Solid State Communications 150 (2010) 561–563

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

# Carbon nanostructure–aSi:H photovoltaic cells with high open-circuit voltage fabricated without dopants

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ARTICLE INFO

*Article history:*
Received 18 December 2009
Accepted 11 January 2010
by S. Das Sarma
Available online 17 January 2010

*Keywords:*
A. Nanostructures
A. Semiconductors
D. Photoconductivity and photovoltaics

ABSTRACT

Recently discovered production techniques allow the synthesis of carbon nanostructured films with large surface areas. The abundance of carbon and the unique properties of these nanostructures, including high transparency and excellent electrical conductivity, make these materials very interesting for photovoltaic applications, in particular in combination with amorphous silicon. We examine the properties of thin carbon nanotube films (buckypaper) and graphene in junctions with undoped amorphous silicon thin films. The observed open-circuit voltages, 390 mV for the carbon nanotube film and 150 mV for graphene, suggest that solar cells with high efficiency can be produced without expensive processing steps like doping, multilayer film deposition in high vacuum, or transparent conducting oxide deposition. The buckypaper cells are stable in ambient conditions for many weeks, at least.



## 1. Introduction

Photovoltaics are a crucial component of a carbon emission-free energy industry [1]. Unfortunately, traditional single-crystal silicon solar cells can cost upwards of several dollars per installed watt, with a per kWh cost several times higher than energy from traditional fossil fuel sources [2]. Thin film solar cells, including ones made of hydrogenated amorphous silicon (aSi:H), have the potential to cut costs because much less material is required to fully absorb sunlight, and because these cells are less brittle and fragile [3]. One pitfall of these materials is that the carrier mobilities are generally lower, so the cells require expensive transparent conducting layers, such as indium tin oxide (ITO), for the top contact [4]. We have produced cells that use undoped aSi:H and either graphene or transparent carbon nanotube networks known as buckypaper. The aSi:H is the primary light absorber. The purpose of the graphene or buckypaper is both to separate charges at the graphene–aSi:H interface, and to serve as a transparent top electrode. Because the carbon film is transparent and conducting, ITO or a similar, expensive transparent conducting oxide is unnecessary. These cells also avoid the use of expensive, toxic doping gases such as $PH_3$ and $B_2H_6$. This reduces the complexity and the cost of manufacturing, and makes the process safer for workers and the cells safer for the environment during use and at the end of life. Additionally, doped aSi:H layers contain high defect concentrations, so using only undoped material may improve mobility through the cell and reduce non-radiative recombination [4].

Solar cells have been made previously using buckypaper on crystalline silicon wafers [5–7], and individual carbon nanotubes have been used for solar cell applications [8]. Carbon nanotubes have also been used as a structure for aSi:H cells to improve light trapping [9], but an aSi:H-CNT junction cell has not been reported. Buckypaper is a promising material for solar cells because it can have high transparency and is a fairly good conductor. Graphene performs even better than buckypaper in terms of both transparency and conductivity [10,11], and has been used both as a transparent electrode [12] and as a component in organic photovoltaics [13]. However, until recently the synthesis of high-quality graphene sheets larger than a few microns was impossible. New chemical vapor deposition (CVD) synthesis techniques now make square centimeter or larger sheets achievable [14], and we have used those techniques in this work.

## 2. Materials and methods

Devices are produced by first depositing 600 nm of aSi:H by plasma-enhanced chemical vapor deposition (PECVD) on patterned ITO on glass substrates purchased from Thin Film Devices, Inc. ITO is used as a back contact because its Fermi level is in a position to create an ohmic contact with aSi:H. It is not

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doi:10.1016/j.ssc.2010.01.013

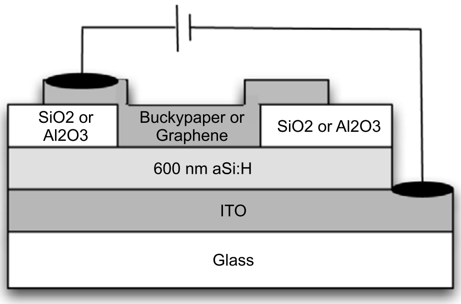


**Fig. 1.** A schematic of device structure. aSi:H is PECVD deposited on patterned ITO substrates. Either $SiO_2$ or $Al_2O_3$ is deposited on top, and a window is patterned and etched. A carbon film is deposited over the window.

important that this layer be transparent, and the ITO could easily be replaced by a less expensive metal. An insulating oxide is deposited on the aSi:H, and then a square window is etched in the oxide. We used either 500 nm of $SiO_2$ or 30 nm of $Al_2O_3$ as insulators, and either a 5 mm or a 500 μm square window. The graphene is grown by CVD on copper substrates using the method of Li et al. [14], then transferred to the device, such that it covers the window. Contacts are made to the ITO back contact and to the graphene above the insulator using silver paint.

