Force- and light-controlled electrical transport characteristics of carbon nanotube 1D/2D bulk junctions

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ARTICLE INFO

Article history:
Received 15 July 2009
In final form 28 September 2009
Available online 1 October 2009

ABSTRACT

Pure carbon bulk junctions are fabricated based on carbon nanotube (CNT) macrostructures and their electrical transport characteristics are investigated. The planar 1D/2D strand-on-film (SOF) junctions show interesting force- and light-controlled transport behaviors. Considering the excellent chemical stability and good mechanical properties (strength, hardness and elasticity) of CNTs, the SOF junctions could find practical and wide applications in electromechanical and optoelectronic devices.

1. Introduction

Bulk junctions made of low dimensional materials are of great importance in the development of high efficiency solar cells and related optoelectronic devices. To establish a rational connection between the microscopic characteristics of nanomaterials with their macroscopic performance, research is now underway for searching new photoactive materials and novel fabrication techniques. One emphasis of current concerns is to eliminate the intervention of conventional semiconductors (e.g. silicon). To this end, it is imperative to find a new kind of materials to provide efficient photon excitation or light energy conversion. In the search for alternative materials, carbon is highly attractive because it is expected to have more diversified properties comparing with silicon and would be highly stable [1,2]. For example, diamond like amorphous carbon (a-C) has been used partially as alternative material of silicon in photovoltaic devices thanks to the feasibility of controlling their conduction type. a-C/Si [3–7] and a-C/GaAs [8] heterojunction photovoltaic cells have been realized through standard deposition and doping techniques and show promising power conversion efficiencies of up to 8%. Carbon nanotube (CNT) based devices showed many interesting characteristics useful for solar cells production such as high mobility, fairly high minority carrier diffusion length, high absorption coefficient and direct energy gaps. CNT thin films have been directly configured as energy conversion materials to replace p-type silicon to create heterojunctions with n-type silicon [9–12]. Initial tests have shown a conversion efficiency of 5–7% at AM1.5. CNTs can also form a rectifying heterojunction with n-GaAs [13] with an efficiency of up to 3.8% under the illumination of a green laser or desk lamp. These results show the possibility to produce CNT-based photoelectric devices with appreciable performance while reducing the use of, or eliminating entirely, the traditional semiconductor layer. Recently, considerable attention has also turned to lightweight, flexible thin film photoelectric devices with reducing cost or increasing efficiency. The first step toward this direction is to realize bulk junctions made of sole carbon as the basic building block of all-carbon devices.

Among the intense studies on CNT-based Schottky junctions, p–n junctions or heterojunctions, crossed CNT (CC) junctions are of particular importance due to their special interface (Fig. 1A) of small contact area and force-controlled intertube conductance [14,15]. Previous studies have addressed certain aspects of the structure, electronic and photoelectric properties of model and real systems involving CC contacts. Potential applications of CC junctions include non-volatile memory [16], electromechanical devices [17,18] and field effect transistors [19–21]. A more recent work considered a geometry in which the relative stability, structure, and conductance of CC junctions are explored [22]. Spatially resolved potential distribution in CC junction devices has also been systematically studied using scanning photocurrent microscopy [23]. In these studies, however, only individual CNTs have been investigated. As mentioned above, to develop and get a comprehensive understanding of all carbon macroscale devices, a more comprehensive study on bulk CNT-based junctions is of particular necessity.

Here we give the first demonstration of the pure carbon bulk junctions based on CNT macrostructures and present the fabrication and characterizations of Schottky devices operated at room temperature. One-dimensional (1D) strands and two-dimensional (2D) films of single-walled CNTs (SWNTs) are chosen as both the metallic and semiconducting components (Fig. 1B). The planar...
1D/2D strand-on-film (SOF) junction shows interesting force- and light-controlled transport responses. Considering the excellent chemical stability and good mechanical properties (strength, hardness and elasticity) of CNTs, the SOF junctions could find practical and wide applications in electromechanical and optoelectronic devices. This work aims to tackle the issues mentioned above from both basic research and engineering application perspectives. Junctions made of sole carbon will help us to explore more complex systems in the future.

