed without high temperature or high vacuum as for the conventional TCO films. However, a common critical issue for these techniques is obtaining high uniformity over the substrates since the NWs tend to aggregate due to the Van der Waals force and capillary force. Recently, T. Y. Kim et al. have developed a formulated AgNW ink with clay platelets that can effectively avoid aggregation and create uniform networks by rod-coating [119].

Whilst the formation of the solution-based NWs is not controllable by the above deposition techniques, aligning the solution-processed AgNWs has become possible with a variety of nanofabrication techniques including the Langmuir-Blodgett technique [120-122], the hydrodynamic focusing method [123], the fluidic alignment [124], the blown bubble [125], the glass capillary [126], and the magnetic-field-assisted electrospinning [127].
2.4.2 Lithographical patterning

Although the solution-processed metal NW networks are easy to fabricate and cost-efficient, the control on both the NW dimensions and network formation is limited. While the resolution of the conventional optical lithography techniques is restrained to microscale by the diffraction limit, recent advancement in the lithographical processes has gone to nanoscale [128, 129], enabling the fabrication of customised nanopatterns.

![Diagram of electron beam lithography](image)

**FIG. 2.4** (a) Schematic diagram of the working principle of the electron beam lithography (EBL). Image from [130] (b) SEM image of the AgNW network on glass substrate fabricated via EBL processes. Image from [131].

Electron beam (e-beam) lithography (EBL) is a direct writing method for creating nanopatterns with the resolution down to sub-10 nm. The basic working principle of the EBL processes is shown in Fig. 2.4(a). An e-beam is excited with a high voltage and injected through a column that controls the beam size. The beam is then focused onto the resist coated on a substrate in arbitrary regions, where reactions (polymer chain cutting for positive resists, cross-linking or polymerisation for negative resists) are triggered within the resist. By immersing the exposed sample in the developer, the written materials either are removed (for positive resists) or stay on the substrate (for negative resists), leaving behind the
patterned resists. After the film coating and lift-off processes, the desired nanopatterns are formed on the substrate.

The dimensions of the nanopatterns are dependent on the e-beam parameters such as the voltage, the column aperture, the beam dwell time, and the dose (total number of electrons) as well as the sensitivity and contrast of the resist materials. It should be noted that for the EBL on non-conductive substrates such as glass and quartz, negative charge can build up on the substrate surface, which can cause beam deflection and thus pattern distortion [132]. This effect can be eliminated by depositing a conductive layer, normally metal or conductive polymer [133], above or below the resist to dissipate the charges.

J. van de Greop et al. have reported the fabrication of the AgNW networks with an area of 50 µm × 50 µm on glass substrate via the EBL processes [131]. The networks are composed of two orthogonal gratings with the widths of the NWs varied from 45 nm to 110 nm (Fig. 2.4 (b)), demonstrating good control over the NW dimensions and the network formation. Similarly, P.-C. Hsu et al. have fabricated the AuNW arrays with the width of 270 nm and an area of 1 mm × 2 mm on quartz substrate [134]. The as-fabricated small-area NW networks are for the fundamental research on their optical and electrical properties.

Nevertheless, the low throughput, high equipment costs and complicity of the EBL processes are only applicable to the small-scale devices for the laboratory-based research. Nanoimprint lithography (NIL), being first introduced by S. Y. Chou et al. [135] in 1995, has pushed the nanofabrication with sub-25 nm resolution towards large scale and high throughput for practical application of the metal NW networks on solar cells. Typical NIL technologies include thermal and UV imprinting, depending on the way of curing the resist.

A typical NIL process flow is given in Fig. 2.5. For the thermal imprinting, a rigid mould with pre-defined nanostructures is imprinted onto a substrate coated with a layer of thermoplastic polymer resist. When the temperature is raised above the glass transition temperature \( T_g \) of the polymer [129], the viscosity of the polymer
will drop significantly and the pattern of the mould can be transferred onto the resist under high pressure. The imprinted pattern is preserved after the substrate is cooled down to the ambient temperature, where the resist returns to the glassy state. After the mould is removed, the residue resist in the patterned regions is etched away by oxygen plasma. Standard film coating and lift-off processes will leave behind the pattern replica on the substrate. In the case of the UV imprinting, a transparent mould is utilised. The imprinted pattern is preserved by curing a low-viscosity resist under the UV light irradiation.

Common hard mould materials are Si or Si-based dielectric materials (SiO₂ and SiNx etc.) that have high mechanical strength and high durability as required for the nanoimprinting. The nanopatterns on the mould for the NIL processes can be defined by EBL, interference lithography (only for periodic structures) or NIL itself [136] combined with anisotropic reactive ion etching (RIE). In the recent years, great effort has gone into developing the high-resolution soft moulds composed of double-layer Polydimethylsiloxane (PDMS) to simplify the mould fabrication, improve the conformal contact with flexible substrates and relieve the de-moulding process [137-139].
In [136] M.-G. Kang et al. have fabricated large-area NW networks with variable metal materials (Au, Al, and Cu), line widths (120 nm and 200 nm) and line thicknesses (40 nm, 60 nm and 80 nm) via thermal imprinting, demonstrating that this technique can be readily applied for various designs. Figure 2.6(a) shows the SEM image of the as-fabricated NWs with a line width of 120 nm on glass. Later on, AgNW networks with a smaller line width of 55 nm and an area of 2.5 cm × 2.5 cm (Figs. 2.6(b) and 2.6(c)) was achieved by employing the shadow evaporation technique [140].

A variation of the thermal imprinting, namely transfer printing, has been developed for the fabrication of metal NW networks [141-143] on flexible substrates. Typically, a PDMS mould replica is made by casting and curing the double-layered PDMS on the patterned resist imprinted by a hard mould. The PDMS is then peeled-off and deposited with a metal layer. Due to the low surface energy of the PDMS, the metal NWs can be transferred onto the substrate through contact printing at elevated temperature and pressure. A finest line width of 70 nm has been reported for this technique [143].
It should be noted that although the dimensions of the lithographically patterned NWs are well controllable, the shape is restrained to rectangular cross-section so far. Also, the evaporated metal NWs are amorphous other than crystalline as the chemically synthesised ones, which means the conductivity of the material is compromised.

### 2.4.3 Electro-chemical methods

A variety of electro-chemical methods for the fabrication of the metal NWs have been developed including the solid-liquid phase arc discharge [144], the electrodeposition through templates with nanopores [145-147], the electrochemical step-edge decoration method [148-150], and the electrospinning [151-155]. Amongst these methods, the electrospinning is emerging as a promising technique for producing metal NWs in high yield and with high quality that are suitable for the solar cell applications.

For a typical electrospinning process (Fig. 2.7(a)), nanofibres\(^3\) (NFs) of polymers containing metal oxide precursors are injected onto an electrically grounded substrate through a sharp conducting tip under the influence of a high electric field. The polymers are removed by annealing at ~ 500 °C in air, leaving behind the metal oxide in the NFs. Calcination of the NFs at ~ 400 °C in a hydrogen atmosphere can lead to the reduction of the metal oxide and the formation of the polycrystalline metal NFs.

By adjusting the experimental conditions such as the magnitude of the electrical field and the concentration of the precursor, the diameters of the NFs can be varied from ~ 25 nm [152] to ~ 270 nm [155]. In theory the NFs can be infinitely long while practically some breakage of the NFs can be generated during the process. In [153] the copper NFs (CuNFs) with a length in the order of cm have been reported.

\(^3\) They are named nanofibres rather than nanowires because they are presenting some fiber-like features such as the high flexibility and the extremely large length.
Figures 2.7(b) and 2.7(c) show SEM images of the CuNF formed network and a single CuNF indicating the continuity of the NF over 100 µm.

The advantages of the electrospinning technique are intrinsically fused junctions between inter-connected NWs (i.e., no junction resistance), well controlled surface coverage and network uniformity, no extra deposition technique required and possible NW alignment with modified experimental setup [153, 156]. However, limited metal materials of the NFs have been reported so far including Cu [153, 155], Ti [157], Fe, Co and Ni [152]. Notably, the CuNF networks were found to have comparable optical and electrical performance to ITO.

### 2.5 Optical and electrical properties of metal nanowire networks

According to the fabrication methods as detailed in the previous Section, the state-of-the-art metal NW networks can be categorised into two types: the random NW networks prepared by chemical methods and the aligned NW networks prepared by lithographical patterning. In this Section we will review and compare the optical and electrical properties of each type of metal NW networks.
2.5.1 Random networks

Transmittance is an important parameter to evaluate the optical performance of the NW networks on solar cells as it links to how much light is available to be absorbed by the solar cells. While it is difficult to build optical model for the random NW networks, the understanding on the transmittance is normally obtained via experimental characterisation on transparent substrates such as glass and polyethylene terephthalate (PET). Transmittance of the metal NW networks is mainly governed by direct light propagation through the open regions among the NWs and the plasmonic light scattering. Empirically, the transmittance value is inversely proportional to the surface coverage of the NWs (i.e., the diameter and quantity of the NWs). Unlike the conventional TCO films, for example FTO, which suffers from decreased transmittance in the infrared region due to the collective excitation of the carrier gas [158], the AgNW networks normally have broadband transmittance in the visible and infrared wavelength range (Fig. 2.8(a)). This broadband feature would be especially advantageous for solar cells with low-bandgap active layers or tandem structures.

FIG. 2.8 (a) Transmittance of a typical AgNW network, fluorine-doped tin oxide (FTO) film and bare glass. The sheet resistance (R_{sh}) for the AgNW and FTO is 9.5 Ω/□ and 7.4 Ω/□, respectively. (b) Transmittance at 550 nm versus R_{sh} of the AgNW networks prepared by different deposition methods. Images from [93].
The diffusive transmittance (haze factor) is considered as another critical parameter for the solar cell application as it characterises the fraction of the scattered light by the NWs that links to the light path enhancement within the solar cells. Under different experimental conditions, the haze factor can be varied in a broad range of 2% to 35% [92, 110, 159]. Obviously, the networks with a higher NW density will lead to a higher haze factor as more NWs can contribute to the scattering. C. Preston et al. have demonstrated that NWs with larger diameters can result in a significantly increased haze factor [159] due to the stronger scattering capability. However, there is always a trade-off between the increased haze factor and reduced total transmittance of the NW networks. An optimised surface coverage of the metal NW network should be evaluated according to the light absorption feature of the specific solar cell.

The electrical conductivity of the random NW networks can be understood by the percolation theory, which is a standard physics model for describing a random network [93, 114, 160, 161]. The expression is given as follows:

\[ R_{sh} = A \cdot (SC - SC_{th})^{-\alpha} \]  \hspace{1cm} (2.1)

where \( R_{sh} \) is the sheet resistance of the network, \( A \) is a parameter that links with \( R_{sh} \) linearly, such as the NW material resistivity, wire diameter and junction resistance. \( SC \) is the surface coverage of the NWs. \( SC_{th} \) is the threshold surface coverage below which the NWs cannot form conductive networks. And critical exponent \( \alpha \) is the dimensionality factor that essentially determines the probability for a NW to participate in an “artery” that transports electrons to the collection terminals (otherwise, the NW can be redundant that leads to a dead-end in the network). The value of \( \alpha \) has been determined from the literature: 1.33 for a two-dimensional (2D) network and 1.94 for a three-dimensional (3D) network [160].

The dependence of \( R_{sh} \) on NW dimensions has been extensively investigated. In [93] D.P. Langley et al. for the first time predicted the minimum achievable \( R_{sh} \) of the AgNW networks with variable NW lengths and densities via the Monte-Carlo simulation. It is concluded that the networks made of longer NWs have lower \( R_{sh} \).
due to the decreased percolation threshold \( (SC_{th}) \) and fewer NW junctions and this has been experimentally confirmed [91]. In theory, smaller NW diameters will result in higher single wire resistivity and thereby higher network \( R_{sh} \). However, increased transmittance should be taken into consideration and it was found in many literatures that thinner NWs can actually result in better overall optical and electrical performance of the networks [35, 91, 92, 99, 119].

Practically, \( R_{sh} \) is also highly related to the distribution and uniformity of the NWs, which is dependent on the deposition methods. Figure 2.8(b) compares \( R_{sh} \) of the AgNW networks prepared by a few popular deposition methods as a function of the transmittance at 550 nm. It can be seen that drop-casting and spin-coating can form more conductive networks with the same transmittance compared to other methods. While drop-casting does not apply to large areas, spin-coating is selected as the deposition method in this thesis. This will be further discussed in Section 4.2.

The materials of the NWs are directly related to \( A \) in Equation 2.1 and thus linearly proportional to \( R_{sh} \) of the network. Silver has been the most popular NW material for transparent electrodes due to its ease of fabrication and high material conductivity. Transparent conductive AuNW network has also been reported in [97] with a \( R_{sh} \) of \(~ 70 \Omega/\square\) and a transmittance of \(~ 75\%\), which is inferior to the typical AgNW networks. Copper NW networks are becoming attractive recently because of the low material cost and comparable optical and electrical performance to the AgNW networks [99, 107, 153, 162]. However, the CuNWs normally suffer from oxidation and chemical corrosion, leading to significantly degraded electrical performance after long-term exposure in high temperatures or the ambient environment. A few techniques have been developed to resolve this issue including the Ni-coated CuNWs by chemical synthesis [163] and the double-layer passivation coating of AZO and Al\(_2\)O\(_3\) by atomic layer deposition [154].

The junction resistance, another important factor associated with \( A \), can be decreased by a few post-deposition techniques such as thermal annealing [25],
electrical annealing [164], plasmonic welding [165], TiO\textsubscript{2} sol-gel treatment [89] and high mechanical pressure [108, 166, 167].

2.5.2 Aligned networks

The electrical conductivity of the aligned metal NW networks is straightforward to understand. The NWs that are in line with the current flow direction can be seen as connected in parallel. For an infinite network, $R_{sh}$ of the networks is expressed in the following equation [168]:

$$R_{sh} = \rho \cdot \frac{P}{W \cdot H}$$

(2.2)

where $\rho$ is the resistivity of the material, $P$ the periodicity, $W$ the width, $H$ the height of the NWs carrying the current. In practice, $R_{sh}$ is normally larger than the ideal value calculated by the above equation due to the broken lines induced during fabrication and amorphous nature of the deposited metal films (i.e., higher resistivity than bulk metals).

Experimental study on the aligned metal NW networks was pioneered by M. G. Kang et al [136, 141] in 2007. The optical and electrical properties of the NW networks with variable metal materials, line widths and line height on glass substrates were investigated. It was concluded that NWs with smaller width can lead to increased transmittance at the expense of increased sheet resistance, but the latter can be compensated by larger wire height. For example, the AuNW network with 200 nm width and 40 nm height has a transmittance of 63\% and a sheet resistance of 7.7 $\Omega/\square$, while that with 120 nm width and 80 nm height has a transmittance of 69\% and a sheet resistance of 5.0 $\Omega/\square$. This finding is in consistent with the theoretical prediction in [168]. Interestingly, the transmittance curves versus wavelength behave quite different with variable NW materials and widths, although the mechanisms were not mentioned in the literature. Soon after this experiment, NWs with smaller width of 70 nm were fabricated to achieve higher
transmittance up to 84% [142, 143]. However, since the height was maintained at 40 nm, the networks exhibited higher sheet resistance of $24 \Omega/\square$.

The physical mechanisms of the light transmission of the one-dimensional (1D) AgNW gratings free-standing in air have been elucidated in [168] via numerical simulation. The transmission of this 1D nanostructure is mainly governed by the propagating modes and resonance associated with surface plasmon polariton (SPP) modes and these modes are sensitive to the light polarisation.

Whilst the study in [168] is purely theoretical, J. van de Groep et al. have explored the case for the AgNW networks on glass substrates both experimentally and theoretically [131]. The AgNW networks are composed of two identical gratings orthogonal to each other (Fig. 2.4(b)) such that they are light polarisation insensitive. Notably, a thin layer of Ge was deposited prior to Ag to reduce the grain size and enhance the quality of the AgNWs. Compared to the random networks, additional optical and plasmonic effects present due to the periodic structures, leading to narrowband features of the transmittance as shown in Fig. 2.9(a). The measured total transmittance (integrated over the air mass 1.5 global solar spectrum) versus $R_{sh}$ with variable periodicity and line width is given in Fig. 2.9(b), demonstrating the superior performance to ITO. The figure of merit in Fig. 2.9(b) inset indicates that networks with thinner NWs and smaller periodicity have better overall performance.

**FIG. 2.9** (a) Measured transmittance of the AgNW networks normalised to that of glass as a function of the wire width ($w$). The periodicity of the gratings is 500 nm. (b) Measured
2.6 Application of metal nanowire networks on solar cells

2.6.1 Substitute for conventional transparent conductive oxide films

The use of metal NW networks as substitute for the conventional TCO front electrode (mainly ITO) has been mostly reported in organic solar cells (OSCs). A typical structure of the OSC is shown in Fig. 2.10. The front electrode on the substrate is in contact with the transparent conductive PEDOT:PSS layer that is used for the enhanced charge injection from the active layer. On the rear side, the negative electrode is in direct contact with the active layer.

![FIG. 2.10 Schematic structure of a typical organic solar cell. Image from [169].](image)

J.-Y. Lee et al. have first realised a functional OSC with the use of the random AgNW electrode in 2008 [25]. The ultralow cell efficiency (0.38%) obtained in their experiments was attributed to the shunt induced by the topography of the...
large-diameter AgNWs\(^4\) (~ 100 nm) and inefficient carrier transport induced by the relatively thick device. Later on, the cell efficiency was significantly improved up to 5.8% by utilising AgNWs with much smaller diameters (~ 30 nm) \([35, 169]\). But it was discovered in \([169]\) that the defects on the AgNW/PEDOT:PSS interface could lead to higher series resistance.

