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Hybrid heterojunction solar cells based on single-walled carbon nanotubes and amorphous silicon thin films

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Abstract

Hybrid heterojunction solar cells based on silicon and single-walled carbon nanotube (SWCNT) thin films have a simple structure and their manufacture employ simple low-temperature processes. Moreover, their progress has been rapid during the last decade, wherein the efficiency of heterojunction solar cells combining hydrogenated amorphous silicon (a-Si:H) and SWCNTs thin film has increased from 0.03% to 8.80%. Here, we present a comprehensive overview of the state-of-the-art on SWCNTs/a-Si:H heterojunction solar cells. In addition to a comprehensive technology review, important special features such as adhesion of SWCNT film to a-Si:H, the interface between SWCNT and a-Si:H, and their influence on the performance of the heterojunctions are included. Future paths for improving the performance of such solar cells are also suggested. Finally, key challenges and trends for further research and development of SWCNTs/amorphous silicon heterojunction solar cells are discussed.

KEYWORDS

amorphous silicon, hybrid heterojunction, single-walled carbon nanotubes, solar cells, thin film

INTRODUCTION

The interest in renewable energy sources has significantly increased along the needs to reduce greenhouse gas emissions as part of the climate change mitigation. Photovoltaics (PV) is one of the future key clean energy technologies and its markets are growing fast (IEA, 2019). Among various solar cell types, crystalline silicon (c-Si) dominates the market showing high power conversion efficiency (PCE) exceeding 26% with heterojunction with intrinsic thin technology based on thin a-Si:H passivating layers and on interdigitated back contacts on n-type silicon wafers (Green et al., 2018; Yoshikawa et al., 2017). But as recent technologies are evolving into flexible, versatile, and portable electronics, there is also demand for manufacturing solar cells in roll-to-roll processes while maintaining an adequate PCE. Such solar cells would be thin, flexible and could be directly incorporated into applications such as buildings, for example, as roofing shingles. The structural complexity and ease of device fabrication are the key factors that determine the cost and the...
viability of future applications. Especially, thin film silicon and a group of nanomaterials and nanotechnologies are rising up as a promising trend due to the reduced usage of materials and adjustable structure at the nanoscale (Lewis, 2007; Stuckelberger et al., 2017).

Thin film solar cells, including the ones made of hydrogenated amorphous silicon (a-Si:H), have been demonstrated as suitable materials for roll-to-roll production with advantages of reduced fabrication cost, increased light absorbivity, reduced thickness of solar cell, thereby reducing material consumption and device weight (Stuckelberger et al., 2017). Additionally, a-Si:H can be deposited on any foreign substrate by plasma enhanced chemical vapor deposition (PECVD) close to room temperature (Stuckelberger et al., 2017). But, as the carrier mobility of a-Si:H is low, they require an expensive transparent conducting layer as the top contact such as indium tin oxide (ITO) (Shah, 2010). However, the ITO film causes not only optical loss due to parasitic absorption at a short wavelength but also open-circuit voltage ($V_{oc}$) degradation due to the plasma damage during sputtering (Gerling et al., 2015, 2016; Holman et al., 2012). Additionally, the ITO electrode has several other disadvantages including high cost, scarcity of material, lack of flexibility, high structural defects, and poor stability at high temperatures. Therefore, ITO-free solar cells have become an important focus of research for next generation PV devices (Choi et al., 2019; Han et al., 2015).

Carbon is the other element (apart from silicon) that is abundantly available in nature, which have a historic contribution in research and human development. Moreover, carbon nanomaterials have become one of most active research fields in the world (Inagaki & Radovic, 2002; Zhang, Terrones, et al., 2016). Among the various carbon nanomaterials, carbon nanotubes (CNTs), in particular SWCNTs, have made a valuable contribution to recent advances in the field of solar cell development owing to a wide range of properties from conductors to semiconductors with variable bandgaps based on their atomic structure (Avouris et al., 2007, 2008; El-Moussawi et al., 2019; Jariwala et al., 2013; Jeon et al., 2018, 2019; Proctor et al., 2017). While the CNTs can have multiple number of walls, SWCNTs exhibit excellent opto-electrical advantages over double and multi-walled CNTs (Iijima & Ichihashi, 1993). In PV devices, it has definite advantages in terms of flexibility, surface area, carrier mobility, chemical stability, and optoelectronic properties (Fu et al., 2018). A thin SWCNT film can be used not only as a perfect window layer in solar cells, but also as a transparent conductive electrode due to its direct sub-band gaps, tunable photoabsorption from the near infrared starting from THz region to the ultraviolet range, and high conductivity (Arnold et al., 2006; Bissett et al., 2012; Jeon et al., 2018, 2019; Jorio et al., 2008; Saito et al., 1998). Moreover, SWCNTs have much higher mechanical resilience than ITO, with a similar work function of $-5.0$ eV and a much lower raw material cost owing to its abundance. For this reason, SWCNTs have been used extensively as a hole transport layer (Q. Fan et al., 2017; Jeon et al., 2018; Qian et al., 2020; P. M. Rajanna et al., 2019; Tune et al., 2020; F. Wang et al., 2015; Xu et al., 2016), even as light absorber (Arnold et al., 2009; Bindl et al., 2010, 2011; Ramuz et al., 2012; H. Wang et al., 2014), and more popularly asp-type transparent electrodes (Barnes et al., 2007; Ellmer, 2012; Jung et al., 2013; Y. H. Lee et al., 1997; P. M. Rajanna et al., 2019; Tune et al., 2012; Tune & Flavel, 2018; Wu et al., 2004) in many solar cell devices and are termed as “heterojunction or hybrid solar cells”, thus replacing brittle ITO, fluorine-doped tin oxide and expensive metal electrodes, especially in c-Si (Q. Fan et al., 2017; Jeon et al., 2018, 2019; Qian et al., 2020; Tune et al., 2012, 2020; Tune & Flavel, 2018; F. Wang et al., 2015), polymer (Aitola et al., 2010; J. M. Lee et al., 2011, 2015), and more recently in perovskite based solar cells (Ahn et al., 2018; Aitola et al., 2016; Ihly et al., 2016; Jeon et al., 2018, 2019; Seo et al., 2019; Zhang, Tan, et al., 2016).

