

# The carbon/silicon heterojunction: the future for carbon based photovoltaics?

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## Abstract

With the increasing demand for alternative energy, great advances have been made in different fields of photovoltaics. Silicon technologies dominate the current solar cell market, but carbon based photovoltaics are known for their potential to be produced at low cost and high volume. In this work the potential of improving the leading silicon technologies using carbon based materials is reviewed. An historical overview is presented for the development of heterojunctions between silicon and five types of carbon: C<sub>60</sub>, carbon nanotubes, graphene, amorphous carbon and conducting polymers (especially PEDOT:PSS). Of these heterojunctions C<sub>60</sub> and amorphous carbon have shown to be the least promising because of low power conversion efficiencies (0.7% and 7.9% respectively). Carbon nanotube/silicon solar cells with efficiencies up to 17% have been reported, but commercial applications of these devices are limited by their small active areas. Graphene and PEDOT:PSS show the greatest potential for improvement of silicon-based photovoltaics because of their low-cost processability and high efficiencies in heterojunction with silicon: 15.6% and 20.6% for graphene and PEDOT:PSS respectively. Also organic-inorganic hybrid tandem photovoltaics (HTPV) are briefly reviewed. HTPV devices have shown decent efficiencies up to 13.2%, but lack absorption in the 600 nm region. If absorption in that region of the solar spectrum is increased HTPV could grow to a leading PV technology because of low production costs and possible features like bendability.

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## Introduction

Silicon and carbon are among the most researched and most abundant elements in nature. Both elements have shown excellent properties for application in photovoltaics over the past decades. The first (selenium based) photovoltaic cell, that could generate electricity from sunlight with an efficiency of 1%, was created in the 19<sup>th</sup> century (Fritts 1883). Nowadays Si-based solar cells are state of the art with efficiencies of over 45% for multi-junction cells (Green 2016). In silicon based photovoltaics three different types of silicon are used: amorphous silicon (a-Si), monocrystalline silicon (c-Si) and polycrystalline silicon (pc-Si). In the field of photovoltaics c-Si has shown to be the most promising technology for reaching high power conversion efficiencies (PCE). The PCE is defined as  $\eta = \frac{V_{oc} * J_{sc} * FF}{P_{in}}$ , where  $V_{oc}$  is the open circuit voltage,  $J_{sc}$  the short-circuit current, FF the fill factor and  $P_{in}$  the incident solar power.

Table 1. Efficiencies of record laboratory-scale devices and typical commercial PV modules of various technologies. The decrease indicates the difference in efficiencies between lab cells and commercial cells based on the same technology. Source: (Darling and You 2013)

PV technology	Lab cell record PCE <sup>33</sup>	Commercial module PCE	% Decrease
c-Si	25.0	20.1 <sup>a</sup>	19.6
p-Si	20.4	14.6 <sup>b</sup>	28.4
a-Si	10.1	5.1 <sup>c</sup>	49.5
CIGS	19.6	12.5 <sup>d</sup>	36.2
CdTe	18.3	12.5 <sup>e</sup>	31.7
OPV	10.7	1.65 <sup>f</sup>	84.6

<sup>a</sup> SunPower. <sup>b</sup> Schott. <sup>c</sup> Uni-Solar. <sup>d</sup> Q-Cells. <sup>e</sup> First Solar. <sup>f</sup> Konarka.

Apart from silicon technologies, many other types of (thin-film) photovoltaics have been developed in the past decades, including but not limited to: dye-sensitized solar cells (DSSC), cadmium telluride (CdTe), copper indium gallium diselenide (CIGS), organic photovoltaics (OPV) and recently hybrid perovskites (HP). Table 1 shows the record PCEs (in 2013) of lab scale solar cells and commercial solar cells for different PV technologies.

The main focus of this work will be on carbon based photovoltaics, because carbon based solar cells (and organic solar cells in specific) can have properties that are not found in silicon, like transparency and bendability. Furthermore organic solar cells can be solution-processed, allowing the possibility of low-cost roll-to-roll production at large quantities. Other carbon-based photovoltaics will also be reviewed here.

### Historic overview of Organic Photovoltaics (OPV)

Until the 1980s, the efficiencies of organic solar cells were far below 1% (Chamberlain 1983). One of the first reported solar cells with a PCE of 1% was the Tang cell (Tang 1986). The active layer of the Tang cell consisted of a bilayer of copper phthalocyanine (CuPc) that acted as donor material, and a perylene tetracarboxylic derivative (PV) as acceptor material. The efficiencies of organic solar cells further increased with the discovery of the bulk heterojunction (Yu en Heeger 1995). In a bulk heterojunction the active layer is a blend of donor and acceptor material and the advantage over bilayer junctions is that there is a very high contact area between the donor and acceptor materials. This results in a shorter average distance between the bulk material and the donor/acceptor interface, which increases the possibility of charge separation at the interface (because carrier diffusion is limited), thereby increasing the efficiency.

A big step in improving the PCE of organic solar cells was made when it was found that PCBM ([6,6]-Phenyl C<sub>61</sub> butyric acid methyl ester) can act as a good electron acceptor in organic heterojunctions. The first cell that made use of PCBM had a PCE of 1% and consisted of a bulk heterojunction between

PCBM and MEH-PPV (Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]) (Yu, et al. 1995). Other device structures, such as tandems consisting of two active layers on top of each other, were also studied (Xue, et al. 2004). Efficiencies of over 6% were achieved for tandems of PCPDTBT:PCBM and P3HT:PC<sub>70</sub>BM (Kim, Lee, et al. 2007), where a single cell of P3HT:PCBM only had an efficiency of 5.0% (Kim, Kim, et al. 2006). Nowadays PCEs of over 10% are achieved for organic tandem cells (You, et al. 2013), as well as for single bulk heterojunction cells (Liu, et al. 2014).

### Current market for solar cells

Organic solar cells, and other thin-film PV-technologies, have been greatly improved over the past 30 years. However, none of these technologies has been able to compete with the silicon technologies in the solar energy market, as displayed in Fig 1.

