© Applied Science Innovations Pvt. Ltd., India Carbon – Sci. Tech. 2 (2009) 98 - 102

# Carbon – Science and Technology

ISSN 0974 – 0546

http://www.applied-science-innovations.com

LETTER

Received : 01/03/2009, Accepted : 15/04/2009

---

# Is Vacuum annealing converts p-type single wall carbon nanotube field effect transistor (in air) to n-type (in vacuum) is universally true (?)

**Prakash R. Somani (*), A. Kobayashi, Y. Ohno, S. Kishimoto, T. Mizutani**

*Department of Quantum Engineering, Nagoya University, Furo-Cho, Chikusa-Ku, Nagoya 464-8603, Japan.*

***Our study on nickel silicide and gold contacted single-wall-carbon-nanotube field effect transistors (SWCN-FETs) is in sharp contrast to earlier published reports of type conversion in SWCN-FETs (from p- to n-) when cycled between air and vacuum, and indicates that (1) band gap of SWCN (2) the extent to which Fermi level of the metal contact gets shifted due to adsorption/desorption of oxygen and (3) relative position of the Fermi level of the metal contact with respect to the top of the valance band of SWCN (in an oxygen-free environment) are some of the important factors that governs such phenomena.***

---

Schottky barrier field effect transistors (FET) employing single walled carbon nanotubes (SWCN) as one dimensional (1D) channel for transport of carriers have attracted lot of interest. This is due to the fact that carbon nanotubes possess high electron mobility (For example, 36,000 $cm^2$/Vs for 1.5 nm thick carbon nanotubes) and velocity, a high current driving capability and an energy band structure with direct transition [1-3]. In general, it is observed that SWCN contacted (contact means source and drain contact) with a high work function metal (like Au, Pd etc.) results in p-type FET whereas a low work function metal contact (like Ca) yields a n-type FET [1-7]. Type of the SWCN FET is also observed to depend on many other factors like unintentional oxygen doping effect in carbon nanotube, change in the Fermi level of contact metal due to oxygen, microstructure of the contact metal, charges in and at the interface of the gate insulator layer, presence of foreign organic molecules at the CN – electrode interface etc. [1, 2, 8, 9]. In the back gate configuration, high work function metal contacted SWCN-FET is observed to show p-type character when measured in ambient air atmosphere (SWCN – in the as synthesized / deposited from). It is observed that such p-type electronic character of SWCN-FET is not the intrinsic property of the SWCN. By simply putting such SWCN-FET in vacuum (generally added with vacuum annealing), the electrical character of the SWCN-FET can be changed from p-type to n-type, including any state in between (i.e. ambipolar state) [1, 2, 10 - 12]. It is interesting to note here that different metals such as Au [11], Ag [10], and Mo [12] were used as source and drain contact metals for fabricating such FETs and SWCNs with relatively small band gap of about 0.6 eV were used [11]. In our previous study, we also observed that a low work function metal like samarium contacted SWCN-FET changes from n-type (in vacuum) to ambipolar (in air) when exposed to air and regains its original performance (both drain current and n-type) when transferred back to vacuum and annealed [7]. Low work function metals like calcium (Ca), samarium (Sm) etc. are known to be more sensitive towards oxygen as compared to high work function metals like Au or Pd. Large number of published reports on type conversion of SWCN FET (from p-type to ambipolar / n-type) when cycled between air and vacuum (generally added with annealing), coins a fundamental question of great importance : ***Is every SWCN-FET (let us talk about p-type FETs made by contacting with high work function metals) will display such type-conversion when cycled between air and vacuum ?***. Our recent studies on nickel silicide contacted SWCN-FETs and earlier work done in our laboratory on gold contacted SWCN- FETs [13], bring out some important facts in this area. We observed that SWCN-FETs fabricated with nickel silicide (source and drain) contacts show significantly stable performance in air and vacuum (even after annealing). No 'type conversion' (i.e. change from p-type to ambipolar or n-type) is observed for such devices. All twenty devices studied show p-type electronic character even when vacuum annealed or in air atmosphere. Similar observation was previously made on gold (Au) contacted SWCN-FETs, in our laboratory. Our results are in sharp contrast to earlier published results by many groups and brings out the importance of (1) band gap of the SWCN and (2) the extent to which the Fermi level of the metal contact gets shifted due to adsorption / desorption of oxygen relative to the positioning of the top of the valance band and bottom of the conduction band of the SWCN.