Among the different methods to grow SWCNTs, aerosol (floating catalyst) CVD method, which produces uniform thin films collected directly on a filter paper (Nasibulin et al., 2011) is found to be one of the most promising and suitable for PV applications (Jeon et al., 2019). These SWCNT thin films have been combined with c-Si to form heterojunction solar cells that have rapidly progressed with PCE of 11–17% in the last decade (Cui et al., 2014; De Nicola et al., 2017; Shi et al., 2012; F. Wang et al., 2015; Zhao et al., 2019). Several reviews exist that highlights the progress made in SWCNT/c-Si solar cells (Hu et al., 2019; Jeon et al., 2018; Jia et al., 2008; Xinming Li et al., 2015; Tune et al., 2012, 2020; Tune & Flavel, 2018). Also, heterojunction solar cells combining a-Si:H and SWCNTs thin film have been reported that have progressed from around 0.03% to 8.80% during the same time (Aleksseeva et al., 2018; Del Gobbo et al., 2011; Funde et al., 2016; P. M. Rajanna et al., 2018, 2019; Schriver et al., 2010). The focus on using SWCNT thin films in a-Si:H is to prevent the use of any standard p-(boron or aluminum) doped a-Si:H or microcrystalline silicon, ITO and other traditional metal layers like Au, Ag, Al, and Cu. And, moreover to utilize the mechanical properties offered by both SWCNTs and a-Si:H, which are potential for flexible and wearable application. In this structure, SWCNTs are proposed as a window layer p-type transparent conductive film (TCF), a potential replacement for all the aforementioned layers and processes, thereby making less energy consuming process technology, minimizing the material consumption, and reducing the net cost. Moreover, as recent technologies are evolving into flexible, versatile, and portable electronics, SWCNTs/a-Si:H heterojunction solar cells looks attractive. However, unlike SWCNTs/c-Si, no reports exist to highlight the progress made in
SWCNTs/a-Si:H thin film heterojunction solar cells. Therefore, in this review, we focus to present the application of SWCNT thin films in a-Si:H solar cells. We briefly discuss the working principles of SWCNTs/a-Si:H heterojunctions and summarize the development of SWCNT thin films in a-Si:H. The adhesion of SWCNT film to a-Si:H, the interface between SWCNT and a-Si:H, and their influence on the performance of the heterojunctions are discussed. This aims to highlight the progress and the advantages of SWCNT thin film as heterojunctions with a-Si:H in PV applications, and to provide possible hints that might help in the further development of SWCNTs-based PV devices.

2 | SWCNTS/A-SI:H HETEROJUNCTION SOLAR CELLS

2.1 | Working mechanism

Solar cells composed of a SWCNT film and Si form a heterojunction device that has been well studied (Jung et al., 2013; Kozawa et al., 2012; Z. Li et al., 2009). The SWCNT film acts not only as charge carrier transport, but also as a photoactive layer (Jia et al., 2008; Tune et al., 2012). The SWCNTs/Si heterojunction follows classical p-n or Schottky theory, where in the photo-generated carriers travel distance is determined by the carrier diffusion length, which is of the same order of magnitude as the cell layer thickness. The electric field responsible for the separation of photo-generated carriers (electron–hole pairs) is concentrated within a very thin zone at the p/n junction or in other words at the closest proximity of the SWCNTs and Si interface, thereby enabling the separation of photo-generated carriers. However, in amorphous silicon materials, the carriers can travel only short distances before recombination. Hence, a uniform electric field needs to be present from the origin of photo-generation throughout the entire cell thickness. This electric field assists carrier travel and immediately separates electron and holes, thereby avoiding recombination. The field assisted travel distance is given by the drift length. Therefore, an intrinsic (i)-layer is inserted between p- and n-layers, to form a pin-diode. For more details on the pin-diode theory, the reader is suggested to review relevant literatures (Schropp & Zeman, 1998; Shah, 2010; Street, 1991). During the last decade, the use of carbon nanotubes in thin film amorphous silicon has been of great interest for researchers as light trapping structures, antireflective coatings, transparent electrodes, and p-type window layer contacting a-Si:H to form heterojunction (Alekseeva et al., 2018; Del Gobbo et al., 2011; Funde et al., 2016; J. Kim et al., 2012; P. M. Rajanna et al., 2018, 2019; Schriver et al., 2010; Tu et al., 2012; Zhou et al., 2014, 2008, 2009). Similar to SWCNTs/c-Si heterojunction (Hu et al., 2019; Jeon et al., 2018; Tune et al., 2012), SWCNTs/a-Si:H also form semiconductor/semiconductor or metal/semiconductor junction as shown in Figure 1a,b. Here, the incident photons are mainly absorbed in i-layer thus generating electron–hole pairs at the close proximity of the p/i interface. The carriers (electrons and holes) drift across a-Si:H (n) or n-type contact like ITO.

![Figure 1](image_url)  Illustration of (a) the SWCNTs film functioning as a p-type layer in semiconductor/semiconductor p-i-n junction; and (b) Schottky junction is formed by a metal/semiconductor interface.
or AZO or metals like In/Ga (Xu et al., 2016), Ti/Au (Jia et al., 2012; Jia, Li, et al., 2011), or Al (Xiaokai Li et al., 2013) that forms an ohmic contact with the amorphous silicon, and a-Si:H (p) or SWCNTs due to the built-in-voltage created by the applied electric field. Electrons are collected across n-type a-Si:H, ITO or AZO and holes are collected at p-type a-Si:H or SWCNTs itself that can be used as a p-type transparent electrode as shown in Figure 1. Furthermore, the front electrode made of Ag (Xu et al., 2015), Au/Cr (De Nicola et al., 2017; Yu, Batmunkh, et al., 2017), or Pt (Cui et al., 2014) contacts the SWCNT film for better transfer of holes to an external circuit. Similar process happens when the metallic SWCNT-film comes in contact with i-layer thus forming Schottky junction as shown in Figure 1b. The differences will be the magnitude of the reverse saturation current and its switching characteristics.

