Fabrication of stable pn junction single-walled carbon nanotube thin films by position selective Cs plasma irradiation method

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Abstract. Stable n-type thin film transistors (TFTs) are fabricated with Cs encapsulated single-walled carbon nanotubes (Cs@SWNTs). The transport property of SWNTs-TFTs clearly changes from p- to n-type characteristic after the Cs plasma irradiation. Based on the systematic investigations, it is revealed that there is an optimum ion energy for the effective Cs encapsulation, which is around 50 eV. Furthermore, it is also found that the n-type feature is stable even in water and high temperature (< 400 ºC) conditions. The pn junction structure is also realized by position selective doping of Cs. This very stable pn junction TFT is important for the practical application of SWNTs-based thin film electronics.

1. Introduction
Thin film transistors (TFTs) are one of the most promising practical applications of single-walled carbon nanotubes (SWNTs) due to their flexible filament-like structure and high carrier mobility [1]. For the fabrication of the industrial electrical devices, it is an inevitable issue to utilize both p- and n-type transistors as basic components of the electrical circuits. Since oxygen and water molecules adsorbing on the surface of SWNTs are known to play a role as an electron acceptor against SWNTs, SWNTs-TFTs show the p-type semiconducting features. Up to now, there are several reports for the fabrication of n-type SWNTs-TFTs by functionalizing the outside surface of SWNTs [2-5]. However, the operation of n-type SWNTs-TFTs is limited only under the specific condition and the fabrication of stable n-type SWNTs-TFTs under the various environmental conditions has not been realized. Here we report the successful fabrication of very stable n-type SWNTs-TFTs by encapsulating Cs atoms in SWNTs with a plasma ion irradiation method [6-10]. Through the systematical investigations, we found that there is a suitable energy range of Cs ions to be encapsulated. This finding is important to realize the high yield encapsulation of Cs atoms inside SWNTs. Since the graphitic network of carbon cells protects the inside Cs atoms from other reactive molecules existing outside of SWNTs, the n-type features are found to be very stable under the various environmental conditions such as air, water, and high temperatures.

2. Experiments
The Cs atom encapsulation is carried out by a plasma ion irradiation method, as shown in figure 1. Cs+ plasmas are generated by a thermal contact ionization method [6-10]. The typical plasma parameters are as follows: electron density \( n_e \approx 10^9 \text{ cm}^{-3} \), electron temperature \( T_e \approx 0.2 \text{ eV} \), and space potential...
Figure 1. Schematic of experimental apparatus.

Figure 2. Typical $I_d$-$V_g$ curves of (a) before (pristine SWNTs-TFTs) and (b) after (Cs@SWNTs-TFTs) Cs plasma irradiation. (c) $I_{on}/I_{off}$ current ratio as a function of $E_{i}$. 
SWNTs are deposited on a SiO₂ (300 nm)/Si substrate. To promote the adsorption of SWNTs, the SiO₂ substrate surface is functionalized by 3-aminopropyltriethoxysilane (APTES) prior to the SWNTs deposition. The pairs of 40-nm-thick Au electrodes are fabricated as source-drain electrodes by a conventional photolithography technique. The length and width between source and drain are 50 μm and 100 μm, respectively. SWNTs-TFTs are put on a SUS plate, which is inserted into the plasma region. The energy of ions is controlled by applying dc bias voltages to the SUS plate. After the Cs irradiation, Cs irradiated SWNTs-TFTs are rinsed by purified water to remove the Cs atoms adsorbing on the outside of SWNTs. The transport properties of SWNTs-TFTs are measured by a vacuum probe station and semiconductor parameter analyzer.

3. Results and discussion

Figure 2 (a) and (b) show typical source-drain current (I₊) vs. gate bias voltage (V₉s) curves of the same device before and after the Cs plasma irradiation, respectively. The source-drain voltage (V_ds) is fixed at 1 V. The threshold voltage of V₉s (V₉sth) clearly shifts to the negative V₉s direction after the Cs plasma irradiation. Furthermore, the currents in the positive V₉s region obviously increase after the Cs plasma irradiation. This indicates the transport property of SWNTs-TFTs drastically change from the p-type to n-type semiconducting features after the Cs plasma irradiation. Hysteresis was often observed in I₊-V₉s curves even before (figure 2(a)) and after (figure 2(b)) the Cs irradiation, which may relate with the water molecule adsorbed along the interlayer between SWNTs and substrate. Suppression of hysteresis is important for the practical application of SWNTs-TFTs. Further progress is required to solve this problem. The mobility of pristine and Cs@SWNTs-TFT is 0.87 and 0.06 cm²V⁻¹s⁻¹, respectively.
In order to identify the optimum irradiation energy of Cs ions, the Cs ion irradiation is carried out under the various energy conditions. It should be noted that the energy of ions ($E_i$) is estimated from the potential difference between the space potential $\phi_s$ in plasmas and the substrate bias voltage $V_{sub}$.