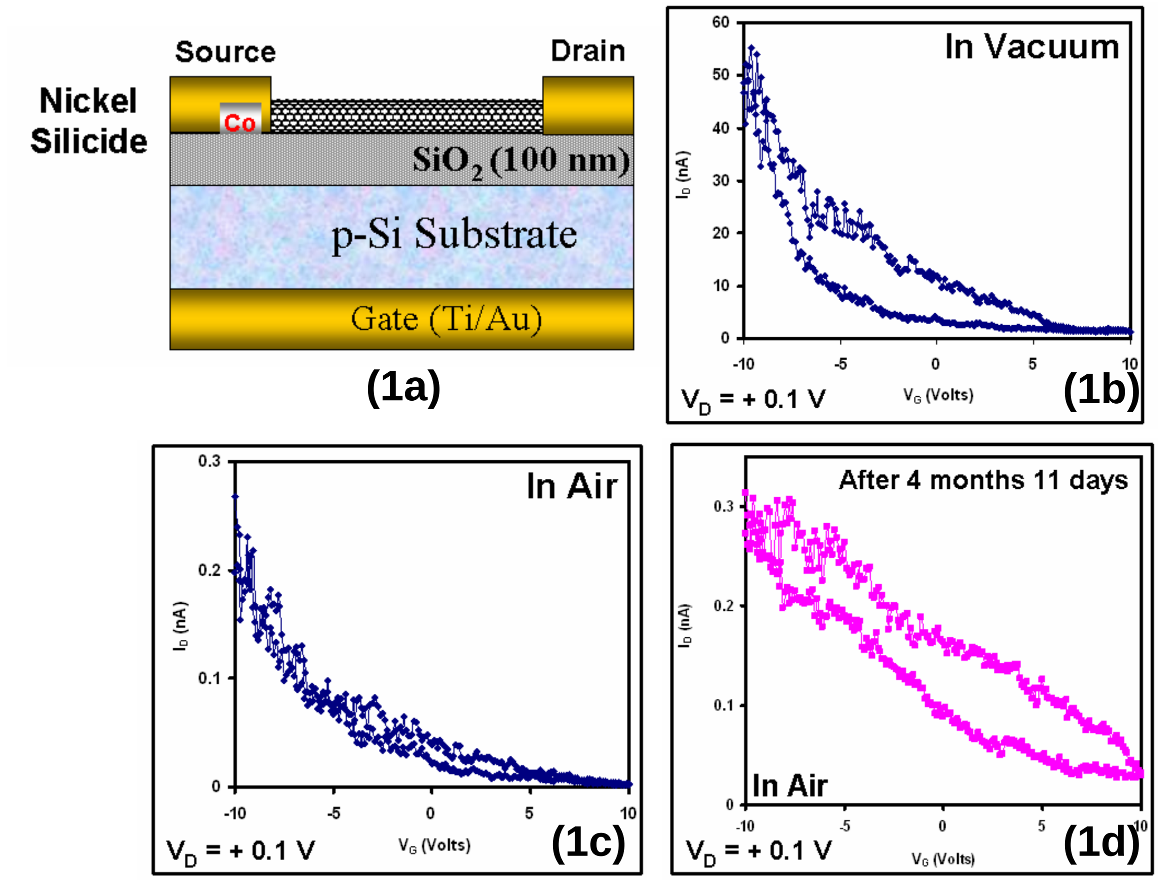


Figure (1) : (a) Schematic of the back gate SWCN FET with nickel silicide as source and drain electrodes, (b) $I_D$-$V_G$ characteristic of the SWCN FET in Vacuum after annealing - showing p-type FET, (c) $I_D$-$V_G$ characteristic of the SWCN FET measured just after breaking vacuum (i.e. in ambient air atmosphere). (d) $I_D$-$V_G$ characteristic of the SWCN FET measured in air after 4 months and 11 days.

We also demonstrate that stable devices that retain their type even after vacuum annealing can easily be fabricated by carefully selecting (a) SWCNs with appropriate diameter and hence band gap and / or (b) metal contact.

