Photo-sensing and photo-conversion investigation of single walled carbon nanotube-silicon interface: role of acid stimulation

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Abstract
Single walled carbon nanotubes (SWCNTs) are emerging as potential candidate in solar applications because of their remarkable structural, electrical and optical properties. In this work, we have reported simple and effective approach for the fabrication of SWCNTs/Si interface which play important role in photo-sensing and photo conversation applications. It is observed that, controlled acid treatment of SWCNTs at room temperature conditions proved helpful for the removal of amorphous carbon and significantly enhanced their photo-sensing response from 4% to 40%, respectively. In addition, it is found that open circuit voltage and current density of SWCNT/Si interface is become increased due to the presence of functional groups. However, Raman analysis also confirms, that acid stimulation significantly affect their crystalline structure. These results are important and compatible with the existing silicon technology without adopting any complex technique.

Introduction
Nowadays, carbon materials are emerging as prominent candidate for the research due to their outstanding physical, electrical and chemical properties [1–4]. Among various carbon materials, carbon nanotubes (CNTs), graphene and carbon nanoparticle, CNTs shows remarkable optical properties viz. tuneable and broadband light absorption which is required in photoconductive applications. Although, the photo-sensing response of nanotubes has produced huge debate with the various studies leading to different interpretations about the cause of photoconductivity [5]. Chen et al [6], have investigated the photo-detecting properties of SWCNTs for the fabrication of prototype infrared (IR) camera. It is well reported and investigated that, nanotubes based photo-detector demonstrates excellent IR detection properties with simple fabrication cost and extraordinary performance [6–7].

However, the addition of few amounts of nanotubes in organic photovoltaic cell (OPC) effectively enhanced the efficiency of cell because of their fast charge transport mobility, good optical absorption near to IR band gaps [8]. The well optimized incorporation of nanotubes especially SWCNTs in polymer/oxides matrix significantly increase the efficiency and stability of OPC [9–12]. In addition, the efficiency of CNT/Si interface based solar cells can be controlled easily using acid stimulated CNTs. The chemical functionalization of the nanotubes with acids e.g. nitric (HNO3) and sulfuric (H2SO4) is very effective for making Si/CNTs interface based solar cells [13–14]. However, the efficiency of Si/CNTs solar cell can be effectively improved by controlled etching of silicon oxide (SiO2) using hydrofluoric acid (HF). The etching time corresponding to the thickness of SiO2 is an important role in the formation of Si/SWCNTs interface. Without the removal of the oxide, device parameters such as Jsc, FF significantly degraded and inconsistent with SWCNTs/Si interface [9].

Although, the understanding of Si/CNTs interface physical behavior is not fully explored/discovered by the researchers. Generally, when a p-type nanotubes is positioned in contact with n-type etched silicon substrate, the energy band bending take place and p-type nanotubes ultimately bends down approach the Fermi level. On the other hand, n-type Si bends move away from the Fermi level [12–14]. It is also expected that a thin insulating layer exists due to native oxide in between Si and CNTs that affect the efficiency and properties of Si/CNTs...
The effect of acid stimulations on the structure of carbon nanotube has been investigated by Raman spectra. The Result and discussions here as sample 1. The nitric acid Pristine SWCNTs were purchased from Global Nanotech, India with more than 95% purity level and labeled Acid stimulation of CNTs Experimental method

Acid stimulation of CNTs

Pristine SWCNTs were purchased from Global Nanotech, India with more than 95% purity level and labeled. The main aim of present work is to report simple steps for the fabrication of SWCNT/Si interface for the study of photo sensitivity and power conversion efficiency properties under illumination of AM1.5 (100 mW cm\(^{-2}\)). It is found that, acid stimulation of SWCNT significantly affect the porous nanotube network and form numerous heterojunctions that improved the SWCNTs/Si interface properties by decreasing interior electrical resistance and support charge carrier separation and their transport. Although, the step by step study of acid treated SWCNTs/Si interface for photocurrent and photo-sensing applications are not commonly investigated in the literature with our best knowledge. The study indicate that SWCNTs/Si interface shows prospective application in optoelectronic devices.