The complexity of the SWCNT film, in which semiconducting and metallic nanotubes coexist leads to the uncertainty at the interface between SWCNTs and a-Si:H. Several individual nanotubes are present in a device, and each forms a heterojunction with the i-layer of a-Si:H. As SWCNTs exhibit semiconducting and/or metallic behavior, a p-i-n junction can be respectively expected for the former (Figure 1a) and a Schottky junction for the latter (Figure 1b).

2.2 SWCNTs as transparent electrodes

The first attempt to create a a-Si/CNT heterojunction was made by Schriver et al. using the carbon nanotube films as buckypaper and graphene in junctions with undoped a-Si thin films as shown in Figure 2a. The measured J-V characteristics of the buckypaper/a-Si heterojunction solar cell is as shown in Figure 2b (Schriver et al., 2010). The produced solar cells were air-stable without additional processing steps like doping, multilayer film deposition in high vacuum, or transparent conducting oxide deposition. In the subsequent year SWCNTs were sprayed on a-Si:H by Gobbo et al. to form Schottky barrier solar cells (Figure 2c) (Del Gobbo et al., 2011). They measured the external quantum efficiency up to 35% at a wavelength of about 460 nm (Figure 2d) and indicated that for lower density SWCNT/a-Si:H heterojunction, nanotubes dominate the photocurrent generation, separation, and transport mechanism thereby splitting the
electron–hole pair generation at the CNT-CNT or CNT-Si heterojunction. However, with increased density of SWCNT/a-Si:H heterojunction more electron–hole pairs are generated in a-Si:H. In the next year, Kim et al. used SWCNT films obtained by vacuum filtration through a mixed cellulose ester membrane as transparent electrodes on a a-Si:H n-i-p solar cell (Figure 3a) (J. Kim et al., 2012). Despite their similar work functions, a Schottky barrier was formed at the SWCNTs/a-Si:H interface that resulted in an inoperable solar cell with a fill factor of 22% as shown in Figure 3b. In order to address this issue, gold nanodots were deposited at the p+a-Si:H/SWCNTs interface (Figure 3a). The nanodots were found to be effective in eliminating the interfacial Schottky barrier thus allowing ohmic contact to form between the SWCNTs and p+ layer without any measurable impact on the $J_{sc}$. This approach led to achieving a respectable FF of 58% which is comparable to that of a a-Si:Hp–i–n solar cell (FF of 62%) with conventional TCO (Figure 3c). In the same year, Khanal et al. used SWCNT films as electrodes to replace the p-layer and back contact in a-Si:H solar cell (Figure 3d) (Khanal et al., 2012). They varied the SWCNTs film thickness and inferred that the optical properties of the nanotubes affect the device performance than does the conductivity (Figure 3e). The cells were illuminated from each side (glass and SWCNTs), and a 25 nm thick SWCNTs film resulted in a PCE of 1.46% (Figure 3f). Funde et al. reported
the first use of aerosol CVD synthesized SWCNT thin films as p-layer and transparent electrodes by a unique technique of dry-transfer in a-Si:H solar cells as in Figure 3g (Funde et al., 2016). Furthermore, the SWCNTs were doped with thionyl chloride (SOCl2) that resulted in an improved PCE of 1.5% from 0.3% for pristine nanotubes (Figure 3h). They highlighted that there exists a substantial potential for further improvement as the parameters of the fabricated device were not optimized in terms of opto-electrical properties of SWCNTs, thickness of nanotube films, and top metal contact. The studies on acid doping and SOCl2 treatment of SWCNTs originated in SWCNTs/Si solar cells by Z. Li et al. (2008). The doping shifts the Fermi level of SWCNTs below $\nu_1$, thus increasing the mobility and carrier density as in Figure 4a (Blackburn et al., 2008; Jeon et al., 2018). As a result, the $S_{11}$ transition is suppressed in the semiconducting SWCNTs and further doping would suppress the $S_{22}$ transition as well (Figure 4b), as observed by near-infrared absorption spectroscopy (Figure 4c).

2.3 | SWCNTs-PEDOT:PSS composite

Recently, it has been shown that both the environment and the substrate material influences the efficient usage of SWCNTs film (W. Li et al., 2019; P. P. Rajanna et al., 2020). The perpetual contact between the nanotubes film and the substrate material or the atmospheric medium impacts the interface properties that consequently effects net efficiency of the solar cell (Xiaokai Li et al., 2013). As an example, at the interface of SWCNTs/Si heterojunction solar cells there exists great profuse of nanotube-silicon junctions where SWCNTs are in physical contact with Si surface. However, within the SWCNT network many nanotubes overlap and suspend on each other without contacting the Si. As a result, the solar cell performance suffers due to the increased recombination at the interface where bare Si surfaces are exposed to air (Jia et al., 2008; Jia, Cao, et al., 2011). To solve this problem, researchers have tried to mix conducting polymers with the SWCNT films to improve their junction density, uniformity, and conductivity (Lin et al., 2013; Sarker et al., 2010; Singh et al., 2008; Xie et al., 2020). Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is a well-researched and commonly used hole transport material, which has high conductivity, work-function, and transmittance (X. Fan et al., 2019). Moreover, injecting PEDOT:PSS on SWCNTs film, the micropores are completely filled and surface roughness is decreased (Q. Fan et al., 2017; P. M. Rajanna et al., 2018). Researchers have therefore combined SWCNTs with PEDOT:PSS to further enhance the performance and form hybrid heterojunction PEDOT:PSS-SWCNTs/Si solar cells (B. Fan et al., 2008; He et al., 2016, 2017; Kymakis et al., 2006; Liu et al., 2017; Thomas et al., 2018). For example, Fan et al. developed an effective way of fabricating hybrid PEDOT:PSS/SWCNT/Si solar cells by placing a SWCNT network on the surface of a Si wafer and then spinning a PEDOT:PSS solution onto it (Q. Fan et al., 2017).