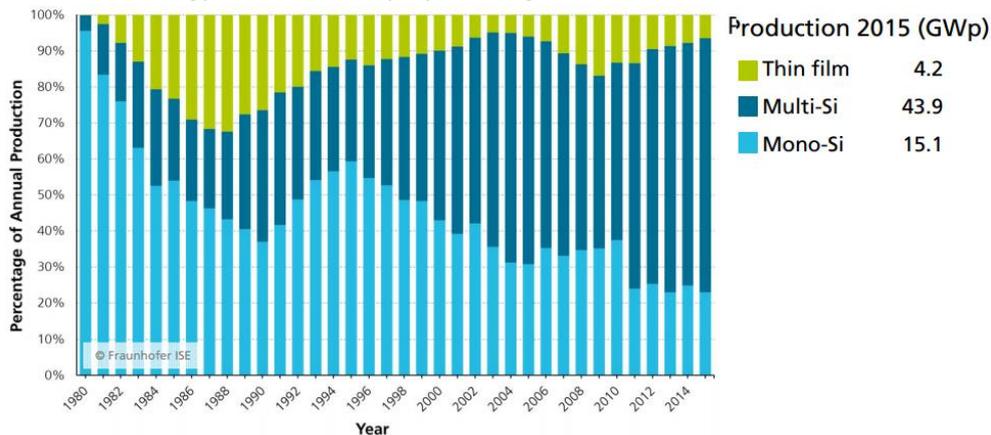


Figure 1. Annual solar energy production. Silicon based photovoltaics hold over 90% of the market in 2014. Source: (Fraunhofer Institute for Solar Energy Systems 2016)

Silicon has always dominated the market of photovoltaics with a current market share of over 90% (Fraunhofer Institute for Solar Energy Systems 2016). The International Technology Roadmap for Photovoltaic (ITRPV) from 2015 shows that the price of energy from Si based solar cells has decreased by more than a factor of 2 over the past 5 years (ITRPV 2015). This indicates that the main limiting factor for further expansion of the solar energy market, the high costs of Si solar cells, is being resolved at the moment.

The ITRPV also predicts that the market share of silicon technologies in photovoltaics will remain unchanged in the near future. What does this mean for the solar energy market? Is there a future for the other photovoltaic technologies? It is likely that other PV-technologies will not be able to compete with silicon in terms of PCEs in the near future. The main shortcomings of Si are the high production costs. OPV technologies, on the other hand, are known for their potential to be produced at low costs and with relatively simple techniques like chemical vapour deposition and spin-coating. Therefore it is likely that OPV can have applications in improving the current silicon technologies as low-cost improvements of c-Si based solar cells, which still require expensive techniques to be fabricated. A low-cost improvement of an expensive Si cell could result in a lower price per unit of produced energy.

This work will address the historical development of heterojunctions of c-Si and five forms of carbon: amorphous carbon (a-C), carbon nanotubes (CNT), graphene, conducting polymers (especially PEDOT:PSS) and C<sub>60</sub>. Heterojunctions were made between c-Si and these forms of carbon have been studied and reported in the literature. An overview of the current state of the art of these carbon-silicon heterojunctions will be presented. Furthermore, organic/inorganic tandems will be reviewed and the potential application of these techniques as low-cost improvements of Si-based photovoltaics will be addressed.

## The C/Si-Heterojunction

### C/Si p-n junction

Most solar cells make use of p-n junction to convert sunlight into electricity. When (a semiconducting form of) carbon and silicon are brought in contact a p-n heterojunction is formed. Upon creation of a C/Si heterojunction between p-type carbon and n-type silicon carriers will diffuse because of a difference in carrier concentration between the materials. Holes are injected into the silicon and electrons are injected into the carbon. As a result of this carrier diffusion process, band bending will occur and a built-in potential will be formed.

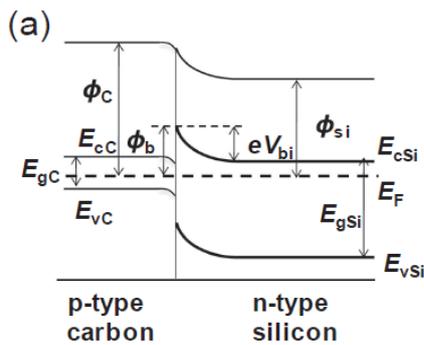


Figure 2. Band bending in a C/Si p-n junction.  $\Phi_C$  and  $\Phi_{Si}$  are the work functions of carbon and silicon.  $E_{gSi}$  and  $E_{gC}$  are the Si and C bandgaps.  $E_{cC}$ ,  $E_{cSi}$ ,  $E_{vC}$  and  $E_{vSi}$  represent the energies of the conduction and valence bands of carbon and silicon respectively.  $E_F$  is the Fermi-energy.  $\Phi_b$  represents the ideal barrier height and  $eV_{bi}$  the built-in voltage. Source: (Xinming, Zheng and Zhu 2015)

When the junction is illuminated with light, photons will be absorbed by the heterojunction. Electrons in the valence band can be excited to the conduction band by photons with an energy higher than the bandgap, creating an electron-hole pair. This photo generated electron-hole pair can be separated by the built-in field. This separation of carriers becomes more effective upon increasing the built-in potential (Xinming, Zheng and Zhu 2015).

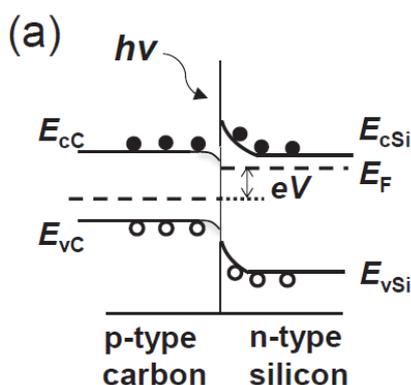


Figure 3. Band diagram of C/Si p-n junction upon irradiation with light.  $E_{cC}$ ,  $E_{cSi}$ ,  $E_{vC}$  and  $E_{vSi}$  represent the conduction and valence bands of carbon and silicon.  $E_F$  is the Fermi energy level and  $V$  is the open-circuit voltage. Source: (Xinming, Zheng and Zhu 2015)

Many forms of carbon are known, ranging from low dimensional structures (fullerenes and CNTs) to carbon based polymers, like PEDOT:PSS. In the following sections heterojunctions of c-Si with each of these forms of carbons and hybrid tandem structures of carbon and silicon will be reviewed.