2. Experimental

SWNT films were prepared by a floating chemical vapor deposition technique with a liquid-free precursor: a solid volatile mixture of ferrocene and sulfur (atomic ratio Fe:S = 10:1) [24]. As prepared SWNT film was subjected to a post purification which employed a combination of oxidations (heat in air at 450 °C for 1 h or immerse in 30% H2O2 solution for 72 h) and rinsing with hydrochloric acid (37% HCl). Smooth and homogenous SWNT thin films were obtained by a post treatment combining the purification, sidewall functionalization mentioned above with water/ethanol competition. When ethanol is dropped into the water, ethanol molecules spread quickly onto the water surface forming a Langmuir monolayer. The formation of SWNT thin film (20–100 nm thick) occurs following the dispersion of the ethanol layer along the water surface and could be easily collected and formed a conformal coating on a target substrate. SWNT strands were obtained by a simple film-to-fiber conversion technique. A strand was drawn out from the SWNT film under stretching to improve the alignment of the nanotube bundles. The SOF junction was then formed as illustrated in Fig. 1C. Copper foils were used as electrodes and silver paste was introduced to ensure the Ohm contact between CNTs and the electrodes. SWNT strands and films used for SOF junctions are approximately 1 cm long and wide.

The samples were characterized by scanning electron microscopy (SEM, Hitachi S3600 N). Electrical transport was characterized by using a Keithley 2602 SourceMeter. The current was measured from zero bias to 4 V, then applied voltage was successively decreased to zero. Similar procedure was followed in the reverse bias region. The measurements were repeated till stable values were reached.
3. Results and discussion

Fig. 1D shows a top view of a typical SOF junction fabricated on a glass slide based on the schematic diagram illustrated in Fig. 1C. The underlying CNT thin film presents the web-like networking of interlinked bundles composed of self-assembled SWNTs (Fig. 1E and F). The strands are generally 20–100 μm thick, consisting of axially aligned SWNT bundles (Fig. 1G and H). SWNT strands and films have similar chirality distributions as they are obtained from the same batch of purified sample.

As shown in Fig. 2A, a typical I–V curve for a SOF junction reveals an asymmetric transport behavior. It is known that bulk CNT samples consist of a mixture of metallic and semiconducting nanotubes with random chirality distribution. Therefore, from the aspect of statistics, the metallic and semiconducting tubes (slightly p-doped) in both strand and films can interact with each other and form four types of intertube junctions (both crossed and parallel) at the SOF interface: SM, MS, SS and MM, where S denotes the semiconducting phase, M denotes the metallic phase and the first Letter represents the phase in the strand, i.e., SM represents the junction between the semiconducting tubes in the strand and the metallic tubes in the film. For individual CNTs, the semiconducting nanotube is depleted at the SM or MS junction by the metallic nanotube, forming a rectifying Schottky barrier [14,15]; while the MM and SS junctions are good tunnel contacts, showing linear transport. Hence, the SOF bulk junction shown in Fig. 2A can be further divided into three parts: an Ohm contact at the junction (MM + SS), the intra-strand and intra-film resistance (R) and an anti-parallel junction pair containing two Schottky junctions with opposite polarities (SM + MS).

The non-linear I–V characteristic of the SOF junction can be expressed by the thermoionic emission model.
where $A$ is the contact area, $A'$ is the effective Richardson constant, $T$ is absolute temperature, $e$ is electronic charge, $\phi_b$ is the barrier height, $k$ is the Boltzman constant, $n$ is the ideality factor. $I_s$ is the reversed saturated current which is negligible. The slope of the linear part of the curve gives the values of ideality factors.

The curve fitting was carried out by first subtracting the linear part obtained near zero bias then fitting with Eq. (1). The corresponding linear and dual rectified transporting $I–V$ curves are shown in Fig. 2B and C. At low bias, the conductance of MM/SS junctions is far beyond that for SM/MS junctions (see Fig. 2D, an enlarged view of Fig. 2B(C)). At high bias (>2 V), a relatively larger current is measured for SM/MS junctions. This might arise from the increasing reverse leakage current or/and the early occurrence of the breakdown of the Schottky junction which is also confirmed by the presence of two breakdown points at high bias shown in Fig. 2A. The SOF Schottky junctions have ideality factors of 25–35, which are still far from that for the ideal diodes due to the weak p-doping of semiconducting SWNTs. Fig. 2E shows the representative signs for these junctions and corresponding energy band diagrams by which the phenomena shown in Fig. 2B and C can be qualitatively explained. In the SM or MS junction, the non-linearity of the $I–V$ curve can be ascribed to the Schottky barrier ($\phi_b$) located on the semiconducting side. In the MM and SS junctions, the linear charge transport results from a finite density of states at the Fermi surface on both sides of the junction.