In the subsequent year, our group reported the synergistic effect of SWCNTs and PEDOT:PSS as a composite p-type transparent electrode to be more effective in forming coupled continuous hybrid heterojunction with a-Si:H as shown in Figure 5a (Alekseeva et al., 2018). The performance of the SWCNTs/a-Si:H, PEDOT:PSS/a-Si:H and SWCNTs-PEDOT:PSS/a-Si:H was compared (Figure 5b). It was found that SWCNTs-PEDOT:PSS composite film has better solar cell output performance with a PCE of 1.6%, FF of 54% and $V_{oc}$ of 0.803 V when compared SWCNTs (PCE of 1.1%) and PEDOT:PSS (1.0%) alone. It was explained that by the introduction of PEDOT:PSS, the

![Figure 4](image-url) Density of states of pristine and doped (a) semiconducting; (b) metallic SWCNTs, respectively; and (c) absorbance spectra of pristine, ethanol densified, and HNO3 functionalized SWCNTs film
micropores of randomly oriented SWCNTs film is filled thereby forming continuous contact with underneath a-Si:H (Figure 5d). Although the FF and $V_{oc}$ was improved when compared to all the previous reported SWCNT/a-Si:H devices, the $J_{sc}$ was lower, owing to the increased absorption of incident photons in the p-type SWCNTs-PEDOT:PSS layer. The improvement in FF and $V_{oc}$ of SWCNT/a-Si:H in Alekseeva et al. could be primarily attributed to SWCNT film synthesis using Aerosol CVD, conformal deposition by dry transfer method, significantly higher electrical properties of SWCNT films, and better interface between SWCNT and a-Si:H (Del Gobbo et al., 2011; Funde et al., 2016; Khanal et al., 2012; J. Kim et al., 2012; Schriver et al., 2010). These results suggest that the SWCNT films should be carefully chosen to further optimize the SWCNTs-PEDOT:PSS composite. Following this, Rajanna et al. reported a SWCNTs/a-Si:H heterojunction solar cell with a much improved PCE of 2.7% by optimizing the thickness of SWCNTs film in the SWCNTs-PEDOT:PSS composite used as p-type layer and transparent electrode (Figure 5c) (P. M. Rajanna et al., 2018). The fabricated devices showed increased PCEs of 3.4% and $V_{oc}$ of 0.9 V with incorporation of PMMA as an anti-reflection layer on top of the SWCNTs-PEDOT:PSS composite (Figure 5c). Moreover, a decrease in the sheet resistance of the SWCNT-PEDOT:PSS (composite) film and an increase in its work function was measured compared to the pristine SWCNT film. This can be attributed, for the fact that every single carbon atom is on the surface exposed to the environment. Therefore, any atom/molecule put on a SWCNT cause changes in their electronic structure and charge transfer between the atom/molecule and a nanotube. Therefore, when PEDOT:PSS is injected it filled micropores in the SWCNT film and, that the holes in the PEDOT:PSS patches can transfer to the interconnected SWCNT network consequently, doping the SWCNTs (Q. Fan et al., 2017; Ki...
et al., 2008; K. K. Kim et al., 2010). Although, a significant progress had been made in SWCNTs/a-Si:H hetero-
junction solar cell from initial PCE of less than 1.0% to 3.4%, yet this was very low and beyond the scope for prac-
tical applications. The challenge was to overcome the problems at the SWCNTs and a-Si:H interface, improve the p-
type transparent electrode, and thereby improve the overall solar cell performance. The significant problems as in-
dicated in the previous works was the large interface resistance, high Schottky barrier leading to band-offsets 
between a-Si:H and SWCNTs, and high series resistance of SWCNTs resulting in high carrier recombination.