### C<sub>60</sub>/Si (0D-carbon)

C<sub>60</sub> has become a widely used electron-acceptor/-transporter in organic photovoltaics after the discovery that ultra-fast photoinduced electron transfer can occur from a conducting polymer to C<sub>60</sub> (Sariciftci, et al. 1992) (Wudl, et al. 1994). Crystals of C<sub>60</sub> are found to be direct band gap n-type semiconductors. Because of the face-centred-cubic structure of these crystals, they show a high electron mobility and have a direct bandgap between 1.5 eV and 2.3 eV (Saito and Oshiyama 1991) (Saito and Oshiyama 1991). The first photovoltaic cell making use of a C<sub>60</sub>/Si heterojunction was fabricated in 1996. Photocurrents were observed for C<sub>60</sub>/p-Si and C<sub>60</sub>/n-Si heterojunctions, with the highest photocurrent for lightly doped n-Si (Kita, et al. 1996). The PCE of this cell was however far below 0.1%, which was mainly caused by a low fill factor of 0.3 and a high resistance in the C<sub>60</sub> film. In order to use C<sub>60</sub> films for PV applications the resistance in the film had to be reduced, which can be done by ion implantation in the film. As a result of ion implantation the carbonaceous film will undergo a structural transition to amorphous carbon (Kastner, Kuzmany and Palmetshofer 1994). Narayanan and Yamaguchi used this principle and created a heterojunction between boron-implanted p-C<sub>60</sub> and n-type silicon. The resistance of the C<sub>60</sub> film was drastically reduced from 35 kΩ to 370 Ω, and the resulting PCE was 0.023% (Narayamam and Yamaguchi 1999). Later they also showed it is possible to fabricate a phosphorous implanted n-C<sub>60</sub>/p-type silicon heterojunction. This cell showed an increased C<sub>60</sub> conductivity, but a PCE of only 0.01% (Narayanan and Yamaguchi 2001). The main reason for this low PCE is an increased series resistance as a result of lattice defects caused by ion implantation. Later on the same research group reported a record-high efficiency for C<sub>60</sub>/Si solar cells of 0.7%. This PCE was achieved by using an excimer laser on the C<sub>60</sub>/n-type Si heterojunction instead of ion implantation (Narayanan, Yamaguchi and Azuma 2002). Even though different techniques to improve the C<sub>60</sub>/Si heterojunction were investigated, the efficiencies of these devices are still very low. The efficiency is mainly limited by the intrinsic conductivity (Xinming Li 2015).

I personally do not see a future in C<sub>60</sub>/Si photovoltaics, mainly because the PCE remains low upon p-type and n-type doping of the C<sub>60</sub>. To make a C<sub>60</sub>/Si heterojunction solar cell it is also required to convert the C<sub>60</sub> into amorphous carbon using dopants or laser irradiation, which makes C<sub>60</sub>/Si cells practically the same as a-C/Si cells (which will be covered in a later section) in terms of their final structure, but with an extra processing step and lower efficiencies. C<sub>60</sub> however has shown, over the past decades, to be very suitable as electron acceptor in organic photovoltaics with conducting polymers like P3HT. In my opinion the future of C<sub>60</sub> in photovoltaics lays in OPV and in the use of C<sub>60</sub> as additives to improve other organic or inorganic photo active materials.

### CNT/Si (1D-carbon)

The discovery of multi-walled carbon nanotubes (MWCNT) (Iijima 1991) and single-walled carbon nanotubes (SWCNT) (Bethune, et al. 1993) (Iijima 1993) dates back to the early 90's. Because of the remarkable electrical properties of CNTs a lot of research has been done on their applications in electronics. SWCNT can be seen as a rolled up sheet of graphene, capped with a semi-spherical fullerene. It is important to note that CNTs are not fabricated in this way. It is merely a method for visualizing their structure. Depending on the axis along which the graphene sheet is rolled up, SWCNT can behave as semiconductors or as metals, as shown in Fig 4.

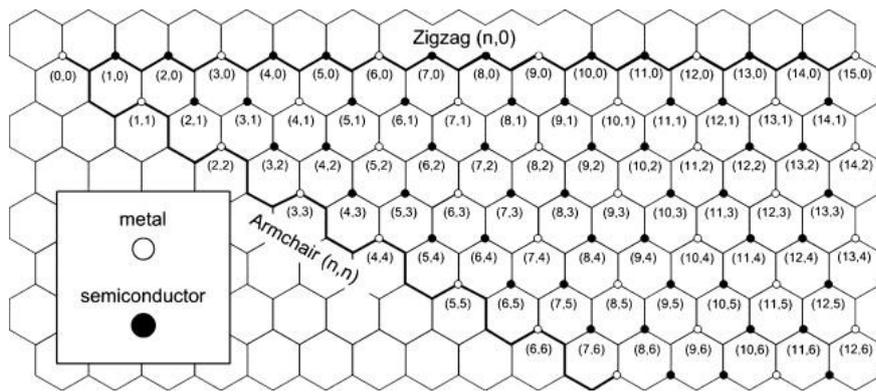


Figure 4. The properties of SWNT are dependent on their structure. SWNTs can be seen as a sheet of graphene rolled into a cylinder along a certain axis. The orientation of this axis determines if a SWNT has metallic (white dots) or semiconductor (black dots) behaviour. Source: (Wernik en Meguid 2011)

Where SWCNTs can be metallic or semiconductors, most MWCNTs show metallic behaviour and allow very high current densities up to  $10^9 - 10^{10}$  A/cm<sup>2</sup> (Wei, Vajtai and Ajayan 2001). Because of their metallic properties MWCNTs (and metallic SWCNTs) have no bandgap. Semiconducting SWCNTs on the other hand do have a tuneable bandgaps, which can range from 0.4 eV to 2.0 eV depending on their structure. Furthermore SWCNTs are very sensitive to oxygen, making it very easy to p-dope them by a reaction with ambient oxygen (Collins, et al. 2000). These properties make SWCNTs very suitable for applications in photovoltaics.