Fabrication of Si/CNTs interface

To fabricate SWCNTs/Si interface, n-type Si wafer was used as substrate. An insulating layer of silicon dioxide (SiO\(_2\)) of 350 nm thickness was deposited on Si wafer. For the metal contact, the desired area of back side of Si substrate was chemically etched with hydrofluoric acid (HF) using Teflon beaker and twizzer. Afterwards, the aluminum (Al) metal was deposited on etched area using thermal evaporator technique. For the fabrication of SWCNTs/Si interface, a shadow mask of desired area was designed and then placed on top of SiO\(_2\) layer. Similarly, various windows were created by selective chemical etching of SiO\(_2\) and then each window makes one active device area. Finally, the well dispersed nanotubes were deposited on active window by using drop-casting method. For making top contact on the fabricated SWCNTs/Si interface, silver (Ag) metal of 150 nm thickness was deposited using thermal evaporator technique. The choice of metal contacts in the fabricated device is based on their work function value relative to the electron affinity of SWCNT/Si interface. The detail of adopted process is shown in figure 1(a). The schematic of electrical measurement setup for fabricated device is shown in figure 1(b). For testing the device, the top contact (Ag) of the CNT film (on oxide) and bottom of Si (Al) were wired such as positive and negative electrodes to finish the entire fabrication process. The I-V and I-T measurement were recorded finally in PC utilizing a program developed in Labview with GPIB control.

Characterizations

The structural studies of all samples were evaluated by recording Raman spectra using Horiba, Lab RAM HR spectrometer coupled with Ar \(^+\) ion laser of wavelength 514.5 nm. To perform the photo-sensing and PV testing, the devices were irradiated under solar simulator at AM1.5 (~100 mW cm\(^{-2}\)), and data were recorded using a Keithley 2400 source meter.

Result and discussions

The effect of acid stimulations on the structure of carbon nanotube has been investigated by Raman spectra. The Raman spectra of as-procured SWCNTs (sample 1) and chemically functionalized SWCNTs (sample 2 and 3) are shown in figure 2(a). The spectra consist of three standard characteristic bands, namely the D band at around 1352 cm\(^{-1}\), G band at 1592 cm\(^{-1}\) and 2D band at 2698 cm\(^{-1}\), respectively. It is also observed that D + G band appeared after the acid stimulation of the nanotubes which confirms that the intrinsic structure of procured nanotubes is retained after functionalization and they become less entangled giving an increased intensity of Raman signal. It is further observed that after functionalization, the D band intensity in sample 2 and 3 is considerably improved, which is mainly due to side wall sp\(^2\)-sp\(^3\) hybridization [15–16] [15–16]. It is well known that, the D to G band intensity ratio (I\(_D\)/I\(_G\)) is related to degree of disorder and is inversely proportional to the
crystalline nature of the nanotubes [15–16]. As shown in table 1, $I_{D}/I_{G}$ ratio for pristine nanotubes is 0.9, which confirms the presence of sp$^2$ hybridization. Furthermore, $I_{D}/I_{G}$ ratio for acid stimulated nanotubes is found to enhance to 1.17 (sample 2) and 1.11 (sample 1) as compared to sample 1 that confirms the attachment of functional groups on the side walls as well as on the ends of tubes. The presence of these groups on the CNTs is mainly considered as defects in their tubular structure [17–18]. It can also be interpreted as: the creation of
defect sites is responsible for the weakening of sp² hybridization and a comparatively strengthened sp³-bonded carbon [17].

In addition, the chemical functionalization of nanotubes resulting to the intercalation of acid molecules inside their lattice that experienced a pressure and hence stress is exerted on them. The experienced pressure is main cause or the up-shifting of wavenumbers of G bands as shown in figure 2(b) [19–2019–20]. However, this stress is responsible for a change in nanotube inter-atomic distance that responsible for shortening of C–C bonds. Another cause of stress could be due to charge transfer between acid molecules and nanotubes and hence holes doping occur in nanotubes [20–2120–21].

The crystallite size ($L_a$) of nanotubes before and after acid stimulation was calculated using following formula [15–1615–16]:

$$L_a = \frac{560}{E^2} \left( \frac{I_D}{I_G} \right)^{-1}$$

Table 1 shows that crystallite size of pristine nanotubes (sample 1) is higher as compared to acid stimulated tubes (sample 2 and 3). In addition, the defect density ($[(1/L_a)^2]$) indicates that acid stimulated nanotubes contains lower defect density in same trends as crystallite size found to decreases in table 1.