2.4 | SWCNTs-PEDOT:PSS-SWCNT fibers as novel transparent electrode

To solve the problems mentioned in the previous section, we proposed a rational design of a novel p-type transparent 
conductor developed using a multicomponent composite that combines the superior properties of SWCNTs with 
PEDOT:PSS, MoO₃ and SWCNT fibers into a single composite (Figure 6a) (P. M. Rajanna et al., 2019). Various configu-
rations were developed and examined as a p-type window layer and electrode in a-Si:H solar cells. A configuration of 
SWCNTs-MoO₃-PEDOT:PSS/SWCNT fibers composite (p-type) measured a record equivalent sheet resistance (Rₚₙ) of 
17 Ω/sq with a transmittance of 90% at 550 nm (Kaskela et al., 2010; P. M. Rajanna et al., 2019). Adsorption doping of 
SWCNT films and fibers by HAuCl₄ is one of the major factors for record Rₚₙ. As all carbon atoms are exposed to the 
environment, any atom/molecule put on a SWCNT causes charge transfer between the atom/molecule and nanotube 
(Ki et al., 2008). As detailed by Tsapenko et al., the adsorption of formed AuCl₄⁻ anions, in which Cl⁻ is the origin for
| Device | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF (%) | PCE (%) | SWCNTs treatment | a-Si treatment | Structures | Remarks | References |
|--------|---------------------|-------------|--------|---------|------------------|----------------|------------|---------|------------|
| 1      | 0.25                | 0.39        | 20.0   | 0.02    | NA               | NA             | Buckypaper/a-Si:H (i)/ITO | First application of CNTs in a-Si solar cells | (Schriver et al., 2010) |
| 2      | 0.30                | 0.50        | 19.0   | 0.03    | NA               | NA             | Ag/SWCNT/a-Si:H(i)/a-Si:H(n)/Cr | SWCNTs transferred on a-Si | (Del Gobbo et al., 2011) |
| 3      | 6.47                | 0.68        | 34.0   | 1.46    | NA               | NA             | SWCNTs/a-Si:H(i)/a-Si:H(n)/FTO | SWCNTs used as p-type electrodes in nip solar cell | (Khanal et al., 2012) |
| 4      | 12.20               | 0.77        | 57.0   | 5.27    | NA               | Triethyloxonium hexachloroantimonate (OA) mixed with dichloroethane | SWCNTs/Au nanodots/a-Si:H(p)/a-Si:H(i)/a-Si:H(n)/Al/ZnO/Ag | SWCNTs are p-doped with triethyloxonium hexachloroantimonate (OA) mixed with dichloroethane and Au nanodots at SWCNTs and a-Si:H (p) interface | (J. Kim et al., 2012) |
| 5      | 11.02               | 0.48        | 29.0   | 1.51    | SOCl$_2$         | HF             | Ag/SWCNTs/a-Si:H(i)/a-Si:H(n)/Al | Dry transfer of SWCNTs film synthesized by aerosol CVD | (Funde et al, 2016) |
| 6      | 3.56                | 0.80        | 54.0   | 1.57    | NA               | HF             | Ag paste/PEDOT:PSS-SWCNTs/a-Si:H(i)/a-Si:H(n)/Al/ZnO | PEDOT:PSS-SWCNTs as p-type composite | (Alekseeva et al., 2018) |
| 7      | 8.99                | 0.90        | 41.8   | 3.40    | NA               | HF             | PMMA/PEDOT:PSS-SWCNTs/a-Si:H(i)/a-Si:H(n)/Al/ZnO | PMMA as anti-reflection layer | (P. M. Rajanna et al., 2018) |
| 8      | 15.03               | 0.91        | 68.2   | 8.80    | HAuCl$_4$        | HF             | SWCNT fibers/PEDOT:PSS-MoO$_3$-SWCNTs/a-Si:H(i)/a-Si:H(n)/Al/ZnO | HAuCl$_4$ doping of SWCNTs film and fibers | (P. M. Rajanna et al., 2019) |
the observed p-type behavior due to its high electronegativity results in a strong HAuCl₄ doping which shifts the Fermi level deeper in the valence band (Ki et al., 2008; K. K. Kim et al., 2010; Tsapenko et al., 2018).

Moreover, the developed p-type composite displayed a high degree of mechanical flexibility with \( \leq 5\% \) change in resistance (Figure 6b). The solar cells made from the developed p-type composite electrode on a-Si:H absorber yielded an outstanding \( J_{sc} \) of 15.03 mA/cm² and record PCE up to 8.8% for SWCNTs/a-Si:H heterojunction solar cells (Figure 6c) which was an effective 18% improvement over a standard n-i-p configured solar cell (Figure 6d). Moreover, SWCNT fibers by itself can be used as replacement for traditional metal contacts due to its high conductivity and simple deposition process (P. M. Rajanna et al., 2019).

Solar cells based on SWCNTs as p-type transparent electrodes in a-Si:H have been studied to substitute standard p-type a-Si:H, transparent conductive oxide such as ITO and FTO, and front metal contacts. The PCEs on rigid structures have progressed steadily from 0.03% up to 8.80% as tabulated in Table 1. Moreover, the mechanical properties of SWCNTs and well-established a-Si:H are promising for future low-cost flexible and wearable solar cells.

3 | SUMMARY AND FUTURE OUTLOOK

Here the recent success in the application of SWCNTs in a-Si:H heterojunction solar cells has been reviewed. The unique structure and extraordinary opto-electrical properties of SWCNTs give them notable advantages for PV applications, and therefore the future direction is undoubtedly SWCNTs based p-type transparent electrodes. Notable progress has been made on the SWCNTs/a-Si:H heterojunction-based devices, however challenges remain in their practical use. For example, the working mechanism of SWCNTs in solar cells has not been fully clarified due to the statistical presence of both semiconducting and metallic nanotubes in a thin film. Also, the performance of SWCNTs based solar cells is determined by the structure and properties of SWCNTs, such as chirality, sheet resistance, and work function (Ren & Wang, 2010). For this, either pure semiconducting or metallic SWCNTs with high purity and quality are needed to fully understand the mechanism.

The fabrication and characterization of SWCNTs based solar cells has been limited to small active area. Large area solar cells are a big challenge. For large area fabrication and performance of SWCNTs based solar cells, a SWCNT film with high transparency and low sheet resistance is desired. Although, significant progress has been made in lowering the sheet resistance at a transmittance of 90% of pristine SWCNTs film, much needs to be done to replace ITO. One of the possible ways is to reduce the inter-tube junction resistance in the most commonly used randomly oriented SWCNTs film that is much higher than the intrinsic tube resistance and the electrical conductivity of SWCNTs film (Fuhrer et al., 2000; Nirmalraj et al., 2009). Recently, carbon-welding on tube-tube junction was proposed to convert inter-tube Schottky contacts into near-ohmic ones (Jiang et al., 2018). To further reduce the inter-tube junction resistance, SWCNT arrays or aligned SWCNTs is another alternative as previously shown in Si solar cells, but mainly with multi-walled nanotubes (Di et al., 2013; R. Li et al., 2014). As SWCNTs have superior properties, an ideal case would be to make high quality aligned SWCNTs (Ma et al., 2011; Seah et al., 2011), whose opto-electrical properties are optimized. On the other hand, front contact fingers should be introduced in SWCNTs based solar cells, which can significantly enhance the FF. SWCNT strips/fibers have been used as front contacts, when the PCE increased to 6.52% from initial 3.97% (Xu et al., 2016). More recently, our group used SWCNT fibers to increase the overall conductivity of SWCNTs as p-type transparent electrode, thereby improving the PCE of SWCNT/a-Si:H heterojunction solar cells (P. M. Rajanna et al., 2019). Moreover, SWCNT fibers itself can be used to replace traditional metal contacts due to their high conductivity and simple deposition process. Therefore, this is good way to increase the efficiency of solar cells, and also, reduce the sheet resistance of SWCNTs film.