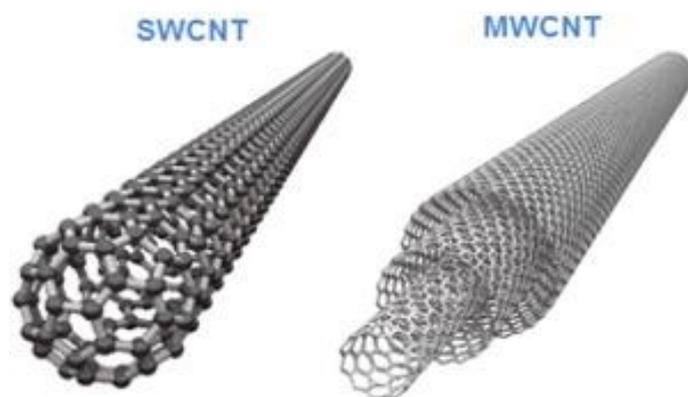


Figure 5. Structure of single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT). Source: (Cividanes, et al. 2013)

The first demonstration of a solar cell that made use of a CNT/Si heterojunction was reported in 2007 (Wei, et al. 2007). This cell consisted of a heterojunction between pristine double walled-CNTs (DWCNT) and n-type doped Si and had a PCE of 1.31%. The low efficiency was mainly caused by a low  $J_{sc}$  and FF (13.8 mA cm<sup>-2</sup> and 19% respectively). The efficiency of this junction was greatly increased by hydrofluoric acid treatment to reduce the thickness of the native SiO<sub>2</sub> layer. This increased the  $J_{sc}$  to 26 mA cm<sup>-2</sup> and the FF to 53%, resulting in a PCE of 7.4% (Jia, et al. 2008).

After the demonstration of DWCNT/n-Si solar cells junctions between SWCNTs and n-type Si were reported. The PCE of the first demonstrated SWCNT/n-Si solar cell was 2.7% (Li, et al. 2009). In recent years studies on SWCNT/Si heterojunctions have shown that chemical doping and changing the alignment pattern of the CNT films can greatly increase the PCE of these heterojunctions (Li, Lv and Zhu 2015). Using this knowledge, record PCEs of 17.0% and 7.53% were achieved for SWNT/n-Si and SWNT/p-Si junctions respectively (Li, Huang, et al. 2014) (Wang, et al. 2015).

Even though the PCE of these junctions was increased from 1.3% to 17% over only 8 years, these PCEs are for very small active areas <1 cm<sup>2</sup> only. For active areas bigger than 2 cm<sup>2</sup> the highest

reported efficiency is 10% (Xu, et al. 2016). Taking into account that to achieve high efficiencies in CNT/Si junctions, very structured alignments of the CNTs and post-treatments are required, CNTs are unlikely to become an economically favourable improvement for Si-based solar cells in the near future.

### Graphene/Si (2D-carbon)

The two-dimensional single atomic layer of carbon (graphene) was isolated for the first time in 2004 (Novoselov, et al. 2004) by Geim and Novoselov, for which they were awarded the Nobel Prize in Physics in 2010. Graphene has very unique properties like near transparency, almost no bandgap, light absorption across a broad spectrum and an incredibly high electron mobility of  $2.5 \times 10^5 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$  (Mayorov, et al. 2011) (Nair, et al. 2008). Because of these metallic like properties graphene is widely studied for its applications in electronics.

The first C/Si heterojunction solar cell that made use of graphene was reported in 2010 (Li, Zhu, et al. 2010). This cell was constructed of a layer of graphene on n-type doped Si and had a PCE of 1.65%. The strategy behind achieving a high PCE in graphene/Si heterojunctions is controlling the number of graphene layers (and thereby the transmittance), increasing the graphene work function to increase the built-in potential in the junction, adding an interfacial layer of graphene oxide or  $\text{SiO}_2$  and increasing the light absorption by adding an antireflection layer (Lin, et al. 2013).

By using p-type chemical doping of graphene, its work function can be increased. Using nitric acid vapor as p-type dopant the PCE of a graphene/n-type Si solar cell was increased to 9.63% compared to 4.98% for a similar cell with pristine graphene (Li, Xie, et al. 2013). Another method of p-type doping is doping with molecular acids, like trifluoromethanesulfonic acid (TFSA), which increased the PCE to 8.6% from 1.9% for the undoped case (Miao, et al. 2012). Combining TFSA doping with p-type doping using Au nanoparticles, that filled the cracks in the graphene layer, resulted in a PCE of 12.3%, where the same cell had a PCE of 7.9% before treatment with TFSA (Ho, et al. 2015).

The record PCE for graphene/Si heterojunction solar cells was achieved by Song et al. by using a  $\text{SiO}_2$  interfacial layer and a  $\text{AuCl}_3$  solution as dopant. This  $\text{TiO}_2/\text{AuCl}_3$ -doped graphene/ $\text{SiO}_2$ /n-Si cell had a PCE of 12.4%, which could be increased up to 15.6% with an anti-reflective coating (Song, et al. 2015).

Overall the efficiency of graphene/n-Si solar cells has increased from 1.65% to 15.6% in only 5 years. This drastic increase can partly be assigned to the fact that doping methods that were used for CNT/n-Si heterojunctions could also be used for graphene/n-Si solar cells. Because of the rapid increase of efficiencies of graphene/Si PV devices and the astonishing intrinsic electrical properties of graphene, graphene could grow out to be one of the leading technologies for low-cost improvement of Si-based solar cells in a matter of years.

### a-C/Si (irregular 3D-carbon)

Apart from very structured forms of carbon (like CNTs, fullerenes and graphene) that show interesting opto-electronic properties, also amorphous forms of carbon (a-C) can be used in electronics. This has been demonstrated in 1979 when a small photovoltaic output was measured in a heterojunction of an evaporated carbon film on mono-crystalline silicon (Bhagavat and Nayak 1979). a-C films can be fully amorphous (explaining their partial transparency), but can also contain diamond-like domains. This is dependent on the deposition technique used for applying the carbon film. The electronic properties of a-C arise from the fact that the hybridization of carbon atoms in the a-C film is a mixture of  $sp^2/sp^3$  and undoped a-C naturally shows p-type semiconducting properties (Veerasamy, et al. 1993). The bandgap of an a-C film can be controlled by the dopant concentration, making it possible to achieve a broad range of bandgaps: 0.2 eV-3.0 eV (Zhu, Wei and Wu 2009). The first carbon-silicon hybrid photovoltaic cell that made use of the p-type semiconductor behaviour of

a-C was created by chemical vapor deposition of 2,5-dimethyl-*p*-benzoquinone on n-type mono-crystalline silicon (H. Yu, et al. 1996). The device structure of this cell is shown in Fig 6.