Figure (1a) shows a schematic device structure of the fabricated SWCN-FET in the back gate configuration with nickel silicide as source and drain contacts. A heavily doped $p^+$-Si wafer with thermally oxidized $SiO_2$ (100 nm) layer was used as the substrate. SWCN was grown directly on the Si substrate by position controlled growth technique [3]. The Co (2 nm) catalyst layer was patterned on the substrate using photolithography, electron beam evaporation and lift-off processes. SWCN was grown using thermal chemical vapor deposition. A mixture of ethanol and argon (100 sccm) was used as a source gas for SWCN synthesis. The total pressure in the furnace was 350 Torr. The growth temperature and time were 800 $^oC$ and 30 min., respectively. Band gap of the SWCNs was between 0.85 eV to 0.95 eV estimated from the photoluminescence measurements [13]. The Au (300 nm)/Ti (100 nm) for the back gate electrode was deposited on the back side of the substrate. Nickel and silicon thin films were deposited on top of another which subsequently yields nickel silicide film after suitable heat treatments in inert gas atmosphere (silicidation process) for the source and drain contacts. Two step annealing process (300 $^oC$ for 30 min. followed by 500 to 650 $^oC$ for 2 – 4 min.) in inert Ar gas atmosphere is used to convert the nickel and silicon bilayer thin films to nickel silicide film [14]. The channel length for the representative reported device was 2 um. SWCN was in the as-synthesized form (i.e. without any intentional doping). Devices were exposed to ambient air atmosphere for few days for oxygen soaking. Electrical measurements were made in a vacuum chamber connected with turbo molecular pump (TMP). Devices were kept under vacuum for 24 hours. Subsequent to this, the devices were vacuum annealed at about 120 $^oC$ for 1 hour and measured for its electrical characteristic. Figure (1b) shows the drain-current ($I_D$) as a function of the gate-source voltage ($V_{GS}$) for the SWCN FET with nickel silicide as source and drain contacts in vacuum (after annealing). Here, the drain-source voltage ($V_{DS}$) was 0.1 V. The $I_D$ increases with negative gate bias ($V_{GS}$) and hence p-type transfer characteristic was obtained. It is observed that even after second or third vacuum annealing step (120 $^oC$ for 30 min in Vacuum), the device shows p-type transfer characteristic. Twenty devices were studied at a time for their performance.