Cells are also made in the same geometry using buckypaper instead of graphene. 20 mL of a solution of CVD-grown multiwall carbon nanotubes (MWCNTs) in 1% aqueous sodium dodecyl sulfate is filtered through a 0.8 μm cellulose filter from Pall Corporation. The filter is dissolved in acetone, leaving a network of MWCNTs (buckypaper). The buckypaper is rinsed with isopropanol and water, then picked up out of the water bath with the aSi:H/oxide device such that it covers the window through the oxide. Contacts are made using silver paint. Fig. 1 shows a schematic of our device structure.

Devices are tested using a Newport xenon lamp with a filter which approximates an AM1.5 solar spectrum. The illumination has an intensity, measured by a calibrated silicon diode, of about 100 mW/cm$^2$.

## 3. Results and discussion

Fig. 2 shows the $J$–$V$ (illuminated current–voltage) characteristics of typical graphene and buckypaper on aSi:H solar cells. The open-circuit voltage ($V_{oc}$) is encouragingly high in both cells, 390 mV for the buckypaper cell and 150 mV for the graphene cell, and no degradation is seen in the buckypaper cells when they are stored in air at room temperature for several weeks. The high $V_{oc}$ is an indication that the band alignment between undoped aSi:H and carbon nanostructures is appropriate for solar cell applications. In our testing apparatus, the buckypaper or graphene acts as a hole transporter, while the aSi:H acts as an electron transport layer. Because MWCNTs and graphene both act as metals, we can analyze the system as a Schottky barrier, as shown in Fig. 3. We have attempted to approximately characterize the Fermi level of the graphene by constructing cells using devices built on crystalline silicon wafers with the same geometry as in Fig. 1. The open-circuit voltage in a graphene–nSi device is 350 mV, while $V_{oc}$ for a graphene–pSi device is −20 mV. Based on the Fermi level and band gap of crystalline silicon, we can estimate that the graphene Fermi level lies between 4 and 4.5 eV, which confirms that it is an appropriate electron donor for a Schottky junction with aSi:H.

The illuminated current–voltage curves generally have fill factors smaller than 0.2. Fill factors this low are rarely seen in photovoltaics literature, and could indicate interesting interface physics. At this point, we do not fully understand the reason for the low fill factors, but we hypothesize that low-energy trap states