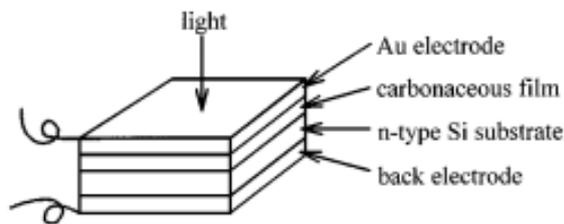


Figure 6. Device structure of first demonstrated a-C/n-type c-Si cell. The carbonaceous film (40 nm) is applied to the n-type Si substrate by chemical vapor deposition of 2,5-dimethyl-*p*-benzoquinone on n-type mono-crystalline silicon. The PCE achieved by this cell is 3.80%. Source: (H. Yu, et al. 1996)

This cell had a PCE of 3.80% and in the same year the efficiency has been increased to 6.45% by making use of a thinner Au top-electrode (H. Yu, et al. 1996). The record PCE of 7.9% has been achieved in 2001 with a boron-doped diamond like a-C layer on a n-type silicon substrate (Ma and Liu 2001). It has also been demonstrated that is possible to make an a-C/p-type Si cell. This has been done by using a phosphorous-doped n-type a-C film on top of a boron doped p-type Si substrate resulting in a cell with a PCE of 2.07% (Krishna, Soga, et al. 1999). The same research group later reported that the PCE of these devices can be increased upon insertion of a 20 nm undoped (p-type) layer of carbon in between the heterojunction. This effect is mainly assigned to an improved quantum efficiency at higher wavelengths for the n-C/p-C/p-Si cell (Krishna, Nukaya, et al. 2001). However, a-C/Si for PV applications develops slowly because of a high density of defects in a-C films and a difficult to control  $sp^2/sp^3$  ratio (Xinming, Zheng and Zhu 2015). Because a high density of defects is inherent to amorphous systems, a-C/c-Si will, in my opinion, not grow to a commercial technology for solar cell applications.

### Conducting polymers/Si (structured 3D-carbon)

Another approach to improve Si solar cells is to deposit a layer of organic semiconducting polymer, like P3HT (Poly(3-hexylthiophene-2,5-diyl)) or PEDOT:PSS (poly (3,4-ethylene-dioxythiophene):polystyrenesulfonate), on top of a silicon-based cell. The advantage of this approach is that the polymer can be deposited at low temperatures and with simple, inexpensive techniques such as spin-coating. This has been demonstrated by Shiu et al. in 2010 for a Si nanowire/PEDOT:PSS heterojunction (Shiu, et al. 2010) and later on by Avasthi et al. who fabricated a junction between n-type c-Si and P3HT by spin-coating a layer of P3HT on top of a doped Si substrate (Avasthi, Lee, et al. 2011). To decrease light absorption by the top electrode PEDOT:PSS was used to replace the previously used semi-transparent Pd layer. Light absorption by the top electrode was decreased, because of the transparency of PEDOT:PSS. However PEDOT:PSS is not as conductive as Pd, therefore a metal grid covering 10% of the surface was added on top of the PEDOT:PSS electrode. This resulted in the device structure shown in Fig 7 with a PCE of 10.1%.

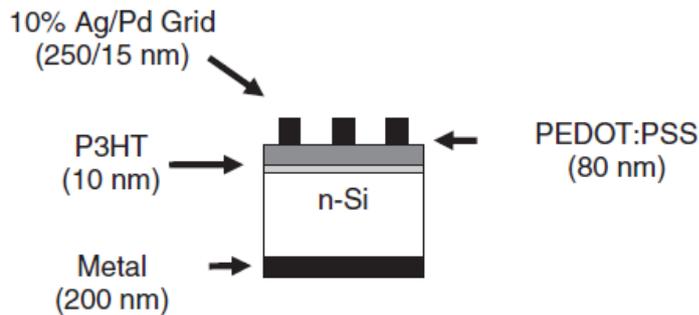


Figure 7. Device structure of n-type c-Si/P3HT/PEDOT:PSS hybrid solar cell with a PCE of 10.1%. P3HT and PEDOT:PSS layers were deposited using spin-coating at low temperatures. (Avasthi, Lee, et al. 2011)

He et al. found that the efficiency could be improved by changing the way the Si surface was terminated from hydrogen terminated (H-Si) to oxide-terminated ( $\text{SiO}_x\text{-Si}$ ). Using this approach the PCE was boosted from 0.02% to 10.6% for a n-Si/PEDOT cell (He, et al. 2012). This incredible improvement of the PCE was mainly assigned to the formation of an unfavourable induced internal electrical field at the H-terminated surface. The  $\text{SiO}_x$ -terminated surface on the other hand has a favourable band alignment with PEDOT, as shown in Fig 8.

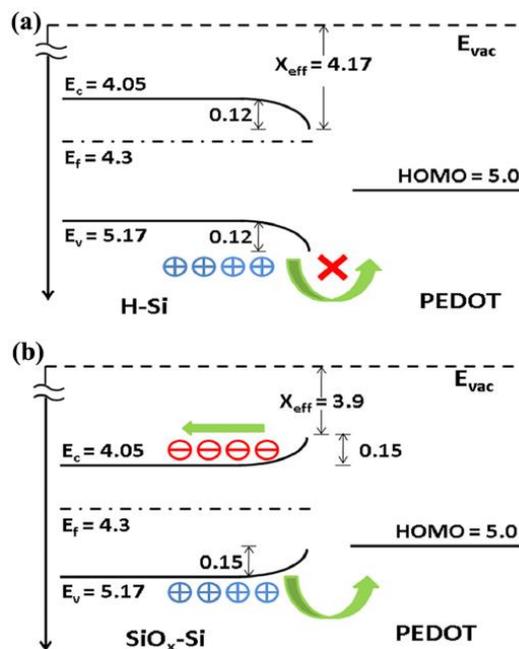


Figure 8. Energy band diagrams of (a) H-Si/PEDOT and (b)  $\text{SiO}_x\text{-Si}$ /PEDOT heterojunctions. Source: (He, et al. 2012)

Apart from the surface of the Si substrate, the doping concentration ( $N_D$ ) of the Si is of influence on the performance of a n-Si/PEDOT:PSS heterojunction. Pietsch et al. found that upon increasing the doping concentration in the silicon, the  $V_{oc}$  could be increased up to 645 mV, resulting in an improved PCE up to 12.6% (Pietsch, Jäckle and Christiansen 2014).