Interestingly, the full width at half-maximum (FWHM) of the G and 2D band of sample 2 and 3 increases significantly on interaction of acid molecules with nanotubes, as can be seen from Table 1. Moreover, a second-order band called G′ and D + G band also appeared in sample 2 and 3. The intensity of G′ band indicates the electrical conditions of the nanotubes. As shown in figure 2(a), the intensity of G′ band in sample 3 is enhanced as compared to sample 2 which clearly confirms higher charge doping in sample 3. In additions, the attachment of functional groups leads to increment in the number of bands close to the Femi level which further facilitate the charge transfer between the carbon atoms [22–2322–23].

Figures 3(a), (b) shows the typical J-V characteristics of SWCNT/Si interface in dark and light under 100 mW cm⁻². It is observed that, the different parameters such as open circuit voltage ($V_{oc}$), Short circuit current ($I_{sc}$), current density (J) and fill factor (FF) of proposed three samples has found to be increased. It means functional groups play important role in the SWCNT/Si interface. It is well known that, acid stimulated nanotubes usually behave as p-type semiconductors and also increased the surface to volume ratio [14–1514–15]. Also, when nanotubes fully expanded on a planar Si substrate, there will be numerous p-n junctions formed due to close contact between SWCNTs and underlying Si wafer. Furthermore, it is found that the sample 3 has highest $V_{oc}$, $J$ and $L_{sc}$ value as compared to all investigated samples. It is because of large surface to volume ratio which affect the mobility of nanotubes and hence promote in exciton dissociation and charge carrier transport phenomena [14, 24].

In order to investigate the photo-sensing behavior of the SWCNTs/Si interface, a bias is applied across the two terminals and corresponding current measured under light illumination and dark as a function of time. Figures 4(a), (b), shows the photo-sensing response of 1% by wt. acid stimulated nanotubes-silicon interface at room temperature. At a fixed bias voltage, the current flowing through the SWCNT/Si instantaneously increased on light illumination, stable after a few seconds and then quickly recovered to its initial current value when the light was switch off. As shown in figures 4(a), (b), these photo response transients, the samples 2 and 3 respond reversibly to light over a number of gas ON and OFF cycles indicating the repeatability of the photo sensor response. A photo response of 28% and 40% has been observed for samples 2 and sample 3, respectively. It is observed that acid infiltration of SWCNTs proved helpful for the removal of impurities such as amorphous carbon/disorder and improved photo response at room temperature. The functionalized SWCNTs/Si based interface exhibit high photosensitivity i.e. 40% as compared to pristine CNTs/Si interface (5%) at room temperature with 1 V. This significant improvement could be due to the photocurrent generation ability of SWCNT/Si interface and the effective charge separation at the functional groups, which is considered as defect in the nanotubes as well as the large number of SWCNT/Si heterojunctions [14]. In addition, the defects in the

| Sample name | D Band Position (cm⁻¹) | D Band FWHM (cm⁻¹) | G Band Position (cm⁻¹) | G Band FWHM (cm⁻¹) | 2D Band Position (cm⁻¹) | 2D Band FWHM (cm⁻¹) | $I_D/I_G$ | $L_a$ |
|--------------|------------------------|---------------------|------------------------|---------------------|------------------------|---------------------|----------|--------|
| Sample 1     | 1390                   | 85                  | 1556                   | 45                  | —                      | —                   | —        | 0.9    | 18.4  |
| Sample 2     | 1346                   | 57                  | 1589                   | 86                  | 2687                   | 88                  | 1.11     | 15.1  |
| Sample 3     | 1346                   | 66                  | 1592                   | 93                  | 2691                   | 93                  | 1.17     | 14.2  |

Table 1. Raman Analysis of three different samples.
Acid stimulated nanotubes work as a localized potential barrier for the separation of photogenerated carriers \[14\].

The calculated response time of pristine SWCNT/Si was 30 ms which is quite large as compared to functionalized SWCNT/Si (10 ms) photosensor. Figure 4(d) shows the comparison in photo response of three different samples under same conditions. The proposed SWCNTs/Si interface does not require any complex and time consuming techniques and is completely friendly with existing silicon technology.

Conclusions

In brief, we observed the role of functional groups in SWCNTs/Si interface for the application of photo-sensor/solar cell response. Here, we reported simple and economic approach for the fabrication of SWCNTs/Si interface which can be applicable to existing solar technology to design on large area. It is observed that, acid stimulation reduces significantly the interior electrical resistance and facilitates additional charge transport.
paths in the porous carbon material, resulting in considerably enhanced photo conversion efficiency and photo-sensing response. The fabricated SWCNTs/Si interface is widely useful in photo-sensor and solar cell applications.