Much effort has gone into relieving the shunting effect induced by the morphology of the AgNWs. J.-W. Lim et al. introduced a brush-painting method to deposit relatively smooth AgNW networks by the sheer stress of the brush \([117]\). T. Tokuno et al. flattened the hanging AgNW junctions by high mechanical pressure \([166]\). D.-S. Leem et al. and R. Zhu et al. increased the thickness of the PEDOT:PSS layer to 150 nm \([26]\) and 200 nm \([89]\) respectively to fully embed the AgNWs. Z. Yu et al. embedded the AgNWs on glass substrate in a cured polymer. After peeling off the polymer, only the surfaces of the AgNWs that were originally in contact with the glass were exposed, presenting flat contact with the successively deposited OSC \([170]\).

On the other hand, the effects of the morphology of the AgNWs can be avoided by engineering the structure of the OSCs. In \([108]\) the AgNWs were first flattened on a glass substrate by mechanical pressure and then laminated on top of the active layer as the cathode in Fig. 2.10, making the device semitransparent. However, significantly increased series resistance was observed due to the poor charge collection of the AgNW network. This lamination technique was also utilised in \([167]\) except that the OSC was deposited from the cathode substrate and the AgNWs were laminated onto the PEDOT:PSS layer, yet shunt was induced by locally thinned device regions. A newly reported technique on dye-sensitised solar cell can resolve both issues of the series resistance and shunt \([27]\): a PEDOT:PSS layer was deposited on the cathode side prior to the AgNWs to ensure ohmic contact of the AgNWs to the active layer and the lateral charge transport in the open regions among the AgNWs; the AgNWs were then deposited on the

\(^4\) It should be noted that with several AgNWs hanging on top of each other, the roughness of the AgNW electrode could be a few times of the diameter of AgNW. The junction regions can stick out of the organic layers and thus easily result in the shunt paths.
PEDOT:PSS layer by the spray-coating method, which is a gentle but effective technique to facilitate the contact without causing shunt.

Shunt is less likely to occur for the OSCs using other types of metal NW networks that naturally have flat NW junctions and smooth surface morphology such as the nanoimprinted [142, 143] and electrospun metal NW networks [153], both of which result in the device performance comparable to that with the ITO electrode without the post-deposition treatments. However, it was found in [153] that the CuNFs were corroded by the acidic liquid PEDOT:PSS during deposition, leading to an increased series resistance of the solar cell. The reaction stopped when the layer was dried and the CuNFs became stable in the device.

As for the inorganic solar cells, D. B. Turner-Evans et al. employed the random AgNW networks as a transparent electrode on a Si microwire solar cell [30]. The highlight of their work was creating ohmic contacts between the $n$-type Si wires and the AgNWs via the Ni particles that were chemically coated onto the Si wires. Although the efficiency was quite low (2.8%) compared to the normal crystalline Si solar cells, it implied the potential of the metal NW networks on other types of solar cells apart from the OSCs.

2.6.2 Hybrid electrodes

While direct contact of the metal NWs with the active layers normally leads to defects of the solar cells as discussed in the previous Section, hybrid electrodes based on the metal NW/TCO composite are becoming increasingly attractive recently. In [81] K.-H. Choi et al. demonstrated the use of AgNWs sandwiched in two sputtered ITO films as transparent electrode on the OSC. The hybrid electrode had superior optical and electrical performance to its ITO reference. Specifically, the diameters of the AgNWs were only ~ 30 nm. In such way, the ITO film on top of the AgNWs did not have to be very thick to fully embed the AgNWs; meanwhile, the protrusions of the hybrid electrode were very small and did not affect the
morphology of the subsequent organic active layers. Without the shunt and the contact defects between the AgNWs and the active layer, the performance of the OSC with the hybrid electrode was higher than that with only ITO due to lower series resistance and enhanced light absorption by the scattering of the AgNWs.

Since indium is a naturally scarce material, the development of indium-free transparent electrodes is becoming more and more important. In [29] similar hybrid structure was applied on the copper indium gallium selenide (CIGS) solar cells except that the ITO was replaced with ZnO. The ZnO film itself was highly resistive but the sheet resistance of the ZnO/AgNW/ZnO hybrid electrode was much lower than that of the ITO film thanks to the superior conductivity of the AgNWs. With the hybrid electrode, the charges can flow laterally in the ZnO film and be collected efficiently from the regions distant from the AgNWs, which would recombine without the ZnO film (Fig. 2.11). The surface coverage of the AgNWs within the hybrid electrode was optimised so that the performance of the CIGS solar cell was greatly enhanced by 19.7% compared to that with the ITO film.

FIG. 2.11 Schematic illustrations of the charge transport and collection from the active layer for the solar cells (a) with AgNWs only and (b) with ZnO/AgNW/ZnO hybrid electrode. (c) and (d) Effective charge collection area (blue regions) for the corresponding electrode. Images from [29].

Nevertheless, the high-vacuum deposition of the TCO films normally requires expensive equipment. Furthermore, for certain types of solar cells, the active layers
can be subject to the high temperatures and ion bombardment during the deposition. The fully solution-processed AgNW/TCO nanoparticle (NP) composite electrodes can potentially resolve these issues. The hybrid electrodes are normally fabricated via individual coating processes of the TCO NPs and the AgNWs. The sequence of the coating may be adjusted for different solar cells. The densely packed TCO NPs have multi-functions on solar cells including reducing the sheet resistance of the AgNW networks [28, 85], improving the mechanical and electrical contact between the AgNWs and the active layer [28, 84, 85, 87], enhancing the charge collection from the open regions among the AgNWs, and minimising the reflection of the solar cells with optimised thickness of the NP layer [82].

ITO [28, 82, 84], ZnO [82, 85-87] and TiO$_x$ [26, 84, 89] are the most commonly used materials for the TCO NPs. Specifically, C.-H. Chung et al. found that the ITO NPs could provide proper energy band alignment for the CIS/CdS solar cell, otherwise current injection from the CIS layer to the CdS layer was limited due to the high work function of the AgNWs [28]. Normally, the ITO NPs are more conductive than the ZnO NPs. But the higher carrier density of the former also caused more parasitic absorption and thus poorer device performance [82]. Although it was expected that improving the conductivity of the ZnO NPs could reduce the lateral transport losses [85], the OSC with the Al-doped ZnO NPs, which are more conductive than the intrinsic ZnO NPs, were found to have negligibly better performance than that with intrinsic ZnO NPs [87]. It should also be noted that the plasmonic absorption of the AgNWs in the hybrid electrodes can result in decreased spectral response of the OSC for the wavelengths below 470 nm [87].

2.6.3 Plasmonic light trapping

Apart from the superb optical transmittance and electrical conductivity, another fascinating feature of the metal NW networks on solar cells is the plasmonic effect induced advanced light trapping, which cannot be realised by the conventional
TCO films. Scattering by the metallic nanostructures has been well-known to cause enhanced light absorption in solar cells via increased light path lengths by angular redistribution of the incident light [171, 172]. This feature is normally broadband with peaks occurring in the vicinity of the surface plasmon resonances (SPRs) of the nanostructures. The light absorption enhancement due to the scattering of the random Ag and Au NWs has been experimentally demonstrated in many literatures [25, 28, 29, 81, 86, 87, 108, 117, 142, 173, 174], most of which are based on OSCs. Only in [173] it was first observed on amorphous Si solar cells (250 nm thick). Soon after that Y. P. Singh et al. systematically investigated the effects of the diameter and periodicity of the circular AgNWs on the light absorption enhancement of the 100 nm thick Si slab [34] by simulation.

Where the SPR of the NWs is excited, narrowband near-field\(^5\) enhancement can occur close to the SPR wavelength. For the solar cells with very thin (less than 100 nm) active layers, whose intrinsic absorption is comparatively weak, this phenomenon can greatly enhance the light absorption in the specific wavelength range. The near-field enhancement in a 50 nm thick Si slab (Fig. 2.12(a)) is shown in Fig. 2.12(c) compared to the case without the AgNWs (Fig. 2.12(b)). The effect of the near-field of the periodic AuNWs on the carrier generation rate of the solar cells was also elucidated in [175]. By tailoring the dimensions, periodicities and surrounding dielectric of the periodic NWs, the wavelengths and magnitude of the enhancement can be well tuned as theoretically predicted in [32] and [31]. It should be noted that near-field enhancement is always accompanied by enhanced absorption in NWs where the SPR occur, which results in decreased absorption in solar cells. T. Z. Oo et al. and M.-G. Kang et al. have experimentally demonstrated the increased quantum efficiency and thereby conversion efficiency of the OSCs due to the near-field enhancement by employing random AuNWs [174] and periodic AgNWs [140] respectively.

\(^5\) The near-field represents the regions in the vicinity of the nanostructures where surface plasmons can take effect, normally within tens of nanometres.
Waveguide mode excited by the metal NWs has also been reported to cause significantly enhanced light absorption within the solar cells (Fig. 2.12(d)) when the following conditions are satisfied: (i) the active layer of the solar cell is thin enough to form a waveguide for highly confining the wavelengths that can be absorbed by the active layer; (ii) the NWs are periodic; (iii) the dispersion relations of the waveguide modes are matched by the NW periodicities and dimensions at the corresponding wavelengths. The related theoretical investigations are given in [31-33, 140].

After all, the actual contribution of the above-mentioned plasmonic light trapping effects to the overall light absorption of the solar cells should be evaluated along with the absorption features of the active layers and the intensity profile of the solar spectrum.
2.7 Conclusions

Amongst the nanomaterial-based transparent conductive networks, Metal NW networks have emerged as promising substitute for the conventional TCO films on photovoltaic solar cells due to the superior optical and electrical properties. Fabrication of the metal NW networks through solution-processed chemical synthesis is relatively cost-efficient and has been well developed. While this approach has less control on the NW dimensions and the network formation, customised design of the metal NW networks can be realised by NIL technique over large areas.

The random and aligned NW networks produced by different methods have their distinctive optical and electrical properties. For the random networks, the electrical conductivity of the random networks is described by the percolation model and is highly dependent on the deposition methods; the understanding on the optical performance is empirically obtained from the experimental measurements. For the aligned networks, the electrical performance of the aligned networks can be simply derived from the Ohm’s law; their optical behaviours are predictable through simulation and the physical mechanisms can be well understood.

The application of metal NW networks on solar cells has been extensively investigated. Directly replacing the conventional TCO films with the metal NW networks, mostly for the OSCs, usually introduces undesirable issues to the solar cells such as current shunt paths and increased series resistance. Hybrid electrodes of TCO and NWs can combine the advantages of the individuals and have been proved to work well on both organic and inorganic solar cells. Additionally, advanced light trapping for the solar cells can be realised by manipulating the plasmonic effects of the metal NWs such as the scattering, the near-field enhancement and the waveguiding.
Chapter 3

Theoretical study on the optical properties of silver nanowire networks

3.1 Introduction

Before the metal nanowire (NW) networks are practically applied onto the crystalline silicon (Si) wafer solar cells as transparent electrodes, a comprehensive understanding on their optical and electrical performance is needed as a guideline for the design of the experiments. It is well understood that plasmons can be generated by the metallic nanostructures under the excitation of the incident light, which can lead to some “abnormal” optical behaviours around the nanostructures [3, 172]. These behaviours are closely related to the material, shape, dimensions and distribution of the nanostructures as well as the surrounding dielectric environment.

Amongst all the metal NW materials, silver is of particular interest in this thesis because of its well-developed synthesis method, high electrical conductivity, good ohmic contact with silicon substrates [176] and relatively good chemical stability. As discussed in Chapter 2, the state-of-the-art silver nanowire (AgNW) networks include gratings or meshes with rectangular AgNW cross-section fabricated by the
lithographic patterning methods and random meshes with circular AgNW cross-section fabricated by the solution-processed methods. The aim of this chapter is to investigate and compare the optical properties of the circular and rectangular AgNW networks [177]. Specifically we are interested in the effects of the light polarization, the density of the AgNWs and the dielectric environment on the transmittance of the networks which are highly relevant for the application on Si solar cells.

This chapter has the following structure. In Section 3.2 we introduce the setup of the numerical models employed throughout the Chapter. In Section 3.3 we elaborate and compare the physical mechanisms of the transmittance of the networks on glass substrate with respect to the shape of the AgNWs. In Section 3.4 we show different mechanisms by changing the substrate material to Si as that in the real case for the solar cells. In Section 3.5 we investigate the effect of a silicon nitride (SiNx) dielectric layer on top of the Si surrounding the AgNWs to simulate the solar cells with anti-reflection coatings. In Section 3.6 we discuss the figure of merit (FoM) of the AgNW networks for each case defined by the total transmittance \( T_{\text{total}} \) weighted over the air mass 1.5 global (AM1.5G) solar spectrum versus an ideal sheet resistance \( R_{\text{sh}} \). Finally we conclude this chapter in Section 3.7.

### 3.2 Methodology

we explore the optical behaviours of the AgNW networks by the finite-difference time-domain (FDTD) method [172]. The simulations are performed with a commercial software package (Lumerical FDTD Solutions [178]). Detailed setups of the simulation models are shown in Fig. 3.1(a). The AgNWs are arranged perpendicularly with each other (in the \( x-y \) plane), representing the mesh structure of the networks. A plane wave in the wavelength range of 300 – 1200 nm (the absorption range for most of the silicon based photovoltaic devices) is used as the
light source with a polarization along the $x$-axis and propagation direction normal to the substrate plane. The AgNWs parallel and perpendicular to the light polarization are named as $p$-AgNWs and $s$-AgNWs, respectively.

FIG. 3.1 (a) Schematic structure of the simulation model setup for circular AgNW networks on glass or Si substrates. The horizontal and vertical arrows within the simulation unit (grey box) represent the polarization and propagation directions of the incident light, respectively. The inset figure shows the two-dimensional (2D) cross-sectional view of the model with the red line indicating the position of the power monitor. (b) Schematic structure of the simulation model of the square AgNW network on glass or Si substrates. (c) and (d) show the schematic structure of the simulation model of circular and square AgNW networks covered with a 75 nm thick SiN$_x$ layer, respectively. The inset figure in (c) shows the measured $n$, $k$ values of the SiN$_x$ layer as a function of the wavelength used for the simulation.

Periodic boundary conditions are applied in the lateral direction for the simulation unit, as indicated by the grey box in Fig. 3.1(a) to simulate the infinite mesh networks. Perfectly matched layer conditions are applied in the vertical direction to avoid the interference effect under the assumption that all the light transmitted through the AgNWs is absorbed by the substrates. According to the convergence requirement, the mesh size for the bulk dielectric is set to be $\lambda/14$ in material,
where $\lambda$ is the smallest simulated wavelength. Refined meshes ($\lambda/150$) are applied for the AgNWs and the interfaces until convergence is achieved to guarantee an ultrahigh accuracy of the simulation [179, 180]. A two dimensional power monitor is placed in plane with the AgNW/Si interface (as indicated by the red line in the inset two-dimensional (2D) cross-sectional view) to record the Poynting power transmitted through the networks, which is then integrated over the monitor area to obtain the total transmitted power for each wavelength.

The diameter of the circular AgNWs is set to be 100 nm, which is the average diameter of the solution-processed AgNWs used in the experiments throughout this thesis. Herein, we are specifically interested in the shape of the AgNWs rather than the dimensions. Therefore, square AgNW networks are selected as representative of the rectangular AgNW networks. The width of the square AgNWs is set to be 89 nm, to keep the cross-sectional area, i.e. the wire conductivity, the same as that of the circular AgNWs. Figure 3.1(b) shows the model for the square AgNW networks on the substrate. The AgNW density is varied by changing the periodicity ($P$) of the networks (i.e., the size of the simulation unit). The values of $P$ studied in this Chapter are 400 nm, 500 nm, 600 nm, 1000 nm, 1500 nm, respectively.

Three cases of commonly used dielectric environment are simulated to represent different practical conditions: AgNWs on glass (Figs. 3.1(a) and 3.1(b)) as the case of the experimental measurement for the transmittance and $R_{sh}$ of the networks, on Si (Figs. 3.1(a) and 3.1(b)) as the case of the application on Si solar cells, and AgNWs on Si covered with a 75 nm thick SiNx layer (Fig. 3.1(c) and 3.1(d)) as the case of the Si solar cells with an anti-reflection coating.

The optical constants of the glass, Si and Ag materials were obtained from Palik [181], and SiNx measured from a commercial crystalline Si wafer solar cell by ellipsometry (Fig. 3.1(c) inset). These experimental data were then fitted by the built-in algorithm from the software to form analytical models as a function of the wavelength, which were used for the simulation.
3.3 Effect of nanowire shapes

We start with investigating the mechanisms that govern the transmittance of the circular AgNW networks on the glass substrate normalised to that of the glass for varying periodicities as shown in Fig. 3.2(a). For the low AgNW density ($P = 1500$ nm), the transmittance remains at a high level above 90%, and appears relatively flat in the whole wavelength range because the periodicity of the AgNWs is larger than the wavelength range studied here. Hence coupling between NWs cannot be observed and the transmittance of the network is mainly governed by the propagating transverse electromagnetic (TEM)-like mode and the scattering effect.