Even further improvement of the efficiency could be achieved by adding a layer between Si and the Al back contact to reduce carrier recombination at the back contact. Suitable materials for this layer are electron transport materials like LiF (Zhang, Liu, et al. 2014) and  $\text{Cs}_2\text{CO}_3$  that reduces the work function of the Al and deflects minority carriers (holes) to reduce carrier recombination, as shown in Fig 9. Using the latter Zhang et al. fabricated a heterojunction cell with an Al/ $\text{Cs}_2\text{CO}_3$ /n-Si/PEDOT:PSS/Ag device structure resulting in a PCE of 13.7%. A similar cell without the hole blocking layer had a PCE of 10.8% (Zhang, Cui, et al. 2015).

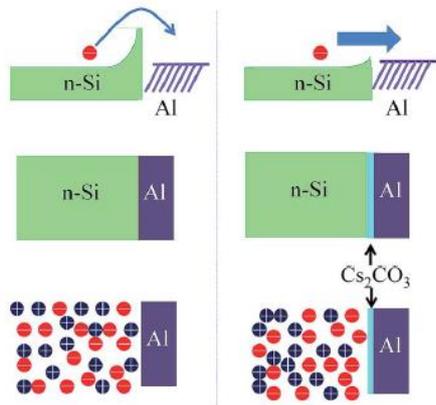


Figure 9. Energy alignment of (a)  $n\text{-Si}/\text{Al}$  and (b)  $n\text{-Si}/\text{Cs}_2\text{CO}_3/\text{Al}$ . For (a) there is a barrier for electrons to be collected at the Al electrode and the electron and hole concentrations are equal at the back interface causing carrier recombination. In (b) the barrier is reduced, because of a lowering of the Al work function improving electron collection at the Al electrode and allowing minority carrier deflection. Source: (Zhang, Cui, et al. 2015)

A big step in further improvement of PEDOT:PSS/Si heterojunctions was made by inverting the device structure. When the junction is at the cell front the efficiency is limited by parasitic light absorbance in the PEDOT:PSS layer. When the device structure is inverted and the PEDOT:PSS layer is placed at the back of the cell, also called the Back-PEDOT structure, the efficiency can be improved up to 17.4% (Zielke, Pazidis, et al. 2014). Since most light absorption occurs in the silicon, placing the PEDOT:PSS layer at the back of the cell did not decrease light absorption of the cell as a whole. Later on the same research group was able to improve the efficiency by changing the PEDOT:PSS composition to get rid of excess PSS, which led to an increased efficiency of 18.3% for a  $n\text{-Si}/\text{PEDOT:PSS}$  junction using the Back-PEDOT structure. They were also able to achieve a very high FF of 80.6%, resulting in a PCE of 20.6% for a  $p\text{-doped Si}/\text{PEDOT:PSS}$  junction using the same device structure (Zielke, Niehaves, et al. 2015). This is to my knowledge the highest achieved PCE for a C/Si heterojunction so far.

To summarise: a layer of PEDOT:PSS can be applied to a silicon solar cell at low cost by for example spin-coating. Since the efficiency of silicon solar cells is increasing rapidly, carrier recombination at the back contact becomes a limiting factor for further improvement of silicon solar cells. The excellent hole-transport and electron-blocking properties of PEDOT:PSS can provide an effective and low-cost solution to this problem by adopting a Back-PEDOT architecture. Furthermore it is predicted that the silicon PV technology might switch from  $n\text{-type}$  to  $p\text{-type}$  silicon (ITRPV 2015) and PEDOT:PSS/Si heterojunctions have shown high PCEs both for  $n\text{-type}$  and  $p\text{-type}$  silicon. Therefore it is likely PEDOT:PSS/Si heterojunctions will be a big player in the field of photovoltaics in the near future.

## Organic-inorganic Hybrid Tandem PV (HTPV)

A fundamentally different approach for using carbon PV technology as a low cost improvement for silicon based photovoltaics is making use of the organic-inorganic hybrid tandem device structure (HTPV). HTPV makes use of a low-cost, low temperature processed solar cell that is placed on top of a more expensive and efficient inorganic, Si-based solar cell by for example printing.

The potential improvement of the PCE of Si-based solar cells by operating them in a HTPV architecture together with an organic solar cell has been modelled by Bailey and McGehee as function of the organic bandgap and the organic absorbance, see Fig 10 and Table 2 (Bailey and McGehee 2012).

