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A novel method to convert metallic-type CNTs to semiconducting-type CNT-FETs

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1. Introduction

Depending on the chirality,[1)] single-walled carbon nanotubes (SWNTs) can be metallic or semiconducting. However, irrespective of synthesis methods, the production of SWNTs always yields a mixture of both types,[2)] with the metallic type being prevalent. Since only semiconducting SWNTs depict the field effect,[3)] semiconducting SWNTs are mandatory for CNT-FETs as well as many sensors.

In this study, we report for the first time a novel plasma treatment to convert metallic carbon nanotubes to semiconducting CNT-FETs by altering the effective chirality of the SWNTs through Ar plasma treatment.

2. Experimental methods

The fabricated SWNT device is shown in Fig. 1. Briefly, a 600nm SiO_2 field oxide layer was first grown on the 4-inch Si wafer. Then, a 150nm Ti layer was deposited by RF sputter, patterned and etched to serve as the bottom-gate metal. Subsequently, a 200nm PE-CVD nitride was deposited as gate dielectric layer. Then, a properly-prepared SWNT/DMF solution was spun on the wafer. After photoresist coating, a negative S/D mask was applied, together with a second Ti layer, to perform the Ti lift off process, leaving the 2nd Ti film only on the S/D regions. Afterwards, a TCP/ICP metal etcher was chosen as the Ar plasma source to treat the SWNTs. An HP-4155A was applied to measure the I_d/V_g transfer curves of the SWNTs before and after each Ar plasma treatment.

3. Results and discussion

As summarized in Table I, we can conclude that both the RF power and the process time strongly affect the yield of working CNT-FETs. Based on these data, we finally settled for an even lower RF power of 20W/20W, and the process time was kept at 1 sec (Experiment V in Table I). From Figs. 2(a)-(d), we can observe the transition from metallic to p-type semiconducting CNT-FETs. The effect of plasma treatment is quite evident since the corresponding transfer curve (the inset of Fig. 2(b)) reveals almost 2 orders of ON/OFF ratio after the 1st Ar plasma treatment. After the 2nd plasma treatment, it can be seen that the ON/OFF ratio increases further to 3 orders (the inset of Fig. 2(c)).

It is worth noting that the as-grown semiconducting CNT-FETs retain their p-type FET characteristics after repetitive plasma treatments (as shown in Fig. 3(a)-(d)).

Figure 4 shows the results of 408 devices measured each time after the 20W/20W/1sec Ar plasma process repetitively. We can see that the number of metallic-type devices drops significantly and the number of devices with 1~2 order ON/OFF ratio increases dramatically, and the number of CNT-FETs with 1~3 order ON/OFF ratio is about 84% after the 1st Ar plasma treatment. These devices are rendered suitable to serve the role of sensors.

A plasma-induced-structure-modification model was proposed to explain the observed conversion. Based on the SWNT band structure, the SWNT will depict metallic behaviors when its symmetric structure is preserved during roll-up.[3)] When the SWNT symmetry is broken, the nanotube will instead depict semiconducting behaviors with small band-gap. This suggests that if we can alter the SWNT's symmetric structure during or after growth, high yields of semicnducting SWNTs are plausible. In the literature, SWNTs grown by PECVD method indeed yield a higher percentage of semconducting-type SWNTs.[4)] This trend is consistent with our finding. The proposed Ar plasma treatment breaks the symmetry of the SWNTs, thus converting the metallic SWNTs into semiconducting FETs. At the same time, the surface of as-deposited semiconducting SWNTs are also affected by Ar plasma, and the extra defects will reduce the SWNT's conductance. So the CNT-FET's conduction current becomes lower after the plasma treatment, as shown in Fig. 3(b)-(d).

4. Conclusion

In summary, semiconducting-type CNT-FETs are realized for the first time using a simple and inexpensive process. It appears to be feasible to use plasma to treat the whole wafer directly. In doing so, the metallic CNTs can be converted to semiconducting FETs without adversely impacting the as-grown semiconducting FET devices with high ON/OFF ratio, as our data show that these as-grown p-type FET devices can withstand the ion bombardment and retain their electrical characteristics.