For higher AgNW densities ($P \leq 1000$ nm), four noticeable features can be observed. To further illustrate the contributions of the $s$-AgNWs and the $p$-AgNWs to the optical behaviours of the networks, we plot the transmittance of the one-dimensional (1D) $s$-AgNWs and $p$-AgNWs for $P = 400$ nm in Fig. 3.2(b). First, a broadband reduction in transmittance occurs at the longer wavelengths beyond 500 nm, which is mainly due to the transmittance decrease of the $p$-AgNWs as shown in Fig. 3.2(b). As explained in literatures [131, 168], the geometry of two
adjacent \( p \)-AgNWs and the air in between can be considered as a metal-insulator-
metal waveguide. For the light above the cut-off wavelength of the fundamental
transverse electric (TE) mode of the waveguide, the mode is transferred from
propagating dominant to evanescent dominant. This cut-off wavelength is
dependent on the dimensions of the waveguide. Indeed, the starting wavelength of
the broadband transmittance reduction is red-shifted with the increased periodicity.

Second, a transmittance dip is present at \( \sim 350 \) nm for all the periodicities, which is
known due to the absorption peak in the \( s \)-AgNWs by the localised surface
plasmon resonance (LSPR) [87, 117]. The Fano-type [182] destructive interference
enhances the dip near the LSPR in the wavelength range of 300 nm – 400 nm,
while above 400 nm, the constructive interference leads to increased transmittance
with respect to the surface area uncovered by the AgNW networks in a broadband
wavelength range [131, 168]. These two effects contribute to the asymmetric
features of the transmittance curves below and above 400 nm.

Third, a second dip presents for the periodicities of 400 nm, 500 nm and 600 nm at
different wavelengths – 600 nm, 740 nm and 880 nm, respectively. It is believed
that this phenomenon is due to the surface plasmon polaritons (SPPs) propagating
along the \( p \)-AgNWs/glass interface excited by the momentum matching of the
periodic \( s \)-AgNWs [131, 168]. This means the excitation of the SPPs requires the
presence of both of the 1D AgNWs. Indeed, as shown in Fig. 3.2(b), this dip does
not exist for the individual 1D AgNWs. This mode is not observed for higher
periodicities because it moved to the wavelength beyond the range studied here.

Finally, the first-order diffraction effects in the vicinity of the periodicity of each
network (except that for \( P = 1500 \) nm) are observed as indicated by the arrows in
Fig. 3.2(a). The enhanced light coupling into the substrate gives rise to the
transmittance increase at the corresponding wavelengths.

It should be noted that the as-studied AgNW networks are insensitive to the light
polarisation due to the symmetric network structure. Therefore, the simulated
transmittance can directly represent the result under the unpolarised sunlight. As
the case for the 1D AgNW gratings under the sunlight, the transmittance should be
the averaged results under the \(s\)-mode and \(p\)-mode incident light (i.e., averaged transmittance of the \(s\)-AgNWs and \(p\)-AgNWs). Figure 3.2(b) compares the
normalised transmittance of the 2D mesh and 1D gratings for the periodicity of 400
nm. Obviously, the 1D grating can outperform the 2D mesh in the whole
wavelength range since the loss mechanisms of the former are reduced to half. This
is an important design criterion for the simulation of metal NW networks on
amorphous Si thin film solar cells in Chapter 6.

Within the same dielectric environment, the optical behaviours of the square
AgNW networks are comparatively investigated. Figure 3.3(a) shows the
normalised transmittance of the square AgNW networks on the glass substrate with
exactly the same periodicities. As indicated by the shape of the transmittance
curves, the same four features as that of the circular AgNW networks are observed.
However, these features are quantitatively different for the two types of AgNW
networks. Figure 3.3(b) compares the transmittance of the circular and square
AgNW networks for the periodicity of 400 nm. Two major changes are observed
for the square AgNW networks: (i) the LSPR is red-shifted from \(~350\) nm to \(~400\)
nm due to the reduced restoring force on the oscillating electrons within the \(s\)-
AgNWs. This could be disadvantageous to the Si solar cells since the absorption
within the AgNWs occurs where the sunlight intensity is high and the spectral
response of solar cells is large. Also, the absorption within the square AgNWs is
higher than that of the circular AgNWs since the energy is more likely to be
confined in the sharp corners. This leads to a more significant transmittance dip at
the LSPR wavelength and decreased transmittance for the wavelengths shorter than
\(~600\) nm. (ii) The propagating SPPs along the \(p\)-AgNWs/glass interface are red-
shifted from \(~600\) nm to \(~640\) nm, and the resulting transmittance dip is more
significant. This is because the larger interfacial area leads to more pronounced
SPPs [131].
3.4 Effect of substrate materials

To investigate the influence of different substrate materials on the optical behaviours of the AgNW networks, the glass substrate is changed to the Si layer as the case for the Si solar cells. The transmittance spectra of the circular AgNW networks normalised to that of the Si are shown in Fig. 3.4(a). Common substrate-independent features similar to those mentioned above are observed including the LSPR of the AgNWs, the cut-off of the fundamental TE mode, and the first order diffraction for the periodicities at 400 nm – 1000 nm.

On the other hand, two different phenomena are observed as a result of the change of the substrate material. First, unlike the periodicity-dependent sharp transmittance dips of the AgNW networks on glass, the wavelengths of the two small transmittance dips on Si consistently lie at ~ 640 nm and ~ 800 nm for all the periodicities. These dips are linked with the hybrid standing SPP modes, which can be excited by the s-AgNWs due to the presence of the high-permittivity substrate. The small gap between the s-AgNWs and the substrate has an effective optical capacitance, giving rise to the collective charge oscillation normal to the AgNW/air.
and AgNW/Si interfaces [183]. Figures 3.4(b) and 3.4(c) show the $|E|^2$ profiles (all the components of the E-field are included) of the 1D $s$-AgNWs at 640 nm and 800 nm for the periodicity of 400 nm. Evidently, energy is highly confined near the interface, leading to an increased absorption within the $s$-AgNWs.

Second, there is an abnormal transmittance enhancement of more than 20% at ~460 nm for the periodicity of 400 nm, which means more light is coupled into the Si layer due to the forward scattering from the AgNWs compared to the bare Si without the AgNWs. To verify this feature, the normalised scattering cross-sections ($Q_{\text{scat}}$, calculated by dividing the scattered power by the incident light intensity and by the geometric cross-section of the AgNWs) of the one dimensional (1D) $s$-AgNWs and $p$-AgNWs into the Si were calculated by the Mie scattering theory as shown in Fig. 3.5. Consistently, there is a scattering peak for the $s$-AgNWs at ~460 nm. When the density of the $s$-AgNWs is high enough, light can be efficiently coupled into the Si layer by forward scattering.

The scattering enhanced transmittance is further confirmed by the $|E|^2$ profile in the $x$-$z$ plane in the centre of two neighbouring $p$-AgNWs (the insets of Fig. 3.5) where the scattering effect of the $s$-AgNWs is most significant (according to our
calculation for the 1D \( p \)-AgNWs, light is mainly reflected rather than transmitted). To make the comparison more visible, we plot the \(|E|^2\) profiles from \( x = -300 \text{ nm} \) to \( x = 300 \text{ nm} \) for all the compared periodicities. For the periodicity of 400 nm, there are areas in Si (at around \( x = 200 \text{ nm} \)) where the scattering effect is overlapping. With the increased periodicity, this overlapping effect becomes weakened (\( P = 500 \text{ nm} \)) and finally almost disappears (\( P = 600 \text{ nm} \)) when two neighbouring \( s \)-AgNWs barely interact with each other. This feature is absent for the glass substrate because the scattering peak of the \( s \)-AgNWs on glass is located at \( \sim 370 \text{ nm} \) (not shown), which is very close to the LSPR. Hence most of the light is absorbed by the AgNWs rather than scattered.

![Graph showing normalized scattering cross-sections and |E|^2 profiles](image)

**FIG. 3.5** Normalised scattering cross-sections (\( Q_{\text{scat}} \)) of the 1D circular \( s \)-AgNWs and \( p \)-AgNWs on Si for light scattered into the Si. The inset figures show the \(|E|^2\) profile in the \( x-z \) plane in the centre of two neighbouring \( p \)-AgNWs for the periodicities of 400 nm, 500 nm and 600 nm at 460 nm. The unit of the scale bars is \((V/m)^2\).

Figure 3.6(a) shows the transmittance spectra of the square AgNW networks normalised to that of the Si. One noticeable change compared to that of the circular AgNW networks is the absence of the hybrid standing SPP modes because the small gap between the \( s \)-AgNWs and the substrate is replaced by a full-area contact. Also, a transmittance increase is observed at wavelengths above 1000 nm for all the periodicities. Figures 3.6(b) and 3.6(c) show the \(|E|^2\) profile of the 1D \( s \)-
AgNWs for the periodicity of 400 nm at 1000 nm and 1200 nm, respectively. Evidently, surface plasmons are excited by the s-AgNWs, creating enhanced E-field intensity at the corners of the AgNWs. The modes shift the field intensity distribution from top corners to bottom corners with the rising wavelengths, enabling increased near-field enhancement within the Si in the vicinity of the two bottom corners.

![Graph](image)

**FIG. 3.6** (a) Transmittance of the square AgNW networks on Si for varying periodicities normalised to that of the Si. The $|E|^2$ profile is plotted for the 1D s-AgNWs for the periodicity of 400 nm at (b) 1000 nm and (c) 1200 nm, respectively. The unit of the scale bars is (V/m)$^2$.

Figure 3.7 compares the normalised transmittance of the circular and square AgNW networks for the periodicity of 400 nm. In addition to the red-shifting of the LSPR, transmittance of the square AgNW networks is decreased in a broadband wavelength range of 370 nm – 1100 nm due to more reflection by the s-AgNWs. This further confirms that the optical properties of the circular AgNW networks can outperform their square counterpart on the Si substrate.
3.5 Effect of surrounding dielectrics

Apart from the substrate materials, the dielectric environment in which the AgNWs is embedded is also of importance to their optical behaviours. To investigate this effect, a layer of 75 nm thick SiNₓ, which is normally used as an anti-reflection coating for the photovoltaic devices, is placed on top of the AgNWs on Si, as shown in Figs. 3.1(c) and 3.1(d). Figures 3.8(a) and 3.8(b) show the transmittance spectra with the circular and square AgNW networks normalised to that of SiNₓ on bare Si, respectively.
FIG. 3.8 Transmittance of the (a) circular and (b) square AgNW networks and on Si covered with a 75 nm thick SiN\textsubscript{x} layer for varying periodicities normalised to that of SiN\textsubscript{x} on bare Si.

Unlike the above two cases where only a narrow transmittance dip is observed in the short wavelength range of 300 – 400 nm, there is a broadband dip in the range of 300 – 800 nm. This can be explained in two aspects. First, the LSPR peak is red-shifted to ~ 580 nm due to the presence of the SiN\textsubscript{x} and Si from the absorbance curve of the AgNWs (not shown). This causes the transmittance minima to move towards the longer wavelengths. Furthermore, according to the normalised absorption cross-section \( Q_{\text{abs}} \) calculated by dividing the absorbed power by the incident light intensity and by the geometric cross-section of the AgNWs) of the AgNW in SiN\textsubscript{x} shown in Fig. 3.9, the LSPR of the s-AgNWs for the two types of the AgNW networks is largely broadened with higher orders occurring when they are embedded in a high-permittivity material, which leads to the broadband characteristics of the transmittance dip.
FIG. 3.9 Normalised absorption cross-sections \( Q_{abs} \) of the 1D circular and square s-AgNWs in the SiN\(_x\) environment.

Second, the disruption of the optimised anti-reflection coating by the AgNWs results in increased reflection in the vicinity of 600 nm, where zero reflection is achieved by a non-disrupted 75 nm thick SiN\(_x\) layer. The oscillation-like behaviour in the shorter wavelengths is due to the interference between the light reflected from the AgNWs/SiN\(_x\) and SiN\(_x\)/air interfaces. A transmittance above 100\% is observed at \( \sim \) 340 nm due to the forward scattering from the AgNWs and less absorption within the AgNWs (Fig. 3.9). In the longer wavelength range above 800 nm, no broadband reduction in transmittance is observed, mainly because the cut-off wavelength of the fundamental TE mode is beyond the wavelength range studied here.

Figure 3.10 compares the normalised transmittance of the two types of the AgNW networks for the periodicity of 400 nm. As expected, the red-shifting of the LSPR and increased reflectance by the s-AgNWs of the square AgNWs leads to a broadband transmittance decrease for wavelengths above 585 nm compared to that of the circular AgNWs.
3.6 Figure of merit

Finally, FoM is used to determine the performance of the two types of AgNW networks as transparent electrodes for the Si solar cells. $T_{total}$ is defined by integrating the transmittance of the AgNW networks over the wavelength range of 300 – 1200 nm with the photon flux of the AM1.5G solar spectrum as the weighting factor for each wavelength. The expression of $T_{total}$ is given by [184]:

$$T_{total} = \frac{\int \frac{\lambda}{hc} I_{AM1.5G}(\lambda) \cdot T(\lambda) d\lambda}{\int \frac{\lambda}{hc} I_{AM1.5G}(\lambda) d\lambda}$$  \hspace{1cm} (3.1)

where $\lambda$ is the wavelength of light in free space, $h$ Planck’s constant, $c$ the speed of light in free space, and $I_{AM1.5G}$ the AM1.5G solar spectrum. For an ideal AgNW network with a unit area, the ideal sheet resistance is calculated by:

$$R_{sh} = \rho_{Ag} \cdot \frac{P}{A}$$  \hspace{1cm} (3.2)
where \( \rho_{Ag} \) is the resistivity of bulk silver and \( A \) the cross-sectional area of the wire [168]. Figures 3.11(a - c) compare the FoMs of the circular and square AgNW networks in the three different structures studied here, respectively, where \( T_{total} \) is normalised to each case without the AgNWs.

**FIG. 3.11 Normalised total transmittance \((T_{total})\) as a function of the sheet resistance of the circular and square AgNW networks on (a) glass, (b) Si and (c) Si covered with a 75 nm SiNx layer.**

Overall, high \( T_{total} \) leads to high \( R_{sh} \) and vice versa. Ideally, as high as more than 85% transmittance could be achieved with \( 3 \ \Omega/\square \ R_{sh} \) for all the structures. As expected, the FoM of the circular AgNW networks are generally higher than that of the square AgNW networks in the same structure. This difference (up to 3%) is comparatively small on glass (Fig. 3.11(a)) since the transmittance of the square AgNW networks is mainly reduced by the change of the LSPR, which is not very significant and only has an effect on a narrow wavelength range. On Si, this difference (up to 15%) becomes much more significant (Fig. 3.11(b)) when the increased reflection of the square AgNW networks comes into play in a broad wavelength range. Similarly, this phenomenon can also affect the square AgNWs on Si embedded in SiNx (Fig. 3.11(c)) with a comparatively large difference (up to
13%). However, the FoM of the circular AgNW networks is also decreased due to the red-shifting of the LSPR and the disruption of the anti-reflection effect.

### 3.7 Conclusions

We comprehensively investigated the optical behaviours of the circular- and square-crosssectioned AgNW networks with varying densities on glass, Si substrates, and Si substrates covered with a layer of SiN$_x$. Different mechanisms that govern the transmittance of the networks were identified and compared. With the same sheet resistance, the circular AgNW networks generally have higher transmittance than the square AgNW networks in the same structure because the latter suffer from more absorption and reflection by the AgNWs.

The major impact of the substrate materials is the change of surface plasmon modes due to the AgNW/substrate interaction. Specifically on Si, increased transmittance with enhancement up to 20% can be achieved with high-density circular AgNWs due to the forward scattering peak in the vicinity of the LSPR. The anti-reflection layer embedding the AgNWs can result in the red-shifting and broadening of the LSPR compared to the case without this layer.

The total transmittance of the AgNW networks under the AM1.5G solar spectrum for each structure as a function of the sheet resistance was calculated. More than 85% total transmittance with only $3 \, \Omega/\square\, R_{sh}$ can be achieved. The presented FoM gives a useful guideline for future design of the AgNW networks as transparent electrodes for photovoltaic devices.
Chapter 4

Silver nanowire networks on crystalline silicon wafer solar cells

4.1 Introduction

Silver nanowire (AgNW) networks have been demonstrated as promising substitute for the conventional transparent electrodes on a variety of solar cells due to their superior optical and electrical performance. Despite of the encouraging results, most of the research is based on the organic or the III-V material solar cells. In this chapter, we demonstrate the use of AgNW networks as transparent electrodes on crystalline silicon (Si) wafer solar cells [118]. Solution-processed AgNW networks are selected for the following reasons: (i) the optical transmittance of the circular AgNW networks is higher than that of the square ones when they are placed on the optically thick Si substrates as revealed in Chapter 3; (ii) low cost and ease of fabrication compared to the lithographically patterned AgNW networks.

This chapter has the following structures. Section 4.2 explains why the spin-coating method is an excellent choice for fabricating the AgNW networks on the crystalline Si wafer solar cells compared to other deposition methods. The spin-coating conditions are optimised in Section 4.3 and highly uniform AgNW networks are
fabricated on glass substrates, whose optical and electrical properties are then characterised and discussed in Section 4.4. Based on these results, we integrate the AgNW networks onto the solar cells, further optimise the experimental conditions, and analyse the results in Section 4.5. Finally we conclude this chapter in Section 4.6.

4.2 Selection of the deposition method

Before we select an appropriate deposition method to fabricate the AgNW networks, we need to address the requirements on the AgNW networks that will be used for the Si wafer solar cells. First of all, the AgNW networks have to be highly transparent and conductive so that minimal power loss is introduced for the solar cells. Secondly, in order to be compatible with the size of the commercialised Si wafer solar cells, the fabrication method of the AgNW networks should be scalable. Thirdly, the distribution of the AgNWs within the networks has to be highly uniform. Any aggregation of the AgNWs will not contribute to the electrical conductivity of the networks but rather block light on the solar cell surface. Furthermore, non-uniformity of the AgNWs could result in the points with a higher or lower resistance. A full-sized solar cell can be considered as numerous “sub-sized” solar cells connected in parallel. If the points with a higher resistance present on some of the “sub-sized” solar cells, the electricity output of the good “sub-sized” cells can be compromised and the overall performance of the cell can be severely affected by these “bad spots” [185].