The work-function of SWCNT films need to be improved for better separation and extraction of photo-generated carriers, that is, the work-function of carbon nanotubes have to be fine-tuned in such a way that the energy levels match with Si. Moreover, the increased work function can increase the barrier height than can result in improved built-in voltage at the interface, thereby resulting in increased \( V_{oc} \). Therefore, effective p-type doping needs to be found that are stable other than the existing acid-based treatments with SOCl₂, HNO₃, chlorosulfonic acid, AuCl₃, and HAuCl₄, which are unstable (Ki et al., 2008; Tsapenko et al., 2018). This result in poor stability of the fabricated SWCNTs based solar cells.

The device architecture of SWCNTs/a-Si:H also needs to be further optimized. Only a few reports exist on the interface between SWCNTs as front electrode and Si (Jia et al., 2012; Tune et al., 2013; Yu, Grace, et al., 2017), but none
exists on the interface between Si and back electrode. Therefore, this needs further investigation for SWCNTs/Si and SWCNT/a-Si:H new type heterojunction solar cells.

Finally, flexible solar cells are becoming of high relevance to the development of flexible and wearable devices (Fu et al., 2018). SWCNTs have excellent flexibility and can be combined with Si thin films like a-Si:H to fabricate flexible SWCNTs/a-Si:H solar cells, respectively. It is envisaged that the SWCNT films are novel p-type transparent conductors in combination with the use of pure high quality semiconducting or metallic SWCNTs that are aligned with better passivation, improved doping stability of SWCNTs, light trapping schemes and nanostructuring can potentially improve future PV devices. Nevertheless, the applications of the novel p-type composite material are not limited to solar cells (P. M. Rajanna et al., 2019). Rational design and room-temperature processing broaden the horizon for transparent and flexible electrode implementation in diverse applications in other fields of science and technology.

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CONFLICT OF INTEREST
The authors have declared no conflicts of interest for this article.

AUTHOR CONTRIBUTIONS
Albert G. Nasibulin: Funding acquisition; project administration; supervision; validation; writing-review & editing.
Peter Lund: Funding acquisition; project administration; supervision; validation; writing-review & editing. Pramod Mulbagal Rajanna: Conceptualization; data curation; investigation; project administration; resources; writing-original draft; writing-review & editing.

NOMENCLATURE
AZO aluminum doped zinc oxide
a-Si:H hydrogenated amorphous silicon
c-Si crystalline silicon
CNTs carbon nanotubes
CVD chemical vapor deposition
FTO fluorine-doped tin oxide
FF fill factor
ITO indium tin oxide
J-V current density-voltage
PV photovoltaics
PCE power conversion efficiency
PECVD plasma-enhanced chemical vapor deposition
PDMS polydimethylsiloxane
PEDOT:PSS poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
PANI polyaniline
PMMA polymethylmethacrylate
SWCNT single-walled carbon nanotube
TCF transparent conductive film
THz terahertz

DATA AVAILABILITY STATEMENT
Data sharing is not applicable to this article as no new data were created or analyzed in this study.
De Nicola, F., Salvato, M., Cirillo, C., Crivellari, M., Boscardin, M., Passacantando, M., Nardone, M., De Matteis, F., Motta, N., De Choi, D., Yoon, H., Kim, K. H., Um, H. D., & Seo, K. (2019). ITO-free carrier-selective contact for crystalline silicon solar cells. Cui, K., Anisimov, A. S., Chiba, T., Fujii, S., Kataura, H., Nasibulin, A. G., Chiashi, S., Kauppinen, E. I., & Maruyama, S. (2014). Air-stable high-efficiency solar cells with dry-processed single-walled carbon nanotube films. Journal of Materials Chemistry A, 2, 11311–11318.

Ahn, N., Jeon, I., Yoon, J., Kauppinen, E. I., Matsuo, Y., Maruyama, S., & Choi, M. (2018). Carbon-sandwiched perovskite solar cell. Journal of Materials Chemistry A, 6, 1382–1389. https://doi.org/10.1039/c7ta09174e

Aitola, K., Kaskela, A., Halme, J., Ruiz, V., Nasibulin, A. G., Kauppinen, E. I., & Lund, P. D. (2010). Single-walled carbon nanotube thin-film counter electrodes for indium tin oxide-free plastic dye solar cells. Journal of The Electrochemical Society, 157, B1831. https://doi.org/10.1149/1.3500367

Aitola, K., Sveinbjörnsson, K., Correa-Baena, J. P., Kaskela, A., Abate, A., Tian, Y., Johansson, E. M. J., Grätzel, M., Kauppinen, E. I., Hagfeldt, A., & Boschloo, G. (2016). Carbon nanotube-based hybrid hole-transporting material and selective contact for high efficiency perovskite solar cells. Energy and Environmental Science, 9, 461–466. https://doi.org/10.1039/c5ee03934b

Alekseeva, A. K., Rajanna, P. M., Anisimov, A. S., Sergeev, O., Bereznev, S., & Nasibulin, A. G. (2018). Synergistic effect of single-walled carbon nanotubes and PEDOT:PSS in thin film amorphous silicon hybrid solar cell. Physica Status Solidi (B) Basic Research, 255(1), 1700557. https://doi.org/10.1002/pssb.201700557

Arnold, M. S., Green, A. A., Hulvat, J. F., Stupp, S. I., & Hersam, M. C. (2006). Sorting carbon nanotubes by electronic structure using density differentiation. Nature Nanotechnology, 1, 60–65. https://doi.org/10.1038/nnano.2006.52

Arnold, M. S., Zimmerman, J. D., Renshaw, C. K., Xu, X., Lunt, R. R., Austin, C. M., & Forrest, S. R. (2009). Broad spectral response using carbon nanotube/organic semiconductor/C 60 photodetectors. Nano Letters, 9, 3354–3358. https://doi.org/10.1021/nl901637u

Avouris, P., Chen, Z., & Perebeinos, V. (2007). Carbon-based electronics. Nature Nanotechnology, 2, 605–615. https://doi.org/10.1038/nnano.2007.300