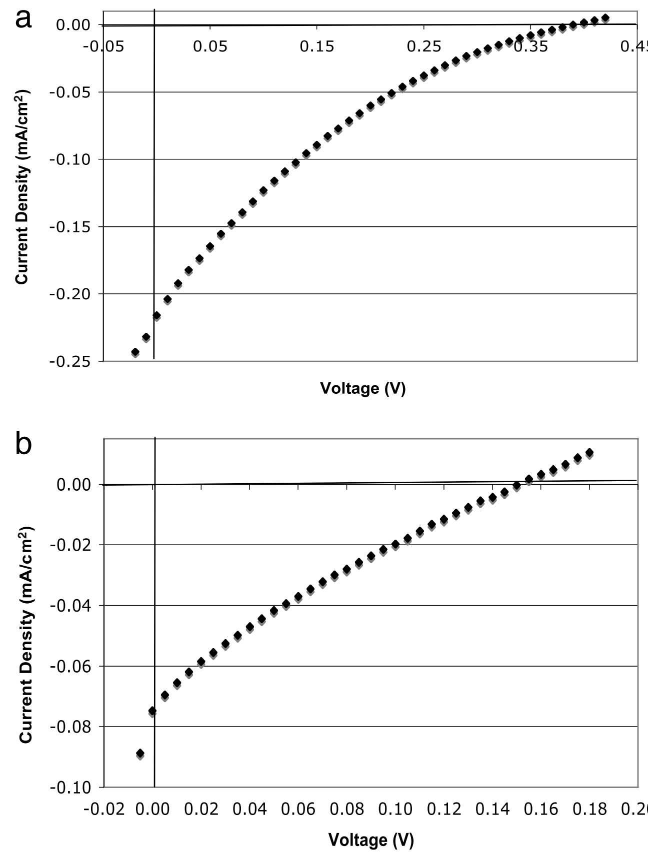


**Fig. 2.** Illuminated current–voltage curves for both buckypaper (a) and graphene (b) on aSi:H cells.

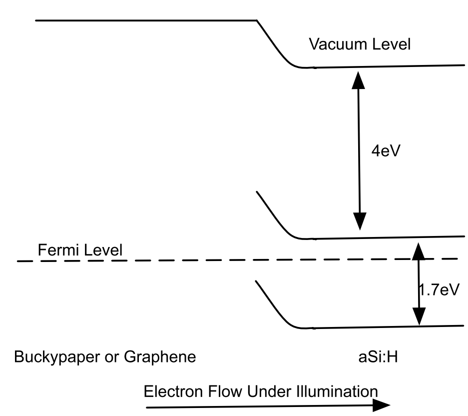


**Fig. 3.** Approximate band diagram for a Schottky barrier aSi:H–carbon nanostructure solar cell.

at the interface may be drastically reducing the currents at voltages close to $V_{oc}$.

The performance of the cells can be improved markedly by increasing the current density. We have tested the conductivities of the buckypaper and graphene films alone using simple two-probe measurements. The resistivities are on the order of hundreds of Ω/□ for graphene and kΩ/□ for buckypaper. These layers do not add series resistances higher than kΩ to the cell, and cannot explain the low currents. The low current and fill factor may be a result of geometrical issues associated with the buckypaper and graphene deposition methods. The carbon films are picked up out of a water bath by the substrate. It is impossible to ensure that they are flat on a microscopic scale, and the quality of the electrical contact between the films and the silicon is unknown. Simple changes in geometry such as varying the window size and oxide

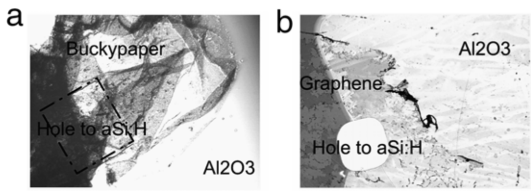


**Fig. 4.** Optical micrographs of devices: a is buckypaper and b is graphene. The side length of the square window is 500 μm.

layer thickness did not have a significant effect on the efficiency of the cells, but a better understanding of the interface geometry could lead to substantial improvements.

The transmittance of the films is high. In the 400–1000 nm wavelength range, graphene grown with this method has a transmittance above 97% [11], and our buckypaper has transmittance between 60% and 85%. Optical micrographs of both devices are shown in Fig. 4, which give a sense of how much light is able to penetrate the films. The transmittance measurement was done on very flat buckypaper, but it is difficult to deposit films on our cells that are flat and free of folds, meaning that much of the cell area is covered by several layers of buckypaper. This reduces the light transmittance through the top contact. No light management strategies have been attempted, and the cells could be improved substantially by improving light management.

## 4. Conclusions

We have produced air-stable solar cells with active layers made entirely from carbon, silicon, and hydrogen that do not require expensive transparent top conducting layers. This is an important step in the quest to directly convert sunlight into usable energy. Geometrical and interface characteristics currently limit the capability of these cells to supply large currents, but high open-circuit voltages indicate that the basic cell design has promise, and that it may be a simple, practical structure for solar cells in the future.

This basic structure has the distinct advantages of avoiding toxic, expensive dopants, and relying on earth-abundant materials. Different geometries could improve light management and absorption, or improve the quality of the electrical contact between the silicon and carbon. In an improved geometry, this amorphous silicon–nanostructured carbon interface could be the basis for highly efficient solar cells made with an inexpensive, scalable production process.

The performance is similar for two different types of carbon nanostructure, graphene and buckypaper, and the basic structure could be adapted to other carbon nanostructures, as well as other thin film semiconductors.

## Acknowledgements

This work was supported in part by the Director, Office of Energy Research, Materials Sciences and Engineering Division, of the US Department of Energy under contract No. DE-AC02-05CH11231 through the sp2-bonded Materials Program, which provided for growth of the graphene films and development of the transfer method, by the National Science Foundation through the Center of Integrated Nanomechanical Systems under Grant No. EEC-0425914, which provided for aSi deposition, and by the Office of Naval Research, which provided for photovoltaic cell design and characterization. M.S. acknowledges support through a National Defense Science and Engineering Graduate Fellowship, and W.R. acknowledges support through a National Science Foundation Graduate Research Fellowship.

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