However, most of the reported deposition methods as reviewed in Chapter 2 such as drop-casting, Meyer-rod-coating, spray-coating and dry transferring, have not shown highly uniform AgNW networks over large areas, which essentially limits their application for large-sized Si wafer solar cells. The non-uniformity of the AgNW networks can be mainly attributed to two mechanisms: (i) when dispersed in the solvent where the AgNWs are free to move, they tend to be attached to each
other by the Van der Waals force; (ii) when the AgNW dispersion is deposited on the substrates, the AgNWs tend to aggregate during solvent evaporation driven by the capillary flow [186].

Fortunately, spin-coating can effectively solve these two issues and avoid aggregations in the following ways. The fast solvent evaporation rate during spinning can significantly reduce the time for the Van der Waals force to take effect. This means, before the AgNWs are attached to each other in the solvent, they are already “pinned” on the substrates. Meanwhile, the centrifugal force due to the high rotation speed can be competitive to the capillary force. More importantly, the size of the substrates used for spin-coating could be arbitrarily large, depending on the requirements of the specific devices. These features make spin-coating an excellent method to fabricate highly uniform AgNW networks on large-sized Si wafer solar cells.

4.3 High-uniformity silver nanowire networks by spin-coating

Figure 4.1 shows a schematic diagram of spin-coating AgNW network on the substrate. The concentrated AgNW suspension in isopropanol was purchased from Seashell Technology, with an average NW diameter of 100 nm and NW length of 30 µm. The AgNW suspension was then diluted by different organic solvents (including acetone, methanol and isopropanol) for spin-coating. The glass substrate was cleaned by ultrasonic bath in acetone, methanol and isopropanol sequentially and finally by oxygen plasma. The oxygen plasma can not only remove the organic impurities and contaminants on the substrate but also increase the wettability of the surface [187], which enables fast spreading of the AgNW dispersion after it is dropped onto the substrate. The uniformity and surface coverage of the AgNW networks on glass substrates can be controlled by a few critical spin-coating parameters, which are discussed below:
• **Organic diluting solvent**: In order to minimise the time for the Van der Waals force to take effect, one needs to select a type of organic solvent with a comparatively high evaporation rate. Indeed, during our experiments, aggregation was more likely to occur by using the solvent with lower evaporation rate under the same experimental conditions. Although acetone can defeat other solvent regarding this criterion, it can easily leave stains on the substrate surface. Hence, methanol was selected in our experiments.

• **AgNW suspension concentration & spin speed**: These two parameters determine how many AgNWs can stay on the substrate after one spin cycle. Ideally, the lower the concentration and the higher the spin speed, the less chance of aggregation for the AgNW networks on the substrates and thus higher uniformity. But this will lead to a lower AgNW density on the substrate for one spin, which means more spin cycles are required in order to achieve the same surface coverage. After numerous trails on these two parameters, we found that by diluting the original AgNW suspension by 150 times and fixing the spin speed at 2000 rpm, least spin times were needed without compromising the uniformity of the AgNW networks.

• **Spin cycles**: This is the only parameter we varied (values between 10 and 30) for the spin-coating to obtain AgNW networks with different surface coverages. Higher surface coverage needs more spin cycles and vice versa. It should be
noted that with the given value of the spin cycles, the surface coverage of the AgNW network was highly repeatable on numerous samples.

Figures 4.2(a) and (b) show the photographs of an as-fabricated 7.6 cm × 5.1 cm glass slide coated with AgNW networks. Note that although this is the largest sample size we have demonstrated, the actual applicable substrate size could be arbitrarily large. From the photographs we can see that the Ag network coating is highly uniform over the entire glass substrate. Figure 4.2(c) shows the scanning electron microscopic (SEM) image of a typical AgNW network with no aggregation.

![Photographs of a 7.6 cm × 5.1 cm glass slide coated with AgNW network. The red dots represent the positions where the scanning electron microscopic (SEM) images are taken on the sample. (c) Processed SEM image for analysing the surface coverage of the AgNW network.](image)

The uniformity of the AgNW networks was further confirmed by analysing five SEM images (each with an area of 0.1 mm²) taken randomly yet distantly enough to represent the whole area on the glass surface (red dots in Fig. 4.2(b)). To determine the resultant NW density on the substrate, we first transferred the images
into black and white binary pixels by image processing software (Fig. 4.2(c)). Note that this step has to be done very carefully so that the diameter of the AgNWs was not changed arbitrarily. The surface coverage of the AgNWs was determined by the ratio of the number of the white pixels to the total number of the pixels of the image. It was found that the variation of the surface coverage was less than 3% over the entire surface for the investigated sample. Such a high level of the uniformity has not been observed on AgNW networks fabricated via other methods, which have a typical surface coverage variation of about 10% [111]. This again reflects the advantages of the spin-coating method.

### 4.4 Optical and electrical properties of silver nanowire networks

Chapter 3 has given a thorough understanding on the optical and electrical properties of the circular AgNW networks through the theoretical calculations. Nevertheless, the models, especially the network formation, are based on the simplification of the real cases for the random AgNW networks. Therefore, it is important to understand their properties through the experiments. Ideally we would like to measure the optical and electrical properties of AgNWs directly on the Si substrate. But because Si wafers are both optically absorbing and electrically conductive, which will interfere the measurement of the AgNWs. Therefore we first fabricated the AgNW networks on glass substrates for investigating the optical and electrical performance of the AgNW networks. According to the theoretical analysis in Chapter 3, the measurement on the glass substrate should be representative enough to evaluate the optical and electrical performance on Si.
4.4.1 Optimisation of annealing conditions

The as-deposited AgNW networks were highly resistive because the AgNWs were still capped by the organic surfactant from the synthesis [25, 94] and they were not effectively connected to each other. Hence, an annealing process was performed in the oven at 200 °C to evaporate the organic materials. Nitrogen atmosphere was applied for avoiding the AgNW oxidation. Temperature higher than 200 °C could easily break the AgNWs and thus made the process less controllable (We have tested that at 300 °C, the AgNWs cannot tolerate for longer than 15 min.).

![Image of sheet resistance (Rsh) of the AgNW networks as a function of the annealing time at 200 °C. The inset figures show the SEM images of the NW junctions fused at 30 min and broke at 71 hours, respectively.]

The sheet resistance ($R_{sh}$) of the AgNW networks was measured by the four-point probe method. Figure 4.3 shows $R_{sh}$ as a function of the annealing time at 200 °C. $R_{sh}$ started to decrease significantly after 30 min when the junction points of the NW connections started to fuse (the left inset of Fig. 4.3), which reduced the contact resistance among the NWs. The lowest $R_{sh}$ was obtained after 2 hours when most of the NW junctions have fused. Further annealing could gradually increase $R_{sh}$ because some of the AgNWs started to break as shown in the right inset of Fig. 4.3. The transmittance was slightly increased after a short-time annealing due to the evaporation of the surfactant and did not change with the time after that.
It should also be noted that for the AgNW networks on the 7.6 cm × 5.1 cm glass slides, $R_{sh}$ was measured randomly over the entire substrate on 20 positions, with variations of only 9% - 14% observed. For other deposition methods, the reported $R_{sh}$ variation is about 55% [114]. This further confirmed the high uniformity of the AgNW networks.

### 4.4.2 Optical transmittance and electrical conductivity

Under the optimised annealing condition of 200 °C for 2 hours, we then investigate the optical and electrical properties of the AgNW networks. The transmittance ($T$) of the AgNW networks on glass substrates was characterised by spectrometry with an integrating sphere. Figure 4.4(a) shows the measured $T$ with variable $R_{sh}$ of the AgNW networks, normalised to the transmittance of the bare glass substrate. $T$ and $R_{sh}$ were controlled by different AgNW surface coverages on the glass surface. As predicted in Chapter 3, the narrow dips of the AgNW transmittance at ~ 350 nm are observed due to the localized surface plasmon resonance (LSPR), and this effect is more pronounced for the denser AgNW networks. A broadband high transmittance for wavelengths longer than 400 nm is observed for the AgNWs, while for a commercial-grade fluorine-doped tin oxide (FTO) film (from NSG Group), the transmittance beyond 900 nm is severely decreased due to the free-carrier absorption in the film [188]. Furthermore, with the same $R_{sh}$ (7 Ω/□), the transmittance of the AgNW network is much higher than that of the FTO in the whole wavelength range.
We use the figure of merit (FoM), defined as the total transmittance ($T_{\text{total}}$) as a function of $R_{\text{sh}}$, to evaluate the optical and electrical performance of the AgNW networks, as shown in Fig. 4.4(b). The definition of $T_{\text{total}}$ was given in Equation 3.1. $T_{\text{total}}$ determines the maximum available solar spectrum after passing the AgNW network that can be absorbed by the solar cell and eventually links to the maximum photocurrent that the solar cell can possibly produce under the Shockley-Queisser limit [189]. The wavelength range was set to 300 – 1200 nm in this work, representing the region that can be absorbed by most types of solar cells in general. Figure 4.4(b) shows that the AgNW networks outperform the indium tin oxide (ITO) films [56], a widely-used transparent conductive oxide (TCO) electrode, once $T_{\text{total}}$ is larger than $\sim$90%. Compared with other state-of-the-art AgNW networks in literature [92], the AgNW networks produced in this work outperform $T_{\text{total}}$ as much as 10% under the same sheet resistance conditions, or vice versa.

We attribute the outstanding performance to the aggregation-free, high-uniformity nature of the AgNW networks. Within an aggregated or non-uniform network, the AgNWs can hang over each other or get isolated without connecting to other NWs,
forming redundant NWs (Fig. 4.5). With an optimised deposition and annealing control process, we can minimise the redundant NWs in a network.

Minimising the redundant NWs is beneficial for improving the optical transmittance and electrical conductivity of the networks for the following reasons. As reviewed in Chapter 2, the electrical conductivity of the AgNW networks can be understood by the percolation model (Equation 2.1). For a three-dimensional percolation network (aggregated networks containing multiple layers and the dangling NWs as shown in Fig. 4.5(a)), both $SC_{th}$ and $\alpha$ are larger compared with a two-dimensional networks (uniform networks free of the redundant NWs as shown in Fig. 4.2(c)), which directly results in larger $R_{sh}$ under the same surface coverage conditions. It can also be understood in such way that a redundant NW has a reduced chance to contact with other NWs in a network, making the network less conductive. While the redundant NWs do not contribute to electron conduction, they reduce $T_{total}$ due to the parasitic absorption and reflection of the light.

Furthermore, when the AgNW networks are applied on the solar cells, the redundant NWs can hardly contribute to the electron transportation. They have small-area point contacts (instead of large-area line contacts) to the Si, which limits their capability to extract the electrons out of the active layer. Compared with most
of the published AgNW networks which suffer from aggregated clusters [111, 190], the aggregation-free, high-uniformity networks fabricated by spin-coating have advantages in their application to solar cells in terms of the optical and electrical properties.

4.5 Silver nanowire networks on crystalline silicon solar cells

4.5.1 Device fabrication

Having the AgNW networks with excellent optical and electrical performances obtained, we carried out the proof-of-concept experiments of integrating the AgNW networks on crystalline Si solar cells for the first time. The solar cells (2 cm × 2 cm × 180 µm) were fabricated in the following processes. Commercial-grade boron doped (p-type) single-crystalline Si wafers went through the standard saw damage etching and RCA cleaning processes (developed by the Radio Corporation of America). Phosphorous doped emitter (n-type) with a sheet resistance of ~ 50 Ω/□ was formed in a diffusion furnace at ~ 850 °C. The as-introduced phosphosilicate glass was removed by hydrofluoric solution. The aluminium full-area rear contact and back surface field were formed by screen-printing the aluminium paste and firing at ~ 800 °C. The front aluminium contact pads were fabricated by a lift-off photolithography process. The native oxide layer was removed by hydrofluoric acid prior to the spin-coating process of the AgNW dispersion on the front surface of the solar cell, ensuring the good contact between the NWs and the silicon. Figure 4.6 shows the structure of the solar cells.
Important parameters of solar cells, such as the series resistance ($R_s$), the external quantum efficiency ($EQE$), the short-circuit current density ($J_{SC}$), the open-circuit voltage ($V_{oc}$), the fill factor ($FF$) and the efficiency ($\eta$) were measured at each step of the fabrication process. Reference cells without the AgNWs were used alongside to exclude the experimental fluctuations other than the AgNWs such as the change of the conductivity of the contact pads and the contact resistance between the contact pads and Si.

### 4.5.2 Solar cell electrical performance

As previously investigated on the glass substrates, the AgNW networks conductivity can be significantly increased after being annealed at 200 °C for 30 min due to the removal of the residual surfactant and fusion of the AgNW junctions. However, the solar cell performance did not improve after the low-temperature annealing process. We attribute to the fact that 200 °C is not high enough to form good ohmic contact between the AgNW networks and the Si. Although the AgNW and Si are physically in touch, a potential barrier of the Fermi level can exist on the AgNW/silicon interface [191], and thus the electrons in the silicon cannot freely travel through the interface to the NWs. It means that the electrons cannot be effectively extracted from the Si to the AgNWs, even though the electrons can easily transport in the network due to the low network resistance.
In order to create the ohmic contact, we performed another critical high-temperature annealing process at 400 °C for up to 5 min in the N₂ atmosphere for the solar cells. Figure 4.7 shows the solar cell performance as a function of the high-temperature annealing time. The effects of annealing on the solar cell performance other than the AgNWs have been excluded by subtracting the data of the reference cell.

A significant efficiency enhancement of 19% (from 4.47% ± 0.02% to 5.32 ± 0.03%) was observed at 1 min. After that the enhancement started to decrease until when the annealing time was prolonged to 5 min, the efficiency dropped back close to the initial value. During the annealing process the variation of the open-circuit voltage ($V_{OC}$) value was negligible, indicating that the surface passivation was not significantly affected by the metal-semiconductor interfacial states. Figure 4.7(b) compares the current density-voltage ($J-V$) curves of the solar cell before the AgNW integration (initial) and with the AgNWs after 1 min annealing. It clearly shows that the variation of the efficiency was mainly affected by $J_{SC}$ and $FF$. Note that the efficiency of the solar cells obtained in our experiments is much lower than that of the normal crystalline Si wafer solar cells due to the absence of the pyramid texture, anti-reflection coating, and gridline metal contacts, which are designed for minimised optical and electrical losses.

It should be noted that the optical and electrical properties of the NWs was unchanged within eighteen months of storage. Hence under normal solar cell operating conditions, degradation of the NW performance is not expected.

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Note that this temperature was selected because we’ve tested that at higher temperature (≥ 500 °C), the AgNWs were easily broken within 1 min. This would make the process difficult to control.
FIG. 4.7 (a) Enhancement of efficiency ($\eta$), short-circuit current ($J_{SC}$), fill factor ($FF$) and open-circuit voltage ($V_{oc}$) of the solar cells as a function of the annealing time at 400 °C. (b) Current density-voltage ($J$-V) curves of the solar cell before the AgNW integration (initial) and with the AgNWs after annealing at 400 °C for 1 min.

The increase of the $J_{SC}$ value may be due to (i) a larger quantity of generated electrons (light absorption) or (ii) a larger quantity of collected electrons. Since the AgNWs do not create light trapping mechanisms for the optically thick Si wafers as discussed in Chapter 3, we attribute the $J_{SC}$ enhancement mainly to reason (ii), the improved electron collection due to the AgNW electrode. Without the AgNWs contacting with the Si, the electrons otherwise have to travel far in the Si before they are collected by the pads. Therefore the chances would be larger for them to recombine with the holes or lose their momentum due to the electrical resistance of the Si.

This mechanism is confirmed in Fig. 4.8, where the series resistance ($R_s$) of the solar cells as a function of the high-temperature annealing time is presented, along with the SEM images of the NW conditions at each time spot. It is found that the $R_s$ value first decreased by 26% at 1 min, and then increased gradually. This trend matches exactly with that of the $J_{SC}$, the $FF$ and the efficiency change. This is understandable because the AgNWs and the Si are connected in parallel with the ohmic contact, which reduces the total resistance for the emitter. Indeed, the measured emitter $R_{sh}$ was decreased from the initial 52 $\Omega/\square$ to 27 $\Omega/\square$ at 1 min, and finally went back to 50 $\Omega/\square$ at 5 min.
This observation is also in line with the condition change of the NWs indicated in the SEM images: from 2 min onwards, the NWs started to turn thinner (Fig. 4.8(b)), then break (Fig. 4.8(c)), and finally became isolated at 5 min (Fig. 4.8(d)). As a result, the optimum annealing time is 1 min, where a good AgNW/silicon contact condition is formed, and the quality of the AgNW networks is not yet compromised. At 5 min, the isolated silver particles can still provide the low-resistance by-pass routes for the electrons at local spots, but the benefits to $R_s$ and the efficiency are limited.

4.5.3 Solar cell optical performance

In order to investigate the optical performance of the solar cells with the AgNWs, we first performed the reflectance measurements. Figure 4.9(a) compares the reflectance of the bare cell before annealing, and the cell with the AgNWs and the
reference cell after 1 min annealing at 400 °C. For the reference cell, a broadband reflectance decrease was observed in the wavelength range of 300 nm – 1000 nm due to the native oxide formation during the experiments, which can introduce anti-reflection effect. For the cell with the AgNWs, the reflectance is further decreased below 400 nm due to the absorption within the AgNWs by the LSPR as predicted in Chapter 3. For the longer wavelengths above 420 nm, the reflection by the AgNWs can surpass the anti-reflection effect by the native oxide, resulting in a broadband reflectance increase compared to the reference cell.