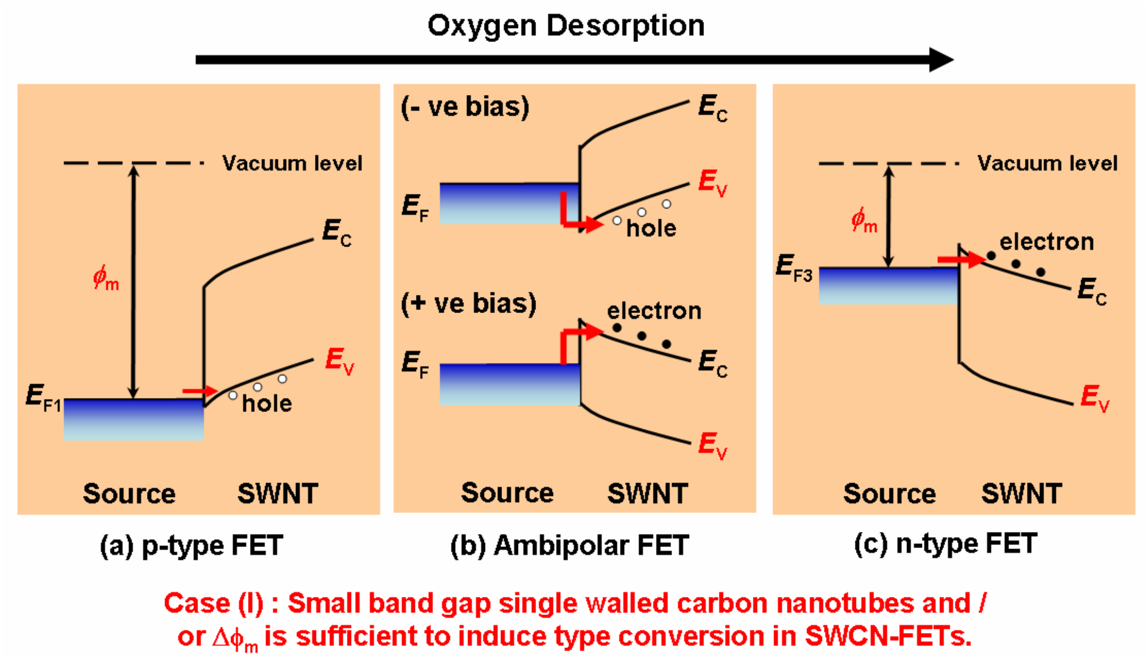


**Figure (2a)**

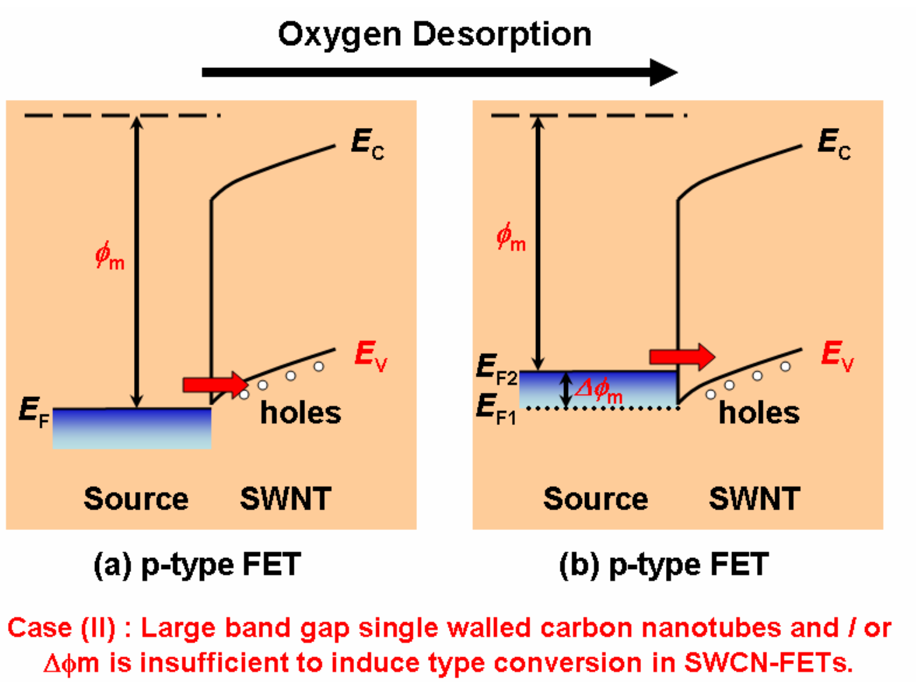


**Figure (2b)**

Figure (2) : (a) Schematic of the source metal and SWCN contact energy level diagram with partial and complete oxygen desorption. Here, $\Delta E_F$ is sufficient to induce SWCN-FET type conversion and band gap of the SWCN is relatively small. (b) Schematic of the source metal and SWCN contact energy level diagram with oxygen desorption. Here, $\Delta E_F$ is insufficient to induce SWCN-FET type conversion and band gap of the SWCN is relatively large.

All the devices show similar p-type behavior even after multiple vacuum annealing steps. Not a single ambipolar or n-type transfer characteristic was observed for such devices in vacuum, after or before annealing.

Figure (1c) shows the variation of the drain-current ($I_D$) as a function of the gate-source voltage ($V_{GS}$) for the same SWCN FET of which the transfer characteristic studied in vacuum is presented in Figure (1b). The drain-source voltage ($V_{DS}$) was 0.1 V. This measurement was made just after breaking the vacuum and exposing the device (s) to ambient air atmosphere. Comparing the transfer characteristics observed in vacuum (Figure 1b) and in air (Figure 1c); it can be seen that $I_D$ decreases by about two orders of magnitude by exposing the device to air atmosphere. However, the type of the device is conserved. All the devices studied are observed to show p-type characteristic even in air atmosphere, with decrease in $I_D$ by one to two orders of magnitude. Figure (1d) presents the transfer characteristic of the same SWCN FET in ambient air atmosphere after 4 months and 11 days. The drain-source voltage ($V_{DS}$) was 0.1 V. The device was stored in ambient air atmosphere for studying the ageing effect on the device characteristic. It is observable that $I_D$ does not change drastically. Hysteresis has increased which might be due to adsorption of humidity from the surrounding atmosphere. In case of other devices studied, similar observation was performed.

Present study indicates that nickel silicide (source and drain) contacted SWCN-FETs display p-type characteristic in ambient air atmosphere or in vacuum (even after annealing). No type conversion (i.e. change from p-type to ambipolar or n-type) is observed for any devices studied.

We believe that type conversion and otherwise in case of SWCN-FETs depends on four factors (1) oxygen induced doping effect in carbon nanotubes (2) the extent / amount of the shift in the Fermi level ($E_F$) of the contact metal due to oxygen attack (3) relative position of the Fermi level of the contact metal with respect to the top of the valance band of the SWCN – in an oxygen free environment and (4) band gap of the carbon nanotube itself. If oxygen induced doping effect is playing a dominant role then one could expect that the SWCN-FETs will show type conversion when cycled between air and vacuum. This is preliminary due to the fact that doping effect will be present in air and absent in vacuum.