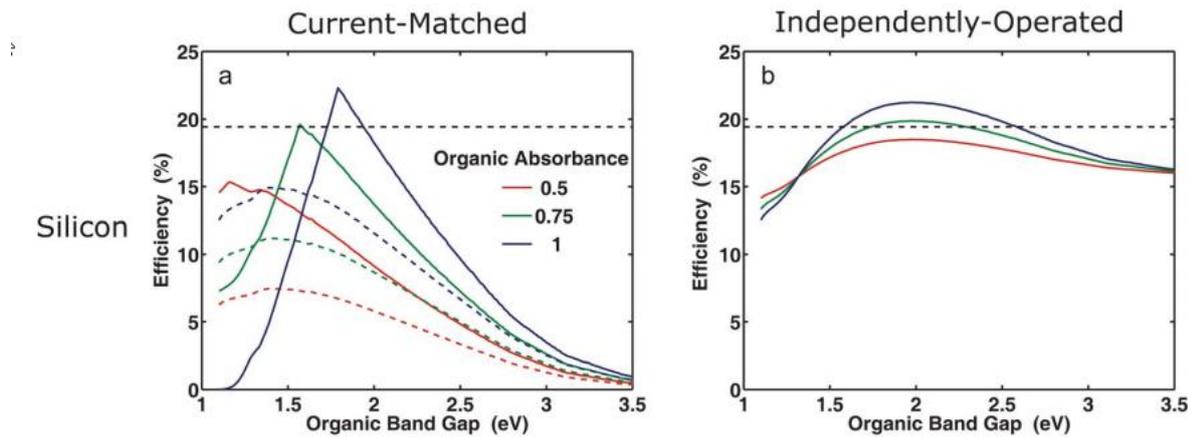


Figure 10. PCE of HTPV devices as a function of the organic bandgap and the organic absorbance for a well-passivated high quality silicon bottom cell. (a) the PCE for current matched (2-terminal) subcells. (b) the PCE for independently operated (4-terminal) subcells. The PCE of the Si-cell without an organic top-cell is displayed as the horizontal black dashed lines. The PCE of the organic top cells without a Si bottom cell are displayed as the coloured dashed lines. Organic top cells were modelled assuming an internal quantum efficiency of 90% and a fill factor of 0.7. Source: (Beiley and McGehee 2012)

Table 2. Efficiencies of HTPV devices with a Si bottom cell for current matched and independently operated architectures. It is assumed that the organic top cell always has the optimal bandgap and absorbs all light above the bandgap energy (taking into account parasitic absorption of the top cell). Source: (Beiley and McGehee 2012)

Scenario	Inorganic only PCE	Current matched		Independently operated		
		Optimal organic $E_g$ (eV)	Tandem PCE	Optimal organic $E_g$ (eV)	Tandem PCE	
Silicon	High quality, good passivation	19.4%	1.79	22.3%	1.98	21.3%
	High quality, no passivation	17.5%	1.79	21.8%	1.93	20.8%
	Low quality, good passivation	15.4%	1.87	19.8%	1.90	18.7%
	Low quality, no passivation	14.2%	1.88	19.8%	1.91	18.6%

The model of Beiley and McGehee predicts the possible increase of the efficiency of Si solar cells can be substantial when operated in a HTPV architecture with an organic top cell with the right bandgap. Efficiencies up to 22.3% have been predicted for high quality Si cells with good passivation. Especially the possibility of increasing the efficiency of low quality Si cells up to a PCE of almost 20% is remarkable and has the potential for achieving low-cost, high efficiency photovoltaics. It is important to note that in HTPV devices amorphous silicon is used as front cell and not crystalline silicon, which has been the main focus of this paper so far. The reason for this is that a-Si has a lower absorption than c-Si, making it suitable for use as front cells when absorption by the back cell is also required. This was not the case for junctions that use the Back-PEDOT architecture because almost all light is absorbed in the silicon in those devices.

Experimental demonstrations of solar cells that make use of the HTPV architecture showed that the interface between the front and back cell is crucial for achieving high efficiencies. Kim et al. fabricated HTPV cells with the device structure shown in Fig 11, making use of PEDOT:PSS and MoO<sub>3</sub> as hole transporting layers (HTL) (Kim, et al. 2011). The device that made use of PEDOT:PSS as HTL showed an interfacial series resistance ( $R_{s,int}$ ) of 63.8  $\Omega$  cm<sup>-2</sup> and a PCE of 0.83%. MoO<sub>3</sub> as HTL resulted in a  $R_{s,int}$  of 50.9  $\Omega$  cm<sup>-2</sup> and a PCE of 1.84%, suggesting that the interfacial series resistance has to be reduced in order to obtain an improved FF (41% in this device) and ultimately achieve high efficiencies in HTPV devices.

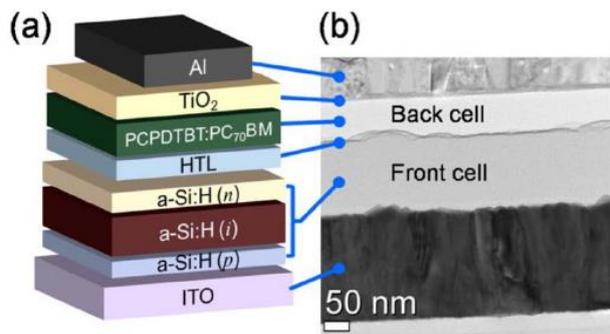


Figure 11. (a) Device structure of HTPV device with PEDOT:PSS and MoO<sub>3</sub> as HTLs and (b) cross-sectional TEM image of the fabricated HTPV solar cell with this structure. Source: (Kim, et al. 2011)

Albrecht et al. improved this structure by using an organic back cell with a higher quantum efficiency and optimizing the recombination contact by replacing ITO with Al-doped zinc oxide (AZO) (Albrecht, et al. 2014). Fill factors of 70% were achieved boosting the PCE to 7.5%.

Because dual junction HTPV devices lack absorption around 600 nm triple junction HTPV cells have been studied. In these cells a second a-Si:H cell with a different p-i-n thickness, in order to make it absorb in the 500-700 nm wavelength region, is incorporated as a middle cell (Fig 12).

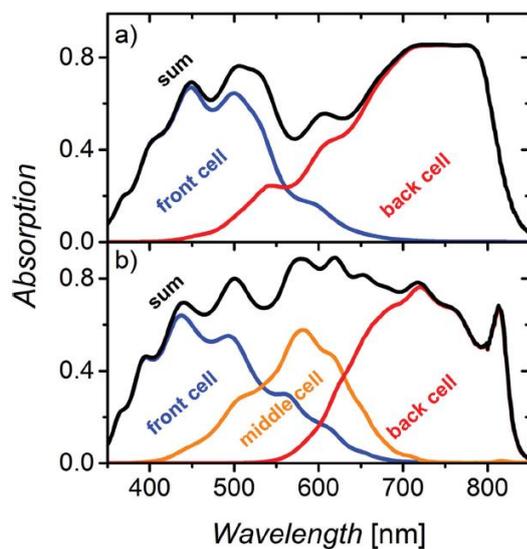


Figure 12. Simulated absorption spectra for (a) a-Si:H/Si-PCPDTBT:PCBM dual junction and (b) a-Si:H/a-Si:H/ Si-PCPDTBT:PCBM triple junction HTPV cells. The coloured spectra represent the absorption for the individual subcells and the black spectra show the sum of these absorptions. Source: (Roland, et al. 2015)

Roland et al. fabricated such a triple junction HTPV cell with a-Si:H/a-Si:H/PMDPP3T:PCBM as active layers. Because of the increased absorption in the mediate solar spectrum and further adjusted recombination contacts leading to a FF up to 80%, efficiencies up to 11.7% were achieved (Roland, et al. 2015).