![Graph showing reflectance and external quantum efficiency (EQE)](image)

FIG. 4.9 (a) Reflectance and (b) external quantum efficiency (EQE) of the bare cell before annealing, and the cell with AgNWs and the reference cell after annealing at 400 °C for 1 min.

We also performed the $EQE$ measurements to further investigate if there is a significant change of light absorption induced by the AgNWs, which can also affect $J_{sc}$ of the solar cells. $EQE$ is defined as the number of the generated electrons over the number of the illuminated photons and thus directly links to the light absorption in the silicon active layer, which can exclude the parasitic absorption of photons in the AgNWs. The experiments were conducted at low light intensity and zero voltage bias, ensuring the solar cell resistance has negligible effects on the electron generation rate. The results are shown in Fig. 4.9(b).

It was found from the reference cell that the native oxide has little impact on $EQE$, except that there is only a slight $EQE$ increase for the wavelengths below 400 nm.
For the cell with the AgNWs, a broadband EQE decrease was observed in the wavelength range of 420 nm – 1020 nm, which is mainly due to the reflection by the AgNWs. By integrating the EQE curve over the air mass 1.5 global (AM1.5G) solar spectrum using Equation 3.1, we found that there are 3% less photons absorbed by the silicon after the AgNW networks are applied. Considering that the other parameters are comparatively unchanged, the 19% efficiency enhancement determined by the I-V characterisation can be safely attributed to the much improved electron collection due to the AgNW networks.

4.5.4 Discussion

So far we have demonstrated the use of the AgNW networks as the transparent electrode on the Si wafer solar cells. For a deeper insight, we are interested in the following issues: (i) is the experimentally obtained solar cell performance the highest that can be achieved with the electrical benefit from the AgNW network? (ii) are there any other potential mechanisms induced by the AgNW network affecting the solar cell performance? And how can we make improvements to achieve the best performance approaching the limit?

To address these issues, we performed some theoretical calculations based on the experimental results. First of all, the pseudo light7 current density ($J_{MP}$) and voltage ($V_{MP}$) at the maximum power point were obtained by inputting the intrinsic parameters of the solar cell into a photovoltaic device simulation program PC1D [192]. The relative electrical power loss due to the lateral current flow on the emitter ($P_{loss \_emitter}$) is then given by [15]:

$$P_{loss \_emitter} = \frac{R_{sh} \cdot D^2 \cdot J_{MP}}{12 \cdot V_{MP}}$$

(4.1)

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7 A pseudo light I-V characteristics of a solar cell is the light I-V characteristics without the effect of the series resistance.
where $R_{sh}$ is the sheet resistance measured from the emitter surface, and $D$ the cell width excluding the contact pads. With the given parameters, $P_{loss_{emitter}}$ should decrease from 61% ($R_{sh} = 52 \, \Omega/\square$ without AgNWs) to 32% ($R_{sh} = 27 \, \Omega/\square$ with AgNWs). This means the relative efficiency enhancement of the solar cell due to the electrical conductivity of the AgNWs should be 29% - the difference of the above two values. Taken the optical loss factor (3%) of the AgNWs into account, the efficiency of the solar cell should increase from 4.47% to 5.69% with a relative enhancement of 26%, larger than the measured enhancement of 19%.

We attribute the discrepancy to the fact that after annealing at 400 °C for 1 min, the contact resistance between the AgNWs and the silicon still exists, although the network itself is already highly conductive. The SEM images of the AgNWs on the solar cell (Fig. 4.10) show that there are some micro-structures on the saw damage etched Si surface. Where the surface is not flat, there are only point contacts between the AgNWs and the Si instead of the line contact where the surface is flat. The total contact resistance ($R_c$) of the solar cell is defined by:

$$R_c = \frac{\rho_c}{A}$$

(4.2)

where $\rho_c$ is the specific contact resistivity determined by the doping density in the Si and the annealing conditions [176, 193], and $A$ the total area of the contacts between the Si and the AgNWs. $\rho_c$ is fixed for a given annealing condition. The point contacts can effectively decreases $A$ and thus increases $R_c$. This hypothesis was confirmed by the fact that a perfect match between the characterisation and simulation of the cell efficiency was achieved if a contact resistance of 0.3 $\Omega$ was inserted in the simulation model.
Therefore, further improvement on the solar cell efficiency can be realised by enhancing the AgNW/Si contact by either decreasing $\rho_c$ or increasing $A$. Techniques such as well controlled rapid high temperature (> 400 °C) annealing and applying physical pressure on the Si surface [108] are the possible solutions.

### 4.6 Conclusions

We fabricated large-size and high-uniformity AgNW networks via the spin-coating method. The high solvent evaporation rate and the centrifugal force of the spin-coating process can avoid the AgNW aggregation by fighting against the Van der Waals force among the AgNWs and the capillary force during the solvent evaporation. We optimised the spin-coating parameters to obtain highly uniform AgNW networks with variable surface coverages. The high uniformity of the AgNW networks was confirmed by analysing the SEM images taken randomly over the entire substrate surface and less than 3% variation on the surface coverage was observed.

We investigated the effect of annealing on the optical and electrical properties of the AgNW networks. We found out that the AgNW networks can achieve the
highest electrical conductivity after annealing at 200 °C for 2 hours. The AgNW networks with varying surface coverages were fabricated on glass substrates. Due to the aggregation-free and high-uniformity nature of the AgNW networks, their optical transmittance and electrical conductivity could be significantly improved and outperform the conventional TCO films. More importantly, the absence of the redundant AgNWs is beneficial for electron transportation on the solar cells.

We also demonstrated the use of the AgNW networks as transparent electrodes for the crystalline Si wafer solar cells for the first time. A critical two-step annealing process was developed for forming the ohmic contact between the AgNWs and the Si. A 19% enhancement on the solar cell energy conversion efficiency could be achieved as a result of the reduced series resistance and increased photocurrent with the AgNW networks. The $EQE$ measurements showed that there were 3% less photons absorbed by the silicon due to the reflection of the AgNWs, which is negligible compared to the electrical benefits.

By analysing the loss mechanisms of the solar cell, we found that larger enhancement was expected with improved contact between the AgNWs and the Si. Therefore, the solution-processed AgNW networks are a promising alternative transparent electrode technology for crystalline Si solar cells due to their superior optical and electrical performance, simple processes and low costs.
Chapter 5

Gold nanomembranes on crystalline silicon wafer solar cells

5.1 Introduction

Having seen the outstanding electrical performance of the silver nanowire (NW) networks on crystalline silicon (Si) wafer solar cell in Chapter 4, the potential of other NW networks also comes into our interest. Ultrathin gold nanowires (AuNWs) have attracted intensive research interest in the recent years due to their ease of fabrication at room temperature, high mechanical flexibility, and plasmonic light trapping effects on the solar cells [98, 102, 103, 174, 194]. Because of the ultrathin nature of the AuNWs, their electrical conductivity is too low to be considered as useful for the Si solar cells with reasonably high transmittance [98, 103, 195]. However, the possibility of using them as different functional parts is yet to be explored. In the previous chapter, we have focused on the electrical benefits of the AgNWs. Herein, we will focus on the optical benefits of the AuNWs [63].

On the other hand, enhancing the optical performances of the indium tin oxide (ITO) thin films, which have been widely used as transparent electrodes on various solar cells due to the superior optical transmittance and electrical conductivity
Chapter 5

[196-200], usually requires costly and complex processes (which will be introduced in the following section). As reviewed in Chapter 2, by combining different types of transparent electrodes, the optical or electrical properties of the composite can be significantly improved compared to that of the individuals [28, 29, 79-81, 83, 89, 90]. In this chapter, we discuss the use of the AuNWs for the enhanced light trapping of the indium tin oxide (ITO) thin films on crystalline Si wafer solar cells.

This chapter has the following structure. Section 5.2 gives a review on the state-of-the-art techniques for enhancing the light trapping effects of the ITO films on solar cells. To start with the experiments, we introduce facile and scalable methods for fabricating the gold nanomembranes (AuNM) and their integration onto the Si solar cells in Section 5.3. The surface morphology of the AuNM/ITO integrated film is investigated in Section 5.4 and the optical properties are investigated in Section 5.5. The optical performance of the solar cell with the AuNM/ITO integrated film is then demonstrated in Section 5.6. Finally, the findings in this chapter are concluded in Section 5.7.

### 5.2 Light trapping of indium tin oxide films

For most of the solar cells that ITO is applied on, the energy conversion efficiency is mainly limited by the insufficient light absorption of the active layers [21, 200, 201]. Light trapping is increasingly important especially when the solar cells are made thinner in order to reduce the material costs. To address this challenge, two light trapping mechanisms have been developed for solar cells built on ITO films:

(i). **Refractive index matching** [196, 202, 203]. One can use ITO films as anti-reflection coatings by utilising the destructive interference between the light reflected from the air/ITO and ITO/active layer interfaces. By finely adjusting the refractive index and the thickness of the ITO films according to the properties of the active layer, the anti-reflection effect can be optimised for the device performance.
(ii). **Generation of roughened surface morphology on ITO films** [204-206].

The scattering effect of the ITO films can be enhanced with this approach. This can redistribute the incident light into large angles and thus increase the total light path length within the active layers.

Due to the nature of destructive interference, approach (i) can only achieve anti-reflection effect in a relatively narrow wavelength range. In contrast, approach (ii) can lead to a broadband light absorption enhancement in solar cells. Therefore, it is generally a more effective approach. However, unlike the other types of TCO films on which textured structures can be formed by controlling the deposition conditions [69, 70, 207], the as-deposited ITO films usually have a flat surface [53].

A variety of post-deposition methods have been reported for creating textured structures on ITO films. One typical way is to dry-etch the ITO films by inductively coupled plasma with an etching mask [205, 208-211]. However, this method includes high-cost equipment, toxic gases and complex processes. More importantly, dry-etching could result in a degradation of the electrical property of the solar cells due to the introduction of defect states on the surface of the active layer [209, 212]. Though one-step wet chemical processes have been reported to etch the as-deposited ITO films using diluted HCl solution or buffered-oxide-etch solution, these methods either require the ITO films to be polycrystalline [213, 214] or include high temperature annealing up to 600 °C [215], which could be incompatible with certain types of solar cells and increase the energy consumption in producing the texturing on the ITO films. Other etching-free methods, such as two-step holographic lithography [216] and nanomoulding [217, 218], have been reported; but the processes are complex and have yet to be proved applicable for large-scale production.

In the following sections, we will demonstrate the use of ultrathin AuNMs to achieve effective texturing of the ITO film on Si solar cells. The Langmuir Blodgett (LB) technique will be first introduced as a fast and easy approach to
fabricate the AuNMs from the chemically synthesised AuNWs and transfer them onto the top surface of the solar cells.

5.3 Device fabrication

To explicitly investigate and compare the light trapping effect of the ITO films on the solar cells with and without the AuNWs, we used planar cells without the conventional surface texture. Prior to the deposition of the AuNWs, the planar single-crystalline Si wafer solar cells were fabricated through the similar processes as introduced in Section 4.5.1. In order to improve the electrical performance of the solar cells, we made the following modifications on the front electrode fabrication: (i) the Al film was replaced by multilayer films of Ti 10 nm/ Pd 35 nm/Ag 500 nm in sequence, which could enhance the metal/Si contact as well as increase the electrode conductivity. (ii) In addition to the contact pad that is solely designed for electrical measurements, parallel metal lines (with a line width of 80 µm and a periodicity of 1.6 mm) perpendicular to the contact pad were also deposited for better current collection.

The ultrathin AuNWs were synthesised by a fully solution-processed, one-step approach at the room temperature [98]. In brief, gold precursor (HAuCl₄) was gradually reduced by triisopropylsilane (TIPS) in the presence of oleylamine (OA). The complete reduction was finished in two days. After purification by centrifugation, the AuNWs were re-dispersed in chloroform. The resulting AuNWs were capped by the OA (Fig. 5.1(a)) with a single-crystalline structure growing in the [111] direction as shown by the transmission electron microscopy (TEM) image (Fig. 5.1(b)). The AuNWs had a diameter of ~2.5 nm and a length up to tens of micrometers, leading to a super large aspect ratio of more than 10000 and high flexibility. Also, the strong hydrophobic interaction between the OA ligands causes the AuNWs to form parallel bundle-like strands (Figs. 5.1(c-e)).
For the deposition of uniform AuNWs onto the solar cell surface, we used the LB technique. Figures 5.2(a–e) show the schematic diagrams of the LB processes. One droplet of the AuNW dispersion in chloroform was spread onto the water surface in the LB trough (Fig. 5.2(a)). The chloroform then evaporated in one second, and the AuNWs were distributed uniformly on the water surface immediately due to their hydrophobic surface, forming a free-floating ultrathin AuNM (Fig. 5.2(b)). Figure 5.2(c) shows the TEM image of the as-fabricated AuNM. Compared to the aggregated bundles by drop-casting as shown in Fig. 5.1(e), the AuNWs within the membrane were highly aligned and uniform. The covering density of the AuNM could be well controlled by adjusting the distance between the two LB barriers and monitored via the surface pressure [98]. By gently attaching the front surface of the solar cell with the solution surface (Fig 5.2(d)), the AuNM could be easily transferred onto the solar cell when it was pulled away (Fig. 5.2(e)).
Figure 5.2(f) shows the enlarged schematic structure of the solar cell integrated with the AuNMs. The LB produced AuNMs can have a high uniformity and a controllable covering density at a large scale up to 300 cm² (depending on the area of the LB trough), which cannot be achieved by other deposition methods such as drop-casting or dip-coating [174]. Furthermore, due to the ultrathin nature, the AuNMs are highly transparent, flexible and mechanically strong, which means they can be conformably attached to substrates and devices with any surface conditions.

Thereafter, a layer of ITO film was deposited on top of the AuNM by radio-frequency (RF) magnetron sputtering at the room temperature. The composition of the ITO target was 90% In₂O₃ and 10% SnO₂ by weight. The chamber pressure was evacuated to $5 \times 10^{-6}$ Torr before the argon gas was injected into the chamber. During the deposition, the RF power was kept at 120 W and the chamber pressure at 5 mTorr. The deposition time was 3 minutes. The solar cells with and without the AuNM (reference solar cell) were deposited with ITO films in the same batch,
labelled as Cell A and Cell B, respectively. Figures 5.2(g) and 5.2(h) show the schematic structures of the fabricated solar cell with the AuNM/ITO integrated film, and the reference solar cell, respectively.

### 5.4 Surface morphology of indium tin oxide films

It is essential to investigate the effect of using the AuNMs on the surface morphology of the ITO films before we understand the light trapping effects of the AuNM/ITO integrated films. Figures 5.3(a–c) show the scanning electron microscopic (SEM) images of the AuNM, ITO film and AuNM/ITO integrated film on the solar cells, respectively. The AuNM appeared as parallel AuNW bundles that are highly aligned on the substrate. For the ITO film deposited on the bare Si, a relatively flat surface was observed. When the ITO film was deposited onto the AuNM, wrinkle-like texturing of the ITO along the AuNW bundles was formed as shown in Fig. 5.3(c).

Since the ITO films were too thin to be characterised by the SEM for cross-sectional view, the enhanced texturing effect on the ITO film by the AuNM was revealed by the atomic force microscopy (AFM) images as given in Figs. 5.3(d–f) for the corresponding films. The root mean square surface roughness ($R_q$) of the AuNM and ITO film on bare Si was 0.78 nm and 1.86 nm, respectively. However, as high as 8.17 nm $R_q$ of the AuNM/ITO integrated film could be achieved, which was three times larger than the addition of the above two values. Instead of forming a surface based on the morphology of the AuNM, the AuNM/ITO integrated film turned out to form tapered-range texturing with the base width around 100 nm and height around 30 nm, as revealed from the one-dimensional (1D) profile of the range extracted from the AFM image at the specified position (Fig. 5.3(g)). The main orientation of the ranges is the same as that of the original AuNM. This feature is attributed to the fact that during the sputtering process, the bombardment of the Ar ion and the plasma induced locally-high temperature could cause the
ultrathin AuNWs to reshape into larger and rougher bundles. As a result, the roughness of the AuNW/ITO integrated film could be significantly increased.

FIG. 5.3: (a – c) SEM images and (d – f) atomic force microscopic (AFM) images of the samples. (a) and (d) AuNMs. (b) and (e) ITO films. (c) and (f) ITO films deposited on the AuNMs. (g) The one-dimensional profile of the texture at the specified position of (f) as indicated by the black line.

5.5 Optical properties of indium tin oxide films

5.5.1 Experimental results

The reflectance of the ITO films were characterised by a spectrometer with an integration sphere. The thickness and refractive index measurement of the ITO films were conducted by the ellipsometry. Figures 5.4(a) and 5.4(b) show the measured reflectance and real part of the refractive index \(n\) of Cell A (with ITO + AuNM) and Cell B (with ITO), respectively. The reflectance of a bare solar cell (without ITO and AuNM) is also given as a benchmark. For Cell B, the decrease of
the reflection was mainly due to the destructive interference between the light reflected from the air/ITO and ITO/Si interfaces, resulting in an anti-reflection effect. The thickness of the ITO film was measured to be 26 nm, and the real part of the refractive index in the range of 1.9 ~ 2.1. These features caused the reflection minima to occur around the wavelength of 200 nm, beyond the wavelength range measurable by the spectrometer.

For Cell A, a broadband reflection decrease compared to Cell B was observed over the wavelength range of 350 – 1100 nm, with the reflection minima red-shifting to 440 nm. The physical mechanisms of the enhanced light trapping can be attributed to the following three reasons.