Avouris, P., Freitag, M., & Perebeinos, V. (2008). Carbon-nanotube photonics and optoelectronics. Nature Photonics, 2, 341–350. https://doi.org/10.1038/nphoton.2008.94

Barnes, T. M., Wu, X., Zhou, J., Duda, A., Van De Lagemaat, J., Coutts, T. J., Weeks, C. L., Britz, D. A., & Glatkowski, P. (2007). Single-wall carbon nanotube networks as a transparent back contact in CdTe solar cells. Applied Physics Letters, 90, 243503. https://doi.org/10.1063/1.2748078

Bindl, D. J., Safron, N. S., & Arnold, M. S. (2010). Dissociating excitons photogenerated in semiconducting carbon nanotubes at polymeric photovoltaic heterojunction interfaces. ACS Nano, 4, 5657–5664. https://doi.org/10.1021/nn1012397

Bindl, D. J., Wu, M. Y., Prehn, F. C., & Arnold, M. S. (2011). Efficiently harvesting excitons from electronic type-controlled semiconducting carbon nanotube films. Nano Letters, 11, 455–460. https://doi.org/10.1021/nl1031343

Bissett, M., Barlow, A., Shearer, C., Quinton, J., & Shapter, J. G. (2012). Comparison of carbon nanotube modified electrodes for photovoltaic photovoltaic heterojunction interfaces. Carbon, 50, 2431–2441. https://doi.org/10.1016/j.carbon.2012.01.065

Blackburn, J. L., Barnes, T. M., Beard, M. C., Kim, Y. H., Tenent, R. C., McDonald, T. J., To, B., Coutts, T. J., & Heben, M. J. (2008). Transparent conductive single-walled carbon nanotube networks with precisely tunable ratios of semiconducting and metallic nanotubes. ACS Nano, 2, 1266–1274. https://doi.org/10.1021/nn080200d

Choi, D., Yoon, H., Kim, K. H., Um, H. D., & Seo, K. (2019). ITO-free carrier-selective contact for crystalline silicon solar cells. Journal of Materials Chemistry A, 7, 2192–2199. https://doi.org/10.1039/c8ta11220g

Cui, K., Anisimov, A. S., Chiba, T., Fujii, S., Kataura, H., Nasibulin, A. G., Chiashi, S., Kauppinen, E. I., & Maruyama, S. (2014). Air-stable high-efficiency solar cells with dry-processed single-walled carbon nanotube films. Journal of Materials Chemistry A, 2, 11311–11318. https://doi.org/10.1039/c4ta01353k

De Nicola, F., Salvato, M., Cirillo, C., Crivellari, M., Boscardin, M., Passacantando, M., Nardone, M., De Matteis, F., Motta, N., De Crescenzi, M., & Castrucci, P. (2017). 100% internal quantum efficiency in polychiral single-walled carbon nanotube bulk heterojunction/silicon solar cells. Carbon, 114, 402–410. https://doi.org/10.1016/j.carbon.2016.12.050

Del Gobbo, S., Castrucci, P., Scarselli, M., Camilli, L., De Crescenzi, M., Mariucci, L., Valletta, A., Minotti, A., & Fortunato, G. (2011). Carbon nanotube semitransparent electrodes for amorphous silicon based photovoltaic devices. Applied Physics Letters, 98(18), 1–4. https://doi.org/10.1063/1.3588352

Di, J., Yong, Z., Zheng, X., Sun, B., & Li, Q. (2013). Aligned carbon nanotubes for high-efficiency Schottky solar cells. Small, 9, 1367–1372. https://doi.org/10.1002/smll.201202995

Ellmer, K. (2012). Past achievements and future challenges in the development of optically transparent electrodes. Nature Photonics, 6, 809–817. https://doi.org/10.1038/nphoton.2012.282
efficiency and stable carbon nanotube-based silicon solar cells. *Advanced Energy Materials, 10*, 1902389. https://doi.org/10.1002/aenm.201902389

Rajanna, P. M., Gilshteyn, E. P., Yagafarov, T., Aleekseeva, A. K., Anisimov, A. S., Neumüller, A., Sergeev, O., Bereznév, S., Marichev, J., & Nasibulin, A. G. (2018). Enhanced efficiency of hybrid amorphous silicon solar cells based on single-walled carbon nanotubes and polymer composite thin film. *ChemSusChem*, 29(10), 105404. https://doi.org/10.1002/cssc.20164657

Rajanna, P. M., Meddeb, H., Sergeev, O., Tsapenko, A. P., Bereznév, S., Vehse, M., Volobujeva, O., Danilson, M., Lund, P. D., & Nasibulin, A. G. (2019). Rational design of highly efficient flexible and transparent p-type composite electrode based on single-walled carbon nanotubes. *Nano Energy, 67*, 104183. https://doi.org/10.1016/j.nanoen.2019.104183

Rajanna, P. P., Luchkin, S., Larionov, K. V., Grebenko, A., Popov, Z. I., Sorokin, P. B., Danilson, M., Bereznév, S., Lund, P. D., & Nasibulin, A. G. (2020). Adhesion of single-walled carbon nanotube thin films with different materials. *Journal of Physical Chemistry Letters*, 11, 504–509. https://doi.org/10.1021/acs.jpclett.9b03552

Ramuz, M. P., Vosgueritchian, M., Wei, P., Wang, C., Gao, Y., Wu, Y., Chen, Y., & Bao, Z. (2012). Evaluation of solution-processable carbon-based electrodes for all-carbon solar cells. *ACS Nano, 6*, 10384–10395. https://doi.org/10.1021/nn304410w

Ren, L., & Wang, S. (2010). Tailoring optical and electrical properties of carbon nanotube networks for photovoltaic applications. *Carbon, 48*, 4397–4402. https://doi.org/10.1016/j.carbon.2010.07.054