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References

[1] Wang Y 1992 Photoconductivity of fullerene-doped polymers Nature 356 585–7
[2] Baughman R H et al 1999 Carbon nanotube actuators Science 284 1340–4
[3] Zhang G L, Zhou R L and Zeng X C 2013 Carbon nanotube and boron nitride nanotube hosted C-60-V nanopeapods J. Mater. Chem. C 1 4518–26
[4] Nair R R et al 2008 Fine structure constant defines visual transparency of graphene Science 320 1308–1308
[5] Ponomarenko L A et al 2008 Chaotic Dirac billiard in graphene quantum dots Science 320 356–8
[6] Chen H Z et al 2013 Infrared camera using a single nano-photodetector IEEE Sensors 13 949–58
[7] Tkix M E, Borondics F, Yu A P and Haddon R C 2006 Bolometric infrared photoresponse of suspended single-walled carbon nanotubes films Science 312 413–6
[8] Hu C et al 2016 Photoresponse properties based on CdS nanoparticles deposited on multi-walled carbon nanotubes RSC Adv. 6 78033–8
[9] Jung Y, Li X, Rajan N K, Taylor A D and Reed M A 2013 Record high efficiency single-walled carbon nanotube/silicon p-n junction solar cells Nano Lett. 13 95–9
[10] Li J, Hu L, Wang L, Zhou Y, Grütner G and Marks T J 2006 Organic light-emitting diodes having carbon nanotube anodes Nano Lett. 6 2472–7
[11] Lee W, Lee J, Yi W and Han S H 2010 Electric-field enhancement of photovoltaic devices: a third reason for the increase in the efficiency of photovoltaic devices by carbon nanotubes Adv. Mater. 22 2264–7
[12] Ponzoni S et al 2017 Hybridized C–O–Si interface states at the origin of efficiency improvement in CNT/Si solar cells ACS Appl. Mater. Interfaces 9 16627–34
[13] Jia Y et al 2011 Achieving high efficiency silicon–carbon nanotube heterojunction solar cells by acid doping Nano Lett. 11 1901–5
[14] Dhall S, Sood K and Nathawat R 2017 Room temperature hydrogen gas sensors of functionalized carbon nanotubes based hybrid nanostructure: role of Pt sputtered nanoparticles Int. J. Hydrogen Energy 42 8392–8
[15] Dhall S, Jaggi N and Nathawat R 2013 Functionalized multiwalled carbon nanotubes based hydrogen gas sensor Sens. Actuators A 201 221–27.
[16] Dhall S and Jaggi N 2015 Structural studies of functionalized single-walled carbon nano-horns Fullerenes, Nanotubes and Carbon Nanostructures 23 942–6
[17] Tessonnier J P et al 2009 Analysis of the structure and chemical properties of some commercial carbon nanostructures Carbon 47 1779–98
[18] Dresselhaus M S, Dresselhaus G, Saito R and Jorio A 2005 Raman spectroscopy of carbon nanotubes Rev. Phys. Rep. 409 47–50.
[19] Murphy H, Papakonstaninou P and Okpalugo T I 2006 Raman study of multiwalled carbon nanotubes functionalized with oxygen groups J. Vac. Sci. Technol. B 24 715–20
[20] Bastwros M, Kim G Y, Zhu C, Zhang K S, Tang X and Wang X 2014 Effect of ball milling on graphene reinforced Al6061 composite fabricated by semi-solid sintering Compos. B 60 111–8
[21] Graupner R, Abraham J, Vencelova A, Seyller T, Hennrich F, Kappes M M, Hirsch A and Ley I 2003 Doping of single-walled carbon nanotube bundles by Brønsted acids Phys. Chem. Chem. Phys. 5 5472–6
[22] Lau C H, Cervini R, Clarke S R, Markovic M G, Matsons J G, Hawyns S C, Huynh S P and Simon G P 2008 The effect to functionalization on structure and electrical conductivity of multi-wall carbon nanotube J. Nanopart. Res. 10 777–89.
[23] Li Z, Zheng L, Saini V, Bourdo S, Dervishi E and Biris A S, 2013 Solar cells with graphene and carbon nanotubes on silicon J. Exp. Nanosci. 8 565–72