1. Due to the height and tapered structure of the texturing, the light path length in the textured AuNM/ITO integrated film is increased, which causes the destructive interference to occur at a longer wavelength.

2. The tapered structure (Fig. 5.3(g)) of the AuNM/ITO ranges can form refractive index gradient, i.e., the effective refractive index is gradually decreased from the bottom to the top. This feature can enhance the anti-reflection effect of the ITO film [205]. Indeed, from the ellipsometry measurement, the overall refractive index of the AuNM/ITO integrated film...
was decreased compared to that of the flat ITO film (Fig. 5.4(b)). Meanwhile, the effective thickness of the AuNM/ITO integrated film was increased (60 nm as measured by the ellipsometry) due to the height of the ranges.

3. The nano-texturing on top of the cells could enhance the scattering from the AuNM/ITO integrated film, which means that the light path length in the Si is increased, enabling the enhanced light absorption in the Si.

Furthermore, it is expected that the anti-reflection effects of the AuNM/ITO integrated film can lead to an additional light trapping mechanism due to the nanotexturing when combined with the conventional micrometre sized pyramid texturing for Si solar cells [12].

### 5.5.2 Simulated results

To confirm the measured features in Fig. 5.4(a), we performed the finite-difference time-domain (FDTD) simulations. To simplify the model, we first considered both the ITO film on cell A and the AuNM/ITO integrated film on Cell B as flat films with effective refractive indices and thickness. The values obtained by the ellipsometry were input into the FDTD simulation. Figure 5.5 (a) shows the setup of the model. Periodic boundary condition is applied on the lateral direction (parallel to the Si surface) to simulate the ITO films with an infinite area, and perfectly matched layer condition is applied on the vertical direction (perpendicular to the Si surface) to avoid interference effects. Power monitors are placed on the ITO and Si surface and above the plane wave source to record the light transmission.
As presented in Fig. 5.4(a), good fitting between the experimentally measured (solid lines) and simulated (dashed lines) reflection of the bare Si and the ITO films on Si is obtained, indicating the high accuracy of the model. The slight deviation between the measured and simulated reflection at wavelengths above 1000 nm is due to the semi-infinite consideration in the model that assumes all the light entering the Si is absorbed, while in reality, part of the light is reflected back into the air from the rear surface due to weak absorption coefficient of the Si in the near infrared wavelength region.

Figure 5.5(b) shows the simulated transmittance ($T$) and absorbance ($A$) of the ITO and AuNM/ITO integrated films on Si from the model. It can be seen that the reflection decrease of the ITO films in the shorter wavelengths below 500 nm is partly due to the absorption of the films. For the AuNM/ITO integrated film, the absorption is larger as a result of the increased effective film thickness compared with the ITO film. This accounts for the decreased transmittance of the integrated film below 400 nm. Nevertheless, the absorption of both the ITO films is negligible in the longer wavelengths, and the transmittance of the AuNM/ITO integrated film is enhanced in a broadband range above 400 nm compared to that of the ITO film due to the enhanced anti-reflection effect.
The above model is based on the assumption that the AuNWs are integrated with the ITO film. However, it is well known that metallic nanostructures can generate plasmonic effects. Therefore, it is also important to understand the plasmonic behaviours of the AuNWs in the ITO film for a further interpretation of the optical properties of the AuNM/ITO integrated film. As was discussed in Section 5.4, the AuNWs reshaped from the uniformly distributed nanomembrane to larger bundles during the ITO deposition. Although it would be difficult to experimentally verify the formation of the reshaped AuNW bundles in the ITO, we can extract the following information from the sample: (i) most of the AuNWs are embedded in the ITO rather than being in contact with the Si surface. (ii) the AuNWs are separated by the OA capping agent as shown in the TEM images in Fig 5.1 and the surface coverage is only about 60% [98]. Hence, it is reasonable to assume that there are individual AuNWs embedded in the ITO dielectric environment.

According to these features, we start with investigating the optical behaviours of the single AuNW in the ITO. Figure 5.6(a) shows the simulation setup. A AuNW with a diameter of 2 nm is embedded in the ITO dielectric environment. Perfectly matched layer boundary condition is applied on every direction of the simulation region. Power monitors are placed inside and outside the total-field scattered-field (TFSF) light source to record the light absorbed and scattered by the AuNW, respectively.

Figure 5.6(b) shows the simulated absorption ($A$) and scattering ($S$) by the AuNW normalised to the source power for the $s$-mode and $p$-mode (light polarisation perpendicular and parallel to the long axis of the AuNW, respectively) incident light. It can be seen that a very small fraction (up to $\sim 5\%$) of light is absorbed by the AuNW in the short wavelengths below 600 nm. This can be partly attributed to the increased absorption of the AuNM/ITO integrated film as shown in Fig. 5.5(b). An absorption peak is observed at 525 nm for the $s$-mode light source due to the localised surface plasmon resonance (LSPR) of the AuNW. Correspondingly, a scattering peak is observed in vicinity. Nevertheless, the total amount of scattered
light by the AuNW is less than 0.01% for both s-mode and p-mode in the entire wavelength range.

![Diagram](image)

**FIG 5.6** (a) Schematic diagrams of the simulation model for the AuNW in ITO with the s-mode light source (light polarisation perpendicular to the long axis of the AuNW). (b) Simulated absorption ($A$) and scattering ($S$) by the AuNW normalised to the light source under the s-mode and p-mode light source (light polarisation parallel to the long axis of the AuNW).

Furthermore, by normalising the absorbed and scattered power to the source intensity and geometrical cross-section of the AuNW, the resulting absorption and scattering cross-sections of the single AuNW are well below 1, which means coupling between adjacent AuNWs is unlikely to occur. Hence, overall, the plasmonic absorption and scattering of the ultrathin single AuNW are too weak to induce noticeable change on the optical behaviours of the ITO film. The enhanced scattering of the AuNM/ITO integrated film as mentioned in Section 5.5.1 is mostly due to the nanotexturing on the surface of the film.

### 5.6 Light trapping of the indium tin oxide films on solar cells

In order to reveal the effect of the improved anti-reflection behaviour of the textured AuNM/ITO integrated film, we carried out the external quantum efficiency ($EQE$) measurement of the solar cells. Figure 5.7(a) shows the $EQE$
curves of the bare cell, Cell A and Cell B. It should be noted that the relatively low $EQE$ compared to the typical single-crystalline Si wafer solar cell is due to the lack of the conventional surface texture as we initially designed for the experiments. Consistently, due to the enhanced anti-reflection effect as described above, a broadband increase of the $EQE$ enhancement for Cell A is observed compared with Cell B, in the wavelength range of 400 – 950 nm.

To further confirm the anti-reflection mechanisms in this range, we present the $EQE$ enhancement (defined by \(\frac{EQE_{\text{sample cell}} - EQE_{\text{bare cell}}}{EQE_{\text{bare cell}}}\)) curves of Cell A and Cell B in Fig. 5.7(b). For Cell B, $EQE$ enhancement was observed at 400 – 600 nm, and the curve is flattened in the longer wavelengths, which is in accordance with the transmittance curve in Fig. 5.5(b). For Cell A, an $EQE$ enhancement peak occurred at ~ 550 nm, matching well with the transmittance peak in Fig. 5.5(b). However, this $EQE$ peak is less significant as revealed by the transmittance peak. This is because for the real solar cell, the heavily-doped emitter can result in weak response in the short-wavelength (300 – 500 nm) range, which means part of the transmitted light does not contribute to the electron-hole pairs that are collected by the $EQE$ measurement system. Noticeably, a small $EQE$ enhancement dip was present at ~ 510 nm, which agrees well with the absorption peak due to the LSPR of the AuNWs in ITO as shown in Fig. 5.6(b).
In the wavelength range below 400 nm, the \( EQE \) was decreased for both cells due to the absorption of the ITO film. For Cell A, the \( EQE \) decrease was larger because of more reflection induced by the red-shifting of the reflection minima as well as more absorption in the ITO. However, the \( EQE \) decreases occurred where the power of the solar spectrum is relatively small. Hence, the overall optical performance enhancement of Cell A was not compromised.

By integrating the \( EQE \) with the air mass 1.5 global (AM1.5G) solar spectrum, the photocurrent density (\( J_{SC} \)) of Cell A was increased from 24.79 mA/cm\(^2\) to 28.06 mA/cm\(^2\), with an enhancement of 13%. This is 5% higher than Cell B, whose \( J_{SC} \) was increased from 25.17 mA/cm\(^2\) to 27.17 mA/cm\(^2\). It should be noted that the \( EQE \), \( J_{SC} \) and efficiency enhancement have been repeatable on different solar cells under the same condition, which proves the reliability of this method.

Table 5.1 One-sun current-voltage (\( I-V \)) characteristics of Cell A and Cell B with and without the ITO films and the corresponding enhancement values for the given parameters.

<table>
<thead>
<tr>
<th></th>
<th>( V_{OC} )</th>
<th>( J_{SC} )</th>
<th>( FF )</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>591.10 mV</td>
<td>24.95 mA/cm(^2)</td>
<td>64.72%</td>
<td>9.54%</td>
</tr>
<tr>
<td>With ITO+AuNM</td>
<td>589.95 mV</td>
<td>26.60 mA/cm(^2)</td>
<td>65.64%</td>
<td>10.30%</td>
</tr>
<tr>
<td>Enhancement</td>
<td>-0.20%</td>
<td>6.63%</td>
<td>1.42%</td>
<td>7.93%</td>
</tr>
<tr>
<td>Cell B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>592.19 mV</td>
<td>25.40 mA/cm(^2)</td>
<td>66.78%</td>
<td>10.04%</td>
</tr>
<tr>
<td>With ITO</td>
<td>587.79 mV</td>
<td>26.57 mA/cm(^2)</td>
<td>66.32%</td>
<td>10.36%</td>
</tr>
<tr>
<td>Enhancement</td>
<td>-0.74%</td>
<td>4.62%</td>
<td>-0.68%</td>
<td>3.13%</td>
</tr>
</tbody>
</table>

The \( EQE \) and \( J_{SC} \) enhancement was confirmed by the current-voltage (\( I-V \)) measurement. Table 5.1 gives the one-sun \( I-V \) characteristics of Cell A and Cell B with and without the ITO films and the corresponding enhancement. It clearly shows that the efficiency enhancement for both cells was mainly due to the \( J_{SC} \) increase, while the \( V_{OC} \) and \( FF \) were only slightly changed. The difference of the one-sun \( J_{SC} \) enhancement between Cell A and Cell B is 2%, which is smaller than
that obtained from the $EQE$ measurement. We attribute this discrepancy to the increased sheet resistance of the AuNM/ITO integrated film ($868 \ \Omega/\square$) compared to that of the ITO film ($629 \ \Omega/\square$).

5.7 Conclusions

We demonstrated the use of ultrathin AuNWs as part of the hybrid transparent electrode with the ITO films for an enhanced light trapping effect on crystalline Si wafer solar cells. Langmuir-Blodgett technique was applied as a facile and scalable method to fabricate and integrate the AuNMs with highly uniform and aligned AuNWs onto the solar cells. Tapered range texturing of the ITO films was formed by the reshaping of the AuNWs during the ITO deposition, leading to an increased surface roughness which is four times larger than that of the planar ITO film. As a result, enhanced anti-reflection effect of the AuNM/ITO integrated film was observed on the solar cell.

The optical properties of the ITO films and AuNWs were also theoretically investigated. A broadband transmittance enhancement of the AuNM/ITO integrated film on Si for the wavelengths above 400 nm was confirmed, while in the shorter wavelengths, more absorption within the film results in decreased transmittance. An absorption peak of the AuNW within ITO due to the LSPR was observed at 525 nm. However, due to the ultrathin nature of the AuNWs, the plasmonic absorption and scattering are too weak to induce any noticeable change on the optical behaviours of the ITO film.

As a result of the improved light trapping effect, $EQE$ of the solar cell with the textured AuNM/ITO integrated film was enhanced over a broadband wavelength range of 400 – 950 nm, with the LSPR effect confirmed at 510 nm. Accordingly, $J_{SC}$ from the $EQE$ measurement was increased by 13%, which is 5% larger than the cell with a planar ITO film. The one-sun $I-V$ measurement further confirmed that the efficiency enhancement of the solar cells was mainly due to the $J_{SC}$ increase.
We also found out that the optical benefits of the AuNM/ITO integrated film was slightly compromised by the increased sheet resistance.
Chapter 6

Metal nanowire networks on amorphous silicon thin film solar cells

6.1 Introduction

In Chapter 4 we have demonstrated the use of silver nanowire (AgNW) network as transparent electrode on crystalline silicon (Si) wafer solar cells. Another important type of Si-based solar cells is the hydrogenated amorphous Si (a-Si:H) thin film solar cell. Compared to the Si wafer solar cells, the costs of the a-Si:H solar cells can be significantly reduced. However, the a-Si:H solar cells generally suffer from lower energy conversion efficiency as a result of the insufficient light absorption by the much thinner active layers. Therefore, using the front electrode with better optical and electrical performances is more critical for a-Si:H solar cells.

In spite of their high electrical conductivity, we have demonstrated in Chapter 3 and 4 that the AgNW networks cannot introduce optical enhancement on crystalline Si wafer solar cells. This is mainly because the wafer solar cells are optically thick and their intrinsic light absorption is already large. However, for the thin film solar cells which suffer from low light absorption due to the significantly reduced active layer thickness, the plasmonic scattering and near-field
enhancement by the metal NWs can potentially introduce optical benefit. Moreover, the thin active layers of the thin film solar cells could form waveguide. This can lead to significant absorption enhancement when the waveguide mode is excited by the periodic metal NWs as reviewed in Chapter 2, which could not be achieved within the optically thick wafer solar cells. In this chapter, we explore the use of AgNW networks as transparent electrodes and light trapping schemes on a-Si:H thin film solar cells [219].

This chapter has the following structures. In Section 6.2 we systematically investigate the optical properties of metal NW networks on a-Si:H solar cells through numerical simulations. The dependence on the shape, dimension, density, position and material of the NWs is discussed as guidance for designing the experiments. The optical and electrical performances of the solution-processed AgNW networks on the a-Si:H solar cells are then experimentally studied in Section 6.3. Finally we conclude this chapter in Section 6.4.

6.2 Theoretical study

The optical behaviours of the AgNW networks on a-Si:H solar cells are first investigated by numerical simulations as guidance for the experiments. In this chapter we only use the n-i-p type structure for two reasons: (i) to rule out any factors that are related to the change of the total volume of the active layer due to the surface morphology of the AgNWs; (ii) as reviewed in Chapter 2, when the active layers are deposited on top of the AgNWs, they can easily be shunted by the surface morphology of the AgNWs. This problem needs to be avoided for the proof-of-concept experiments.

In this section we discuss the simulation for the solution-processed circular AgNWs and lithographically patterned rectangular metal NWs individually. An important conclusion was given in Section 3.3 that the one-dimensional (1D) gratings can optically outperform the two-dimensional (2D) meshes due to less
reflection. Therefore, only the 1D grating structures are considered in this section for the optimised light absorption in solar cells.

The numerical simulations are performed by the finite-difference time-domain (FDTD) method. Figures 6.1(a) and 6.1(b) show the details of the models for the circular and rectangular NWs on n-i-p a-Si:H solar cells, respectively. A 500 nm Ag film is placed at the bottom as the rear reflector and metal contact. The 100 nm ZnO film in between the Ag film and the a-Si layer acts as a charge collection layer. The thickness of the a-Si layer is set to be 300 nm, which is the typical thickness of the practical a-Si:H solar cells. Indium tin oxide (ITO) films with variable thicknesses \( t \) are placed above the a-Si layer for passivation, charge collection and anti-reflection. Periodic 1D AgNWs with variable dimensions sit on top of the ITO film. The optical constants of Ag material were obtained from Palik, and ITO, ZnO and a-Si:H measured from a typical n-i-p a-Si:H solar cell. For a given structure, the cases for the incident light with polarisation normal (\( s \)-mode) and parallel (\( p \)-mode) to the gratings are both simulated, which contribute equally to the unpolarised sunlight.

**FIG. 6.1** Schematic structures of the simulation models for the 1D (a) circular silver nanowires (AgNWs) on n-i-p a-Si:H solar cell with variable indium tin oxide (ITO) thickness \( t \), AgNW diameter \( d \) and periodicity \( p \); (b) rectangular NWs with variable ITO thickness \( t \), NW width \( w \), height \( h \) and periodicity \( p \).
The optical performance of the a-Si:H solar cells is evaluated by the light-generated current density \((J_L)\), which is calculated according to the following equation:

\[
J_L = e \cdot \int_{300nm}^{800nm} \frac{\lambda}{h} I_{AM1.5G}(\lambda) \cdot A(\lambda) d\lambda
\]  

(6.1)

where \(e\) is the electron charge, \(\lambda, h, c, I_{AM1.5G}\) the same definition as in Equation 3.1, and \(A\) the absorbance of the a-Si:H layer calculated by the subtraction of the transmittance of the power monitors above and below this layer.

### 6.2.1 Circular silver nanowires

We first optimise the periodicity and ITO thickness for the structure in Fig. 5.1(a). The diameter of the AgNW is fixed at 100 nm, which is the averaged value of the solution-processed AgNWs as given in Chapter 4. The solar cell with an optimised ITO thickness of 60 nm without AgNWs \((J_L = 14.16 \text{ mA/cm}^2)\) is used as a reference. Figures 6.2(a-c) show \(J_L\) of the solar cells with AgNWs normalised to that of the reference cell. For the \(s\)-mode incident light (Fig. 6.2(a)), relatively large \(J_L\) values are observed in a narrow-featured area near \(p = 400 \text{ nm}\) due to the excitation of the waveguide modes. For all the periodicities, the normalised \(J_L\) reaches the highest values at \(t = 40 – 60 \text{ nm}\) with an insignificant difference (less than 3%) in this thickness range. This is mainly due to the optimised anti-reflection effect of the ITO film.