The plasma parameters are measured by a Langmuir probe. The saturated source-drain current ($I_{ds}$) at p (negative $V_{gs}$) and n (positive $V_{gs}$) region in $-40 \leq V_{gs} \leq 40$ range is defined as $I_{onp}$ and $I_{onn}$ respectively. The saturated source-drain current ($I_{ds}$) ratio of n- to p-channel ($I_{on}/I_{onp}$) is utilized as a guidepost to estimate the conducting type of SWNTs-TFTs (figure 2(c)). We defined the device as n-type characteristic when $I_{on}/I_{onp}$ is higher than $I_{onp}$ and $V_{gs}$ shift to negative $V_{gs}$ direction compared with that of pristine device. Since pristine SWNTs thin film is intrinsic semiconductor, it is natural that p-type conduction is appeared even in Cs@SWNTs thin film transistor. Because the space potential in plasmas is -3 V, only electrons are irradiated to SWNTs-TFTs under the condition of $V_{sub} = 0$ V. In this case, the averaged $I_{on}/I_{onp}$ is $\approx 0.2$, which indicates SWNTs-TFTs work as the p-type semiconducting devices. With an increase in the ion energy, the clear transition from p- to n-type features is observed around $E_i = 20$ eV. The n-type transitions of SWNTs-TFTs are found up to $E_i = 60$ eV. Interestingly, the conducting type of SWNTs-TFTs does not change when the irradiation energy is over 80 eV. In order to identify the meaning of this threshold energy of Cs ion irradiation, the Raman measurement is carried out for the Cs irradiated SWNTs. We use the intensity ratio of G-band to Si-band (520 cm$^{-1}$) ($I_G/I_S$) as a sign of the amount of SWNTs. It is to be noted that the $I_G/I_{S}$ is almost the same for each sample before the Cs irradiation. Since $I_G/I_S$ drastically decreases under the condition of $E_i > 80$ eV, SWNTs should be damaged in this high irradiation-energy range. Based on these results, it is found that there is an optimum irradiation energy range of Cs encapsulation, which is around $E_i = 50$ eV and the conducting type of SWNTs-TFTs does not change in the case of high energy ($E_i > 80$ eV) Cs ion irradiation due to the ion bombardment effects.

To confirm the stability of Cs encapsulated SWNTs (Cs@SWNTs), Cs@SWNTs-TFTs are soaked in the purified water for certain periods. Figure 3 shows soaking time dependence of $I_{ds}$-$V_{gs}$ curve of Cs@SWNTs with exactly same device. The decreasing of $I_{ds}$ and slight $V_{gs}$ shift to positive direction are observed between 0h (figure 3(a)) and 4h soaking (figure 3(b)), which should be caused by washing out of Cs atoms from SWNTs outside surface. Noticeably, the $I_{ds}$-$V_{gs}$ does not show an obvious change after 8h (figure 3(c)) and the n-type feature is still maintained even after 12h soaking (figure 3(d)). This indicates that the origin of the transition from p- to n-type property should be caused by the encapsulated Cs atoms inside SWNTs, which is very stable even in the water. The stability of further longer scale such as week or month is under investigations. We also measure the stability of Cs@SWNTs-TFTs under the other conditions. The clear n-type feature is still observed in the air and after the high temperature ($< 400 ^\circ$C) annealing. This very stable n-type TFTs is important for the fabrication of SWNTs-based high performance thin-film electronic devices.

The pn junction structure is also fabricated by position selective doping of Cs. Prior to the Cs irradiation, the half of SWNTs channels is covered by polymer to prevent Cs ions doping. The basic device structure is same with pristine SWNTs-TFTs and Cs@SWNTs-TFTs. Figure 4 shows a typical $I_{ds}$-$V_{gs}$ curve of Cs@SWNTs/pristine SWNTs junction TFT. The clear rectifying characteristic can be obtained, which indicates the pn junction structure is formed by our position selective doping method.

4. Conclusion

We have succeeded in the fabrication of very stable n-type SWNTs-TFTs with Cs@SWNTs. It is found that the transport property of SWNT-TFTs clearly changes from p- to n-type after the Cs plasma irradiation. Furthermore, the n-type property is very stable under the long time soak in water, air exposure, and after the high temperature annealing. The pn junction structure is also realized by position selective doping of Cs. This stable pn junction SWNTs-TFTs is very important for the industrial fabrication of high performance electrical circuits with SWNTs-TFTs.

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