It is further confirmed that the contact force between the strand and the film has a significant influence on the electrical transport behavior of the SOF junction from the force-controlled conductance measurements. We applied a compressive force up to 50 mN to the strand, and recorded the transport characteristics of the SOF junction. A non-linear-to-linear transition is clearly identified from the $I–V$ curve development as the applied compressive force is increasing (Fig. 3A). When the applied force is less than 5 mN, the $I–V$ curves show a typical non-linear dual Schottky rectification feature (Fig. 3B and region I of C), similar to that shown in Fig. 2. This has been explained by the presence of a finite intertube potential barrier that impedes ballistic electron transport between tubes. As theoretically predicted, for individual CNTs, the most stable junction geometry has the smallest conductance which increases rapidly as force is applied [22]. However, this condition is hardly to be met in our case due to the random distribution of nanotube chirality and homogeneous arrangement of the tube bundles within the underlying film. As the applied force is further increased, the CNTs deform significantly at the junction. The charge density in the contact region becomes sizeable as the CNTs become closer and more deformed, resulting in a significant overlap of intertube wave function. This yields an increasing conductance (region II of Fig. 3C) and a non-linear-to-linear transition. As the applied force is up to 20 mN, the conductance reaches its saturated state (region III of Fig. 3C) and the corresponding $I–V$ curves show a completely linear Ohm contact behavior. It has been theoretically confirmed that for crossed intertube junctions the C–C bonds interlinking the tubes can form with increased contact forces [22]. Therefore, the potential barrier disappears under higher applied forces. When the external force is released, the $I–V$ curve is recovered accordingly with minor hysteresis, suggesting that the radial deformations of tubes and bundles have been recovered after the external force has been removed. This result differs from the theoretical prediction that the interlinking bonds survive even after the contact forces are released and whole structure is fully relaxed [17,18]. The force-controlled reversible transporting characteristics indicate the possibility and importance of the SOF junctions in electromechanical device applications.

The photo-response of the SOF junction is further investigated. Instead of mapping the photocurrent distribution, the whole junction is evaluated under the illumination of spectrum and power density comparable with AM1.5. As shown in Fig. 4, the SOF junction operated at 10 mN shows a distinct photodependent non-linear effect. The transport characteristics (both conductance and $I–V$ curve shape) are reversible and can be well tuned by varying the intensities of the incident light. For example, under the illumination of the 50 mW/cm$^2$ light, the $I–V$ curve unambiguously shows the light modulated non-linearity of the SOF junction.
The decreased conductance at higher incident intensities can be partially attributed to the heating effect which increases the intra-strand and intra-film resistance. While the physical mechanism of the variation and photodependence of the transport characteristics of the SOF junction upon illumination remains to be investigated, this light-controlled performance of the anti-parallel Schottky junctions does suggest the application of the SOF junction as a light sensor or a light-controlled rectifier. With our new experimental observation, the devices can be constructed much more easily in a pure carbon manner in macroscale. The level of performance could be adjusted by choosing the CNT strands with appropriate dimensions or by varying the contact length between strand and film.

4. Conclusions

To conclude, we report for the first time the bulk junctions based on CNTs. It has been revealed that the SOF interface give rise to an anti-parallel pair of Schottky junctions. The force- and light-controlled behaviors provide deep insights of future application of pure carbon devices in electromechanical and light-controlled devices. Future focus is to develop optimal design of CNT-based heterojunctions, including band gaps modulation, control of band structure, rectification behavior and interface buffer layer. The emphasis will be on the SOF junction performance on flexible substrates and its possible use as photovoltaic cells upon functionalization and cooperation with other photoactive materials. It is expected that after complete development, pure carbon devices may become more economical than silicon-based devices, and the cost would be extremely low and unlike silicon, it is highly chemically and environmentally stable.

Acknowledgements

This work is supported by National Science Foundation of China (#50972067), Program for New Century Excellent Talents in University (#NCET-08-0322) and the Scientific Research Foundation for the Returned Overseas Chinese Scholars (#20091020304), State Education Ministry of China.

Appendix A. Supplementary material


References