It can also be seen that \(J_L\) of the solar cells with AgNWs tends to approach that of the reference cell when the AgNW periodicity increases. The similar behaviour is observed for the \(p\)-mode incident light except that the \(J_L\) values are smaller due to more reflection from the AgNWs. This indicates that with optimised anti-reflection effect of the ITO film, the AgNWs do not introduce additional light trapping effects but rather reflect the light. The same phenomenon is also observed when we decrease the AgNW diameter (results not shown).
The normalised $J_L$ under the unpolarised sunlight is calculated by averaging the results for the $s$-mode and $p$-mode, as shown in Fig. 6.2(c). To reveal the detailed mechanisms, we plot the absorbance of the a-Si:H layer for the structure with $t = 60$ nm and $p = 1$ µm in Fig. 6.2(d), where $J_L$ starts to increase, as indicated by the dashed lines in Fig. 6.2(c). Indeed, compared to the reference cell, the AgNWs under both $s$-mode and $p$-mode light result in reduced absorption in the a-Si:H layer in a broadband wavelength range of 430 – 600 nm due to the stronger reflection.

![FIG. 6.2](image)

We then further investigate the effect of the AgNW position on the optical performance of the solar cells. Figure 6.3(a) shows $J_L$ as a function of the top ITO thickness ($t_{top}$) while maintaining $t = 60$ nm, $d = 100$ nm and $p = 1$ µm for the
structure given in the inset plot. The optimised $J_L$ is observed for $t_{top} = 20$ nm with very little difference in the range of $t_{top} = 15 - 25$ nm. The absorbance curves of the a-Si:H layer are given in Fig. 6.3(b). Compared to the AgNWs uncovered by ITO ($t_{top} = 0$), the AgNWs covered by 20 nm ITO ($t_{top} = 20$ nm) can introduce a broadband absorption enhancement. This phenomenon can be attributed to the change of the plasmonic behaviours of the AgNWs.

Figures 6.3(c) and 6.3(d) show the normalised scattering cross-sections ($Q_{scat}$) for the light scattered into the a-Si:H layer and the normalised absorption cross-sections ($Q_{abs}$) of the AgNW with $t_{top} = 0$ and $t_{top} = 20$ nm, respectively. Evidently, for the wavelengths above 500 nm, the $s$-mode absorption in the a-Si:H layer is enhanced.
due to the increased scattering cross-section of the AgNW with $t_{top} = 20$ nm. In the wavelength range of 370 – 500 nm, the increased $s$-mode absorption in the AgNW with $t_{top} = 20$ nm leads to decreased absorption in the a-Si:H layer, and vice versa for the wavelengths below 370 nm. Under the $p$-mode light illumination, the anti-reflection behaviour of the ITO film is blue-shifted due to the disruption of the ITO film. Thus the $p$-mode absorption is enhanced in a broadband range below 500 nm. For the AgNWs covered by thicker ITO layers, $J_L$ starts to decrease mainly because of higher absorption within the AgNWs.

### 6.2.2 Rectangular metal nanowires

As can be concluded from the previous section, compared to the AgNWs, the ITO thickness is a more important parameter affecting the overall optical performance of the a-Si:H solar cells due to the anti-reflection effect. Therefore, we first optimise the ITO thickness with rectangular AgNWs. To start with, we use the AgNW dimensions that are preliminarily optimised for the a-Si layer without the ITO film: $w = 110$ nm, $h = 90$ nm, $p = 700$ nm. As expected, highest a-Si absorption is found for $t = 60$ nm, where the best anti-reflection effect is achieved.

With maintained ITO thickness of 60 nm, we then re-optimise $w$ and $h$ for variable $p$. The results are shown in Fig. 6.4(a). The largest $J_L$ of 14.21 mA/cm$^2$ is achieved at $w = 70$ nm, $h = 90$ nm, and $p = 500$ nm. This is slightly higher than that of the reference cell without the AgNWs, as indicated by the black dotted line. To further understand the effect of the AgNW dimensions on the optical performance of the solar cell, we plot $J_L$ as a function of $w$ and $h$ for $p = 500$ nm in Fig. 6.4(b). Under the $s$-mode light, relatively large $J_L$ enhancements are observed for the AgNWs with the dimensions of 50 nm < $w$ < 110 nm and $h > 50$ nm due to strong scattering effect. For the AgNWs smaller or larger than these dimensions, $J_L$ is significantly reduced by strong AgNW absorption or reflection. Under the $p$-mode light, thinner AgNWs lead to larger $J_L$ because of less reflection. Overall, under the unpolarised
light, the width of the AgNW is a more critical parameter than the height that leads to the change of $J_L$.

![Graph](image1)

**Fig. 6.4** (a) Optimised $w$, $h$ and $J_L$ for variable $p$ of the AgNWs on top of 60 nm ITO layer. (b) $J_L$ as a function of $w$ and $h$ for $p = 500$ nm. (c) Absorbance of the a-Si:H layer with optimised AgNW dimensions for $p = 500$ nm on top of 60 nm ITO layer, referenced to the cell without the AgNWs. (d) $Q_{scat}$ for the light scattered into the a-Si:H layer and $Q_{abs}$ of the optimised AgNW.

The mechanisms of the $J_L$ enhancement with optimised AgNW dimensions for $p = 500$ nm are elaborated by the absorbance curves of the a-Si:H layer, as shown in Fig. 6.4(c), referenced to the cell without the AgNWs. It can be seen that the enhancement is mainly attributed to the broadband $s$-mode absorption increase in the longer wavelength range above 570 nm, although in the shorter wavelengths the absorption is decreased compared to the cells integrated with the circular AgNWs. Noticeably, the sharp absorption peak at 700 nm is due to the excitation of the waveguide mode under the $p$-mode light. Figure 6.4(d) shows $Q_{scat}$ for the light scattered into the a-Si:H layer and $Q_{abs}$ of the AgNW. Indeed, compared to the circular AgNWs (Fig. 6.3(c)), $Q_{scat}$ and $Q_{abs}$ of the rectangular AgNWs are
increased in the longer and shorter wavelengths, respectively, agreeing well with the absorption features in Fig. 6.4(c).

Again, the position of the AgNWs with a fixed ITO thickness of 60 nm is investigated. Figure 6.5(a) shows \( J_L \) as a function of \( t_{\text{top}} \) with optimised AgNW dimensions and periodicity. Unlike the circular AgNWs as shown in Fig. 6.4(a), \( J_L \) of the solar cells integrated with the rectangular AgNWs is inversely related to \( t_{\text{top}} \). Figure 6.5(b) shows the \( Q_{\text{scat}} \) and \( Q_{\text{abs}} \) of the AgNW with \( t_{\text{top}} = 20 \) nm. It can be seen that when the rectangular AgNWs are covered by the higher-index ITO layer, the \( s \)-mode \( Q_{\text{abs}} \) is increased in a much wider wavelength range of 300 – 600 nm compared to that of the circular AgNWs (Fig. 6.3(d)). This finding is similar to that observed in Section 3.5. Overall, the increased absorption in rectangular AgNWs outweighs the enhanced scattering effect, and thus leads to the reduced \( J_L \).

![Figure 6.5(a)](image)

**FIG. 6.5(a)** \( J_L \) as a function of \( t_{\text{top}} \) for \( t = 60 \) nm, \( w = 70 \) nm, \( h = 90 \) nm and \( p = 500 \) nm. The inset plot shows the simulated structure of the AgNWs sandwiched in ITO film. (b) \( Q_{\text{scat}} \) for the light scattered into the a-Si layer and \( Q_{\text{abs}} \) of the 1D AgNW with \( t_{\text{top}} = 20 \) nm.

As reviewed in Chapter 2, apart from the dimensions of the NWs, the material of the NWs is another parameter that can be varied by the lithographical patterning methods. Therefore, the effect of NW material on the optical performance of the a-Si:H solar cells is also investigated. Figure 6.6(a) shows the optimised \( J_L \) as a function of \( p \) for a few popular metals including Ag, aluminium (Al), gold (Au), and copper (Cu). Obviously, Ag has the best optical performance amongst all the compared metals, followed by Al, Au and Cu in sequence. This phenomenon can
be explained by the plasmonic behaviours of the metal NWs. Figures 6.6(b) and 6.6(c) show the fraction of light scattered into the a-Si:H layer ($f_{\text{a-Si}}$ calculated by $Q_{\text{scat}}$ to a-Si:H divided by total $Q_{\text{scat}}$) and $Q_{\text{abs}}$ of the metal NWs ($w = 70$ nm, $h = 90$ nm) under the unpolarised light, respectively. Although the AuNWs and the CuNWs have stronger scattering capabilities than the AgNWs, they absorb more light in the entire wavelength range. On the other hand, the AlNWs absorb less light in the shorter wavelengths below 500 nm, but their scattering ability is weaker than the AgNWs in the longer wavelengths.

FIG. 6.6 (a) Optimised $J_L$ of the a-Si:H solar cells with AgNWs, AlNWs, AuNWs and CuNWs for variable $p$. The fraction of light scattered into the a-Si:H layer ($f_{\text{a-Si}}$ calculated by $Q_{\text{scat}}$ to a-Si:H divided by total $Q_{\text{scat}}$) and $Q_{\text{abs}}$ of the metal NWs ($w = 70$ nm, $h = 90$ nm) under the unpolarised light are shown in (b) and (c), respectively.
6.3 Solution-processed silver nanowire networks on amorphous silicon solar cells

6.3.1 On bare amorphous silicon layers

Having shown the optical behaviours of the AgNW networks on a-Si:H solar cells, we then investigate their electrical performances through experiments. Solution-processed AgNW networks are first selected as the low-cost approaches and proof-of-concept demonstration on the solar cells. We start with studying the intrinsic electrical behaviours of the AgNW networks on bare a-Si:H solar cells by fully replacing the conventional transparent conductive oxide (TCO) films with the AgNW networks.

The n-i-p a-Si:H layers with a total thickness of 300 nm were deposited on stainless steel sheets by the plasmon-enhanced chemical vapour deposition (PECVD) method. The AgNW network with a sheet resistance \( R_{sh} \) of \( \sim 20 \, \Omega/\square \) was spin-coated onto the top of the bare a-Si:H layer. The front metal contact pads (10 nm Ti/300 nm Ag) were fabricated by electron beam evaporation for electrical measurements. The sample then went through the optimised annealing condition as described in Chapter 4 (200 °C for 30 min followed by 400 °C for 1 min in N\(_2\) atmosphere) to ensure efficient charge collection and transport by the AgNWs.

Figure 6.7(a) shows the current density-voltage \((J-V)\) curve of the as-fabricated solar cell. The inset plot and the table show the structure and important parameters of the solar cell, respectively. Although the sheet resistance of the AgNW network \( \sim 20 \, \Omega/\square \) is low enough as transparent electrode (comparable to that of the typical ITO film), the open-circuit voltage \((V_{OC})\), short-circuit current \((J_{SC})\), and fill factor \((FF)\) of the solar cells are all abnormally low, leading to an ultralow efficiency \((\eta)\) of 0.5%. Figure 6.7(b) shows the external quantum efficiency \((EQE)\) of the solar

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8 The fabrication of the a-Si:H layer and ITO films throughout this chapter was performed by A/Prof. Guofu Hou at Nankai University.
cell. Compared to $EQE$ of the bare a-Si:H solar cell that is predicted by the numerical simulation, the measured $EQE$ of the a-Si:H solar cell with the AgNW networks is much lower in the whole wavelength range. According to the inset scanning electron microscopic (SEM) image of the solar cell, the separation among the individual AgNWs can be up to tens of micrometres, which are much larger than the carrier diffusion lengths of the doped a-Si:H layer (hundreds of nanometres) [20]. Therefore, most of the light-generated charges would recombine on the surface before they are collected by the AgNWs. This also explains the ultralow $V_{OC}$ as observed in Fig. 6.7(a).

FIG. 6.7 (a) Current density-voltage ($J$-$V$) curve of the bare a-Si:H solar cell with the AgNW network as transparent electrode. The inset plot and table show the structure and important parameters of the solar cell, respectively. (b) External quantum efficiency ($EQE$) measured from the a-Si:H solar cell with the AgNW network and predicted by the numerical simulation. The inset figure shows the scanning electron microscopic (SEM) image of the AgNW network on the solar cell. The scale bar is 20 µm.

6.3.2 On top of indium tin oxide layers

It can be concluded from the above Section that when AgNW networks are applied on a-Si:H solar cells as the transparent electrodes, charge collection layers are required for better electrical performances of the solar cells. In this section we investigate the use of the AgNW networks on top of an ITO film on the a-Si:H solar cell. The thickness of the ITO film is fixed at 60 nm for an optimised anti-
reflection effect on the solar cells according the simulated results presented in the previous section.

The ITO film with $R_{sh}$ of $\sim 80 \, \Omega/\square$ was deposited by the thermal evaporation method in order to avoid damages to the a-Si:H surface that would be otherwise introduced by the sputtering processes. The metal contact pad was fabricated on top of the ITO film. The area of the solar cell is 0.3 cm$^2$. The initial performances of the as-fabricated solar cells were measured after the metal contact pad fabrication.

After spin-coating of the AgNWs, a critical issue we need to address for the as-deposited AgNWs on the a-Si:H solar cell is the annealing conditions. Since the AgNWs are in contact with the ITO films, the two-step annealing process that is designed for creating the AgNW/Si ohmic contact is not necessarily applicable. More importantly, the second high temperature (400 °C) annealing step can degrade the quality of the a-Si:H layers, leading to significantly decreased $V_{OC}$ and $FF$ of the solar cell (results not shown). In order to avoid such issue, we decreased the annealing temperature down to 150 °C, which is below the deposition temperature of the a-Si:H layer. Meanwhile, the annealing time was extended to 2 hours to ensure reasonably low $R_{sh}$ can be achieved for the AgNW networks.

After annealing, the AgNW network on top of the solar cell (Cell A) has a $R_{sh}$ of $\sim 20 \, \Omega/\square$. A reference cell (Cell B) without the AgNWs was used alongside to monitor any solar cell performance change induced during the annealing process. Specifically, Cell A and Cell B were deposited in the same batch with similar solar cell performances for easy comparison. Figures 6.8(a) and (b) show the $J-V$ curves of Cell A and Cell B, respectively. The corresponding solar cell structure and important parameters are given in the inset figures and tables.

For Cell B, the efficiency was slightly increased (with an enhancement of 12.9%) after annealing, mainly because annealing can enhance the contact between the Ag pad and the ITO, as evidenced by the $FF$ increase. For Cell A, a larger efficiency

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9 The AgNW network was fabricated based on the correlation between the sheet resistance and the spin-coating parameters that have been obtained on the glass substrates under the same annealing condition.
enhancement of 16.4% was observed compared to that of Cell B. We attribute the extra enhancement to the high electrical conductivity of the AgNW network. With the use of the AgNW network, the charges collected by the ITO film would preferentially travel to the nearby highly conductive AgNWs. As a result, they could lose less momentum and have more chances to be finally collected by the contact pad than those would otherwise travel only in the less conductive ITO film as for Cell B. This explains the $J_{SC}$ increase for Cell A. The $FF$ enhancement for Cell A (12.5%) was also higher than Cell B (11.9%) due to less resistive loss on the front electrode, which is clearly indicated by the change of the squareness of the $J-V$ curves. The open-circuit voltages for both cells were also slightly increased but their effects on the efficiency improvements were insignificant.

The influence of the AgNW networks on the optical performances of the solar cells was investigated by the $EQE$ measurements. Figures 6.8(c) and (d) show $EQE$ of Cell A and Cell B, respectively. For Cell B, $EQE$ was increased in the entire wavelength range after each step, which can be attributed to the improved charge collection efficiency as a result of the better contact between the metal pad and the ITO film (also evident from the $FF$ increase in Fig. 6.8(b)). On the contrary, for Cell A, $EQE$ was decreased for the wavelengths below 550 nm due to the reflection of the AgNWs, agreeing very well with the simulated results in Fig. 6.2(d).

By integrating $EQE$ multiplied by electron charge over the air mass 1.5 global (AM1.5G) solar spectrum, we can obtain $J_{SC,EQE}$ as given in the inset tables in Figs. 6.8(c) and (d). It is interesting to note that the change of $J_{SC,EQE}$ is not necessarily in consistent with the change of $J_{SC}$ obtained from the $J-V$ measurement. This is because for the $EQE$ measurement, $J_{SC}$ is unaffected by the resistance of the front electrode (see Section 4.5.3), while for the $J-V$ measurement, the actual current flowing through the front electrode is much larger so that the series resistance can have much bigger impact on $J_{SC}$ due to the resistive power loss.
We then further increase the electrical conductivity of the AgNW networks to investigate if extra efficiency improvement can be achieved. A denser AgNW network with a final $R_{sh}$ of $\sim 10 \, \Omega/\square$ was fabricated on Cell A. However, we found that the efficiency was not improved (results not shown). According to Equation 4.1, when the cell size is small and the AgNW network is sufficiently conductive,
the resistive loss due to the lateral current flow on the AgNW network is ignorable so that further increasing the conductivity will not introduce noticeable electrical benefits to the solar cell performance. On the other hand, the highly conductive AgNW networks will be more advantageous on large-size solar cells or solar modules, which are more vulnerable to the resistive loss on the front electrodes [220].