The record PCE of 13.2% for these devices has been achieved by Tan et al. for a triple junction cell with the device structure shown in Fig 13 (Tan, et al. 2016). This high efficiency was achieved by optimizing the thickness of the individual cells (90/1000/150 nm for the front/middle/back cells respectively) and the interconnecting layers and by using a light-trapping textured front electrode. Making use of a textured front (Fig 13a) increased the PCE to 13.2% compared to 10.4% for a similar flat device (Fig 13b).

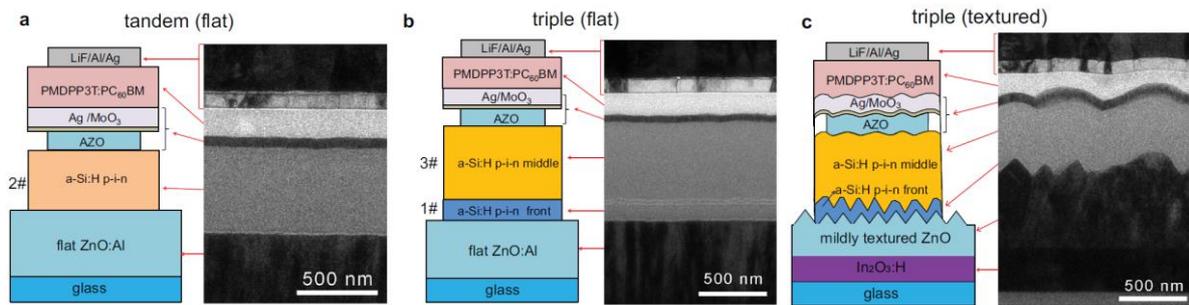


Figure 13. Device structure and corresponding TEM images of (a) *a*-Si:H/PDPP3T:PC<sub>60</sub>BM dual junction, (b) flat *a*-Si:H/*a*-Si:H/PDPP3T:PC<sub>60</sub>BM triple junction and (c) textured *a*-Si:H/*a*-Si:H/PDPP3T:PC<sub>60</sub>BM triple junction HTPV solar cells. Source: (Tan, et al. 2016)

The main disadvantage of this high efficiency triple junction cell is the fact that it needs to be precisely textured, which increases the production costs. The same research group however also improved the flat dual junction hybrid HTPV cell by making use of a stack of AZO/Ag/MoO<sub>3</sub> as interconnecting layer between the organic and inorganic cell. The role of the thin Ag layer (1 nm) was to improve the AZO/MoO<sub>3</sub> contact to make it more ohmic. A PCE of 11.6% was reported for this device (PCE of individual cells were 8.4% and 5.5%). It is noteworthy that the efficiency is higher in the tandem device than the flat triple junction device. The main reasons for this are the higher  $V_{oc}$  and FF in the tandem device. In triple junction HTPV cells the middle *a*-Si:H cell is current-limiting because of low absorption of *a*-Si:H in the 500-700 nm region. This also explains why the record PCE was achieved for a cell with a very thick middle cell (1  $\mu$ m) with additional light trapping by the front electrode.

To further improve triple-junction HTPV devices two approaches are possible. The first approach is to increase the efficiency of the middle *a*-Si:H cell by further improving light trapping. This has the disadvantage that textured devices are more costly to produce and textures interfaces tend to reduce the  $V_{oc}$  and FF (Tan, et al. 2016).

The second approach is to replace the *a*-Si:H middle cell by an organic solar cell with a good absorption in the 500-700 nm region.

If HTPV devices become more efficient they might become a good alternative for c-Si technologies. The two main advantages of HTPV are that both *a*-Si and organic solar cells can be flexible, making a lot of possible new applications possible, and *a*-Si and organic solar cells are relatively cheap compared to c-Si solar cells, that are very costly to produce.

## Conclusion and outlook

The state of the art of carbon/silicon heterojunctions has been reviewed for various types of carbon. Amorphous carbon and fullerenes have shown to be the least suitable of the studied carbon materials for C/Si heterojunctions, because of their low PCEs of 7.9% and 0.7% respectively. CNTs have been used to achieve high PCEs of up to 17% in C/Si heterojunctions. These efficiencies are however only achieved for very small active areas. For active areas over 2 cm<sup>2</sup> no efficiencies of over 10% have been reported. Because of the small active areas and the requirement of expensive post treatment of CNT/Si devices to achieve decent efficiencies I do not expect CNTs will be used as a cost-effective improvement for Si solar cells in the foreseeable future.

Graphene/Si heterojunctions have developed at an astonishing speed. The PCE has increased from 1.65% to 15.6% in only 5 years. This increase can however be partly assigned to the fact that existing technologies for CNTs could also be used for graphene. A major advantage of graphene is that it can be deposited at low costs and at low temperatures using chemical vapour deposition. Combined with its astonishing electrical properties this makes graphene a very good candidate for cost effective improvement of existing Si PV technologies. Also PEDOT:PSS has shown to be a good candidate for this purpose because of its excellent conductivity and hole transporting and electron blocking properties. PEDOT:PSS might even be the most suitable candidate to improve Si solar cells, because of the possibility to reduce carrier recombination at the back contact which is becoming a limiting factor for increasingly efficient c-Si solar cells.

Also HTPV has been briefly reviewed. These devices have shown decent efficiencies up to 13.2%, but lack absorption in the 600 nm region. When this problem is resolved, by for example the use of a second organic active layer that absorbs in this region of the solar spectrum, HTPV might grow to be a low-cost alternative for crystalline silicon solar cells. Also the possibility of HTPV devices to be flexible poses interesting new applications that are not possible for c-Si, because crystalline materials are intrinsically not bendable.

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