Saito, R., Dresselhaus, G., & Dresselhaus, M. S. (1998). *Physical properties of carbon nanotubes*. Imperial College Press. https://doi.org/10.1142/p080

Sarker, B. K., Arif, M., & Khondaker, S. I. (2010). Near-infrared photoresponse in single-walled carbon nanotube/polymer composite films. *Carbon, 48*, 1539–1544. https://doi.org/10.1016/j.carbon.2009.11.065

Schrömer, M., Regan, W., Loster, M., & Zettl, A. (2010). Carbon nanostructure-aSi:H photovoltaic cells with high open-circuit voltage fabricated without dopants. *Solid State Communications, 150*(13–14), 561–563. https://doi.org/10.1016/j.ssc.2010.01.013

Schröpp, R. E. I., & Zeman, M. (1997). *Amorphous and microcrystalline silicon solar cells: Modeling, materials and device technology*. Boston, MA: Springer. https://doi.org/10.1007/978-1-4615-5631-2

Seah, C. M., Chai, S. P., & Mohamed, A. R. (2011). Synthesis of aligned carbon nanotubes. *Carbon, 49*, 4613–4635. https://doi.org/10.1016/j.carbon.2011.06.090

Seo, S., Jeon, J., Xiang, R., Lee, C., Zhang, H., Tanaka, T., Lee, J. W., Suh, D., Ogamoto, T., Nishikubo, R., Saeki, A., Chiashi, S., Shiomi, J., Kataura, H., Lee, H. M., Yang, Y., Matsuo, Y., & Maruyama, S. (2019). Semiconducting carbon nanotubes as crystal growth templates and grain bridges in perovskite solar cells. *Journal of Materials Chemistry A, 7*, 12987–12992. https://doi.org/10.1039/c9ta02629k

Shah, A. V. (2010). *Thin-film silicon solar cells* (1st ed.). EPFL Press. https://doi.org/10.1201/b16327

Shi, E., Zhang, L., Li, Z., Li, P., Shang, Y., Jia, Y., Wei, J., Wang, K., Zhu, H., Wu, D., Zhang, S., Cao, A. (2012). TiO2-coated carbon nanotube-silicon solar cells with efficiency of 15%. *Scientific Reports, 2*, 884. https://doi.org/10.1038/srep009884

Singh, I., Bhatnagar, P. K., Mathur, P. C., Kaur, I., Bharadwaj, L. M., & Pandey, R. (2008). Optical and electrical characterization of conducting polymer-single walled carbon nanotube composite films. *Carbon, 46*, 1141–1144. https://doi.org/10.1016/j.carbon.2008.04.013

Street, R. A. (1991). *Hydrogenated amorphous silicon*. Cambridge University Press. https://doi.org/10.1017/cbo9780511525247

Stuckelberger, M., Biron, R., Wyrsch, N., Haug, F. J., & Ballif, C. (2017). Review: Progress in solar cells from hydrogenated amorphous silicon. *Renewable and Sustainable Energy Reviews, 76*, 1497–1523. https://doi.org/10.1016/j.rser.2016.11.190

Thomas, J. P., Rahman, M. A., Srivastava, S., Kang, J. S., McGillivray, D., Abd-Elah, M., Heinig, N. F., & Leung, K. T. (2018). Highly conducting hybrid silver-nanowire-embedded poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) for high-efficiency planar silicon-on-organic heterojunction solar cells. *ACS Nano, 12*(9), 9495–9503. https://doi.org/10.1021/acsnano.8b04848

Tsapenko, A. P., Goldt, A. E., Shugla, E., Popov, Z. I., Maslakov, K. I., Anisimov, A. S., Sorokin, P. B., & Nasibulin, A. G. (2018). Highly conductive and transparent films of HAuCl4-doped single-walled carbon nanotubes for flexible applications. *Carbon, 130*, 448–457. https://doi.org/10.1016/j.carbon.2018.01.016

Tu, W. C., Chang, Y. T., Wang, H. P., Yang, C. H., Huang, C. T., He, J. H., & Lee, S. C. (2012). Improved light scattering and surface plasmon tuning in amorphous silicon solar cells by double-walled carbon nanotubes. *Solar Energy Materials and Solar Cells, 101*, 200–203. https://doi.org/10.1016/j.solmat.2012.01.038

Tune, D. D., & Flavel, B. S. (2018). Advances in carbon nanotube–silicon heterojunction solar cells. *Advanced Energy Materials, 8*, 1703241. https://doi.org/10.1002/aenm.201703241

Tune, D. D., Flavel, B. S., Krupke, R., & Shapert, J. G. (2012). Carbon nanotube-silicon solar cells. *Advanced Energy Materials, 2*, 1043–1055. https://doi.org/10.1002/aenm.201200249

Tune, D. D., Flavel, B. S., Quinton, J. S., Ellis, A. V., & Shapert, J. G. (2013). Single-walled carbon nanotube/polyaniline/n-silicon solar cells: Fabrication, characterization, and performance measurements. *ChemSusChem, 6*, 320–327. https://doi.org/10.1002/cssc.201200600

Tune, D. D., Mallik, N., Fornasier, H., & Flavel, B. S. (2020). Breakthrough carbon nanotube–silicon heterojunction solar cells. *Advanced Energy Materials, 10*, 1903261. https://doi.org/10.1002/aenm.201903261

Wang, F., Kozawa, D., Miyauchi, Y., Hiraoka, K., Mouri, S., Ohno, Y., & Matsuda, K. (2015). Considerably improved photovoltaic performance of carbon nanotube-based solar cells using metal oxide layers. *Nature Communications, 6*, 6305. https://doi.org/10.1038/ncomms7305

Wang, H., Koileiat, G. I., Liu, P., Jiménez-Osés, G., Lai, Y. C., Vosgueritchian, M., Fang, Y., Park, S., Houk, K. N., & Bao, Z. (2014). High-yield sorting of small-diameter carbon nanotubes for solar cells and transistors. *ACS Nano, 8*, 2609–2617. https://doi.org/10.1021/nn406256y
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