6.3.3 Sandwiched in indium tin oxide layers

According to the simulated results in Section 6.2.1, the optimised AgNW position is on top of 40 nm ITO and covered by 20 nm ITO, which can lead to enhanced scattering effect for the a-Si:H solar cell compared to the AgNWs on top of 60 nm ITO. Having demonstrated the benefits of the AgNWs to the electrical performance of the a-Si:H solar cell in the previous section, we then further experimentally investigate the effect of AgNWs with the optimised position on the optical performance of the solar cell.

Initially, a 40 nm ± 5 nm\(^{10}\) thick ITO layer with \(R_{sh}\) of ~ 192 \(\Omega/\square\) was deposited onto the a-Si:H layer. During Step 1, the AgNW network with \(R_{sh}\) of ~ 20 \(\Omega/\square\) (after annealing at 150 °C for 2 hours) was integrated onto Cell C, with a reference cell (Cell D) without the AgNWs used alongside to exclude the effect of annealing. Figures 6.9(a) and (b) show the \(J-V\) curves of Cell C and Cell D, respectively. As expected, the efficiency of Cell C with AgNWs was significantly improved compared to Cell D mainly due to the increase in \(FF\). It should also be noted that the efficiency enhancement of Cell C (28.8%) is much larger than that of Cell A, since the electrical benefit of the AgNWs is more pronounced on the less conductive ITO layer.

\(^{10}\) The error could be subject to thickness measurement.
FIG. 6.9 (a) and (b) $J$-$V$ curves of the a-Si:H solar cells with two-layer ITO films as charge collection layers. The inset plots and tables show the respective structure and important parameters of the solar cells. (c) and (d) $EQE$ curves of the a-Si:H solar cells. (a) and (c) are the results for Cell C (with AgNWs sandwiched in the ITO layers). (b) and (d) are the results for Cell D (reference cell without AgNWs).

Figures 6.9(c) and (d) show the $EQE$ curves for the corresponding solar cells. It is interesting to note that the total light absorption for Cell C with 40 nm ITO was not inferior to Cell A with 60 nm ITO according to $J_{SC, EQE}$, while $J_{SC}$ obtained from the $J$-$V$ measurement for Cell C was smaller than the Cell A. The discrepancy of $J_{SC}$ can be attributed to the different conductivity of the ITO films. Although the
AgNW networks with the same $R_{sh}$ were applied on Cell A and Cell C, the charges need to travel within the ITO before they are collected by the AgNWs, where more resistive loss is induced for Cell C with thinner and less conductive ITO.

During Step 2, a 20 nm ± 5 nm ITO layer was deposited on top of Cell C and Cell D, resulting in a total ITO thickness of 60 nm. As shown in Figs. 6.9(c) and (d), the broadband $EQE$ enhancement for Cell C compared to Cell D agrees well with the theoretical prediction in Fig. 6.3(b). However, an unexpected broadband $EQE$ decrease in the short wavelengths occurred for the cells in Step 2 compared to that in Step 1, leading to significantly decreased $J_{SC}$ and the final efficiency (Figs. 6.9(a) and (b)). It is considered that the two-step deposition process could result in degraded overall quality of the ITO film compared to the continuous deposition processes. Therefore, although in theory the structure of AgNWs sandwiched in ITO is optimised for the optical performance of the a-Si:H solar cell, it is not practically preferred in terms of the overall solar cell performance and the fabrication complexity.

**6.4 Conclusions**

We theoretically investigated the optical performances of metal NW networks on a-Si:H solar cells dependent on the ITO thickness, the shape, dimensions, density, position and material of the NWs. It was found that the ITO thickness is a critical parameter affecting the overall optical performance of the solar cells due to their anti-reflection effects. The optimised ITO thickness is 60 nm regardless of the NW parameters.

According to the simulated results, absorption of the a-Si:H layer with the circular AgNWs is decreased due to the increased reflection compared to that without the AgNWs. The optimised AgNW position is on top of 40 nm ITO and covered by 20 nm ITO, where enhanced scattering outweighs the absorption by the AgNWs. For the rectangular AgNWs, the optimised AgNW dimensions are $w = 70$ nm, $h = 90$
nm, and $p = 500$ nm, with which a slight increase in $J_{SC}$ ($0.05$ mA/cm$^2$) was obtained due to enhanced scattering in the longer wavelengths. Unlike the circular AgNWs, the optimised position for the rectangular AgNWs is on top of 60 nm ITO since they suffer from more absorption when being embedded in the ITO film. Given the fabrication flexibility, the material of the rectangular NWs was also investigated and it was found that Ag can outperform other metals due to either less absorption or stronger scattering ability.

We experimentally investigated the use of solution-processed AgNW networks as transparent electrodes on a-Si:H solar cells. When the AgNWs were applied on the bare a-Si:H layer, the solar cell suffered from ultralow efficiency due to poor charge collection. We showed that with a 60 nm thick ITO film underneath the AgNWs as charge collection layer and anti-reflection layer, the use of AgNW network could result in an efficiency enhancement of 16.4%, of which 6.7% was attributed to the high conductivity of the AgNW network. We also demonstrated the use of the AgNWs with the theoretically optimised position. Although the enhanced scattering by the AgNWs was experimentally observed, the ITO film suffered from degraded quality from the two-step deposition process and resulted in poorer solar cell performance than the cells with continuous ITO films.
Chapter 7

Conclusions

7.1 Thesis conclusions

In this thesis we theoretically and experimentally investigated the application of metal nanowire (NW) networks as transparent electrodes and light trapping schemes on Si-based solar cells. A wide range of topics were covered including the fabrication methods of metal NWs, the integration methods of NWs onto solar cells, the application of NWs with different materials, the optical and electrical properties of the metal NW networks and their influence on the solar cell performances. Several major achievements were made in this thesis as follows:

1. Theoretical investigation on the optical properties of silver NW (AgNW) networks dependent on the NW shape, the substrate material and the dielectric embedding material, with detailed physical mechanisms elaborated.
2. Fabrication of large-size, high-uniformity AgNW networks by the spin-coating method, achieving superior optical transmittance and electrical conductivity to the conventional transparent conductive oxide (TCO) films.
3. Experimental demonstration of the AgNW network as transparent electrode on crystalline silicon (Si) wafer solar cell and development of the two-step
annealing process for efficient current collection, with a 19% efficiency enhancement achieved.

4. Experimental demonstration and theoretical investigation of the enhanced light trapping of gold NW/indium tin oxide (ITO) integrated film on crystalline Si wafer solar cell, with a 13% light absorption enhancement achieved.

5. Theoretical investigation of the optical performances of metal NW networks on hydrogenated amorphous Si (a-Si:H) solar cells dependent on a wide range of parameters.

6. Experimental demonstration of the electrical and optical performances of AgNW networks on a-Si:H solar cells with up to 29% efficiency enhancement achieved.

7. Development of an optimised integration processes of AgNW networks onto a-Si:H solar cells considering the effect of annealing to the active layers, the effect of AgNW position on the practical solar cell performances and the complexity of the processes.

First of all, we obtained a thorough and comprehensive understanding on the optical behaviours of AgNW networks through numerical simulations. The optical transmittance of the circular and rectangular AgNW networks that can be produced by different fabrication methods were comparatively studied. The physical mechanisms that govern the optical transmittance were identified with variable AgNW densities and incident light polarisations.

By changing the substrate materials from glass to Si, we found that different surface plasmon modes and scattering effects can be excited due to the AgNW/substrate interaction. When the AgNWs are embedded in a silicon nitride anti-reflection layer, the localised surface plasmon resonance (LSPR) of the AgNWs is red-shifted and broadened compared to the case of AgNWs in air. The figures of merit of the circular and rectangular AgNWs within these dielectric environments were presented. We concluded that ideally, more than 85% total transmittance under the air mass 1.5 global (AM1.5G) solar spectrum with only 3
$\Omega/\Box R_{sh}$ can be achieved for the AgNW networks. The circular AgNWs can optically outperform the rectangular AgNWs on Si substrates due to less absorption and reflection by the AgNWs.

Based on the above findings, we for the first time experimentally demonstrated the use of solution-processed circular AgNW network as a low-cost and high-performance transparent electrode on the crystalline Si wafer solar cell. Highly uniform AgNW networks with variable surface coverages were fabricated on large-size substrates with areas up to 7.6 cm $\times$ 5.1 cm by the spin-coating method. Due to their aggregation-free nature, the AgNW networks demonstrate superior optical transmittance and electrical conductivity to the conventional TCO films.

An optimised two-step annealing process was developed for the AgNW network on the solar cell – the first low-temperature (200 °C) step for obtaining high electrical conductivity of the network to ensure efficient charge transport and the second high-temperature (400 °C) step for creating the ohmic contact on the AgNW/Si interface to ensure an efficient charge collection from the Si. A 19% enhancement on the solar cell energy conversion efficiency was achieved due to the high conductivity of the AgNW network. We showed that only 3% less photon absorption was introduced by the AgNW, which is negligible compared to the significant electrical enhancement. Detailed loss mechanism analysis showed that larger efficiency enhancement could be achieved with improved AgNW/Si contact.

Apart from the AgNW networks, we also investigated the potential application of other metal NWs on crystalline Si wafer solar cells. Inspired by the hybrid electrode concept, we utilised the ultrathin gold NWs (AuNWs) in combination with the ITO films for the enhanced light trapping effect on the solar cells. Using the Langmuir-Blodgett technique, we fabricated the gold nanomembranes (AuNMs) with highly uniform and aligned AuNWs and transferred them onto the solar cells. Through the surface morphology characterisation, we found that tapered-range nanostructures were created for the ITO films deposited on top of the AuNMs. The
textured AuNM/ITO integrated films present enhanced anti-reflection behaviour compared to the planar ITO film deposited under the same conditions.

According to the numerically simulated results, we confirmed that the AuNM/ITO integrated film on Si substrate can introduce a broadband absorption enhancement in the Si for the wavelengths above 400 nm compared to the planar ITO film. A further insight of the plasmonic behaviours of the AuNWs showed that a small absorption peak occurs at 525 nm for the AuNWs embedded in ITO due to the LSPR. However, due to the ultrathin nature of the AuNWs, the plasmonic absorption and scattering of the AuNWs are too weak to introduce noticeable change on the optical properties of the AuNM/ITO integrated film.

The enhanced light trapping effect of the AuNM/ITO integrated film on the solar cell was demonstrated by the external quantum efficiency enhancement in a broadband wavelength range of 400 – 950 nm. The LSPR effect of the AuNWs was also confirmed at 510 nm. As a result, the total light absorption of the solar cell was increased by 13%, which is 5% larger than the cell with planar ITO film.

Finally, we investigated the use of metal NW networks as transparent electrodes on a-Si:H thin film solar cells. The optical performances of the metal NW networks on a-Si:H solar cells were theoretically studied based on the practical device structure. A wide range of parameters were optimised including the ITO thickness, the shape, dimensions, density, position and material of the NWs.

For the a-Si:H solar cells with circular AgNWs, light absorption is mainly decreased by the reflection from the AgNWs. The optimised AgNW position is on top of 40 nm ITO and covered by 20 nm ITO, where enhanced scattering outweighs the absorption by the AgNWs.

For the a-Si:H solar cells with rectangular AgNWs, the optimised AgNW dimensions are 70 nm in width, 90 nm in height, and 500 nm in periodicity, where the light-generated current is slightly increased due to the enhanced scattering in the longer wavelengths. The optimised AgNW position is on top of 60 nm ITO instead sandwiched in two ITO layers. We also showed that the AgNWs could
outperform other metal NWs such as the AuNWs, the AlNWs and the CuNWs, all of which have either more absorption or less scattering ability than the AgNWs.

We experimentally demonstrated the use of solution-processed AgNW networks as transparent electrodes on a-Si:H solar cells. By using the AgNW network on top of 60 nm ITO film as the charge collection and anti-reflection layer, a 16% efficiency enhancement was achieved, of which 4% was due to the high conductivity of the AgNW network. We also experimentally observed the enhanced scattering by the AgNWs on top of 40 nm ITO and covered by 20 nm ITO, as predicted by the simulated results. However, the ITO film suffered from degraded quality from the two-step deposition process and resulted in poorer solar cell performance than the cells with continuous ITO films.

In summary, this thesis presents innovative research on the applications of metal NW networks on Si-based solar cells. The thorough understanding on the optical and electrical behaviours of the metal NW networks provides important guideline for engineering the NWs on the solar cells. Given the encouraging electrical and optical performances as well as the well-developed fabrication processes, the metal NW networks can be very promising substitute for the conventional TCO films. The functions of the metal NW networks that were experimentally demonstrated in this thesis opens up the possibility of their future applications on Si-based solar cells.

7.2 Future outlook

In Chapter 6 we have demonstrated that AgNW networks can effectively improve the electrical performances of the a-Si:H solar cells as part of the transparent electrodes. In this section we propose some future work based on these results to further explore the applications of AgNW networks.
7.2.1 Towards higher solar cell performances

We demonstrated the outstanding electrical performances of the AgNW networks on planar \textit{n-i-p} a-Si:H solar cells. To obtain higher photocurrent, one usually creates textured structures on the substrate for the enhanced light trapping within the active layers. On the other hand, higher photocurrent would result in more resistive loss on the top electrode with maintained \( R_{sht} \) according to Equation 4.1. Therefore, it is expected that the use of highly conductive and transparent AgNW networks can lead to more efficiency improvement on textured a-Si:H solar cells.

We investigated the optical behaviours of the AgNWs on a-Si:H solar cells and found that the AgNWs mainly causes absorption losses to the solar cells due to reflection. In the nanotechnology field, extensive research has been carried out on the plasmonic [221, 222] or dielectric [7] nanoparticle-enabled absorption enhancement for the a-Si:H solar cells due to their strong scattering ability. By using the AgNWs in combination with the nanoparticles, it is expected that both the electrical and optical performances of the a-Si:H solar cells can be improved and large efficiency enhancement can be achieved.

In Chapter 4 we showed the broadband transmittance of the AgNW networks, while for most of the TCO films, transmittance is decreased in the longer wavelengths due to the free-carrier absorption. The broadband feature was not utilised for the a-Si:H solar cells in this thesis because they can only absorb light for up to 800 nm. Nevertheless, it is very promising for the high-efficiency Si thin film solar cells such as the microcrystalline Si solar cells [223] and the micromorph Si tandem solar cells [224, 225], which have a broader light absorption range of up to 1200 nm.
7.2.2 Using nanoimprinted silver nanowire networks

In Section 6.2.2 we showed that the optimised rectangular AgNW networks can optically perform better than the circular AgNW networks on a-Si:H solar cells due to enhanced scattering in the longer wavelength range. Furthermore, it is expected that the electrical performance of the former can also outperform the latter due to the following reasons: (i) the optimised AgNW density is much higher than the solution-processed AgNWs, which means the resistive loss on the charge collection layer would be much lower; (ii) the AgNWs are well-aligned and thus there are no redundant AgNWs that do not contribute to the electrical conductivity of the networks; (iii) there are no junction resistances for the lithographically patterned AgNW networks.

In Section 6.3.2 we concluded that the highly conductive AgNW networks would be more advantageous for large-size solar cells. Amongst the state-of-the-art lithographical patterning methods, nanoimprinting lithography (NIL) is the only candidate that has the capacity for producing large-area and high-resolution nanostructures. So far we have successfully fabricated small-area (100 µm × 100 µm) AgNW gratings with controllable widths on Si substrates by NIL. Figures 7.1(a) – (c) show the SEM images of the AgNW gratings with the optimised width of 70 nm. The thickness of NWs can be down to 30 nm as shown in Fig. 7.1(d). The NIL process development for the large-area AgNW gratings is still ongoing.
FIG. 7.1 (a) Scanning electron microscopic (SEM) image of the nanoimprinted AgNW gratings with an area of 100 µm × 100 µm. The scale bar is 20 µm. (b) Enlarged SEM image (a). The scale bar is 5 µm. (c) Enlarged SEM image of (b) showing the width of the AgNW gratings is 70 nm. (d) SEM image of the AgNW gratings with a width of 30 nm on a different sample. The scale bars for (c) and (d) are both 200 nm.

The other advantage of the nanoimprinted AgNW networks over the solution-processed ones is that the former intrinsically have smooth surface morphology, i.e., no hanging junction. This is particularly important when the AgNW networks are applied onto the p-i-n type a-Si:H solar cells since otherwise shunting problems would easily be introduced, especially when the charge collection layer is designed to be thinner than the hanging NW junction regions.
7.2.3 Using indium-free materials for charge collection layers

In Chapter 6 we used ITO film as a charge collection layer, which are normally used as front electrodes for the \( n-i-p \) type a-Si:H solar cells because of high optical and electrical performances and comparatively low deposition temperatures. However, for the solar cell applications, cost and environment friendly are becoming increasingly important criterion, both of which cannot be satisfied by the indium material. Therefore, there is a high demand that other indium-free materials to be used for the a-Si:H solar cells.

As a charge collection layer, the material does not have to be as highly conductive as ITO films. The charges injected from the active layer only need to travel for up to a few micrometres to be collected by AgNWs, which act as the main charge transporter. As an extension of this thesis, the preferential alternative materials could be intrinsic or aluminium-doped ZnO films since they have low material costs, mature fabrication technologies, decent electrical conductivity and similar optical constants to the ITO films. It should be noted that in terms of their application on \( n-i-p \) type a-Si:H solar cells, a few practical issues need to be taken into consideration for the active layers such as low-temperature deposition (less than 150 °C) and evaporation techniques [226, 227] rather than sputtering.

Other low-cost alternative materials could be metal oxide nanoparticles [82, 87], graphene films [36, 37, 228], and carbon nanosheets [38], etc., which have been demonstrated on various organic or inorganic solar cells. For these materials, there could be potential challenges on a-Si:H solar cells regarding the electrical contact between the charge collection layer and the active layer as well as light trapping manipulation.
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