In case of SWCNs with relatively small band gaps contacted with metals which do show significant change in its Fermi level ($\Delta E_F$) and hence work function ($\Delta\phi_m$) under oxygen influence – will show type conversion (i.e. type change from p-type in air to ambipolar or n-type in vacuum) when cycled between air and vacuum. Earlier studies reported support this fact **[11]**. This can be understood with a schematic of the energy level diagram of the SWCN and the contact meal as depicted in Figure (2a), in which partial oxygen removal shifts the Fermi level of the contact metal up in energy scale enabling injection of both electrons and holes leading to ambipolar FETs; whereas complete removal of oxygen shifts the Fermi level of the contact metal near to the bottom of the conduction band edge (Ec) of SWCN leading to n-type FETs. In such devices, amount of change in the Fermi level of the contact metal ($\Delta E_F$) is sufficient to induce a type conversion in SWCN-FETs when cycled between air and vacuum. Small band gap of the SWCN will play a positive role for type conversion.

However, the situation can be quite different in case of SWCNs with relatively large band gaps and / or contacted with metals which are quite immune to oxygen attack (i.e. metals of which Fermi level does not change to a large extent even under oxygen attack). Energy level diagram corresponding to this case is schematically shown in Figure (2B). In such a case, $\Delta E_F$ will be insufficient to induce a type conversion in SWCN-FETs. Large band gap of the SWCN and small value of $\Delta E_F$ will help to retain the type of the device even when oxygen is completely removed from the device. It should be noted here that the relative position of the Fermi level of the contact metal with respect to the top of the valance band of the SWCN – in an oxygen free environment – will also play an important role in such devices.

In the present case of SWCN-FETs with nickel silicide as source and drain contacts, we feel that both the factors (i.e. relative immunity of contacts towards oxygen attack as well as relatively large band gap of the SWCN) is playing a crucial role in retaining the type of the devices same in air and in vacuum.

In conclusion, every SWCN-FET (Schottky barrier type) made by contacting with high work function metals may not change its type when cycled between air and vacuum. Band gap of the SWCN, the extent / amount of the shift in the Fermi level ($E_F$) of the contact metal due to oxygen attack and relative position of the Fermi level of the contact metal with respect to the top of the valance band of the SWCN – in an oxygen free environment (all) will play an important role in such processes. Stable devices that retain their type even after vacuum annealing could easily be fabricated by carefully selecting SWCNs with appropriate diameter and hence band gap, and / or metal contact.

**Acknowledgement :**

This work was partially supported by the Grant-in-Aid for Scientific Research on Priority Area of MEXT – Japan.

**References :**

[1] Ph. Avouris, Acc. Chem. Res. 35 (2002) 1026.
[2] V. Derycke, R. Martel, J. Appenzeller and Ph. Avouris, Nano Letters 1/9 (2001) 453.
[3] T. Mizutani, Y. Ohno and P. R. Somani "Carbon Nanotube Field Effect Transistors", in "Carbon Nanotubes : Multifunctional Materials" Ed. P. R. Somani and M. Umeno, Applied Science Innovations Pvt. Ltd., January 2009, pp 87-119.
[4] Y. Nosho, Y. Ohno, S. Kishimoto, T. Mizutani, Nanotechnology 17 (2006) 3412.
[5] T. Mizutani and Y. Ohno, Proc. SPIE Int. Soc. Opt. Eng. 5732 (2005) 28.
[6] Y. Nosho, Y. Ohno, S. Kishimoto, T. Mizutani, Appl. Phys. Lett. 86 (2005) 073105.
[7] P. R. Somani, A. Kobayashi, Y. Ohno, S. Kishimoto, T. Mizutani, "N-type single walled carbon nanotube field effect transistors with samarium as contact electrodes", talk presented at Japan Society of Applied Physics

(JSAP) 69th Autumn Meeting 2008, Chubu University, Japan (2-5 September 2008).
[8] D. Phokharatkul, Y. Ohno, H. Nakano, S. Kishimoto, T. Mizutani, Appl. Phys. Lett. 93 (2008) 053112.
[9] B. K. Kim, J. J. Kim, H. M. So, K. J. Kong, H. Chang, J. O. Lee, N. Park, Appl. Phys. Lett. 89 (2006) 243115.
[10] T. Kamimura, K. Matsumoto, Jpn. J. Appl. Phys. 44/4A (2005) 1603.
[11] V. Derycke, R. Martel, J. Appenzeller and Ph. Avouris, Appl. Phys. Lett. 80/15 (2002) 2773.
[12] A. Javey, Q. Wang, A. Ural, Y. Li, H. Dai, Nano Letters 2/9 (2002) 929.
[13] N. Moriyama, Y. Ohno, T. Mizutani, Private Communication.
[14] R. T. P. Lee, L. T. Yang, T. Y. Liow, K. M. Tan, A. E. J. Lim, K. W. Ang, D. M. Y. Lai, K. M. Hoe, G. Q. Lo, G. S. Samudra, D. Z. Chi, Y. C. Yeo, IEEE Electron Device Lett. 29/1 (2008) 89.