Acknowledgments

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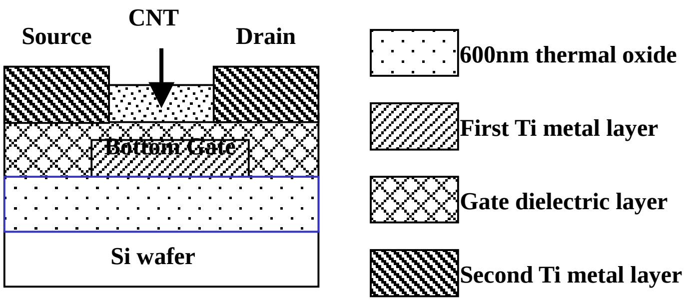

Fig. 1. Cross-sectional diagram of the device.

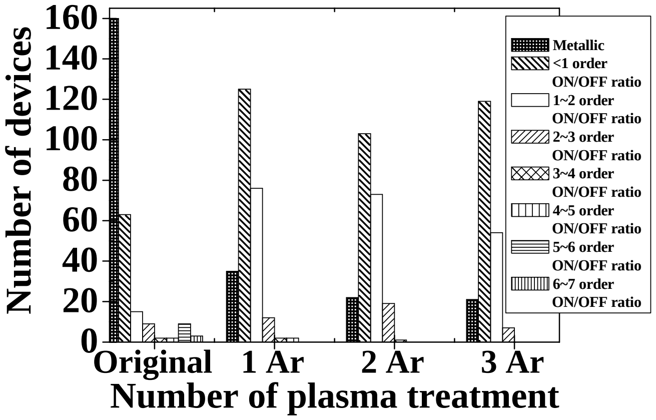

Fig. 4. Measured results of 408 devices after repetitive Ar plasma treatments. The number of metallic-type CNTs drops abruptly after plasma treatment, while devices with ON/OFF ratio less than 10 increase noticeably, and devices with 1~2 order ON/OFF ratio also increase dramatically from 15 to 76 devices.

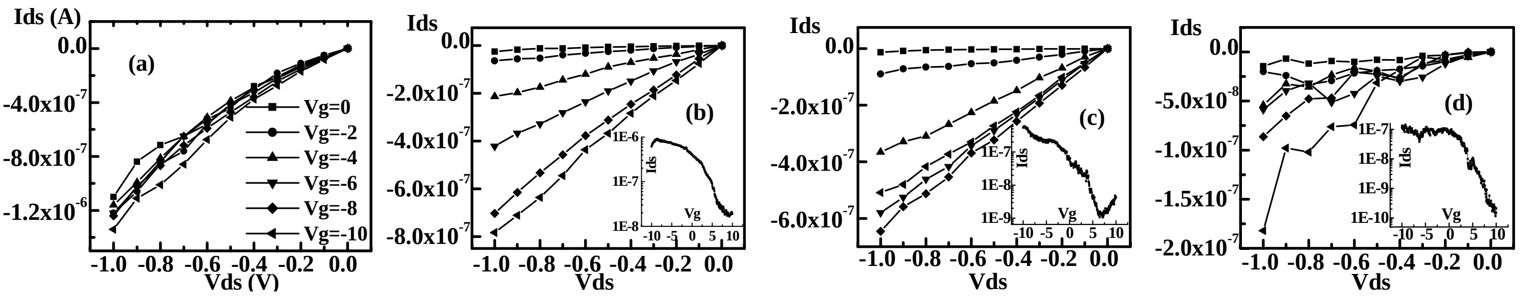

Fig. 2. Ids-Vds characteristics of (a) an as-grown metallic CNTs, (b) after the first Ar plasma treatment under 20W/20W/1sec condition, (c) after the 2nd Ar plasma treatment, and (d) After the 3rd Ar plasma treatment. Insets show the corresponding transfer characteristics.

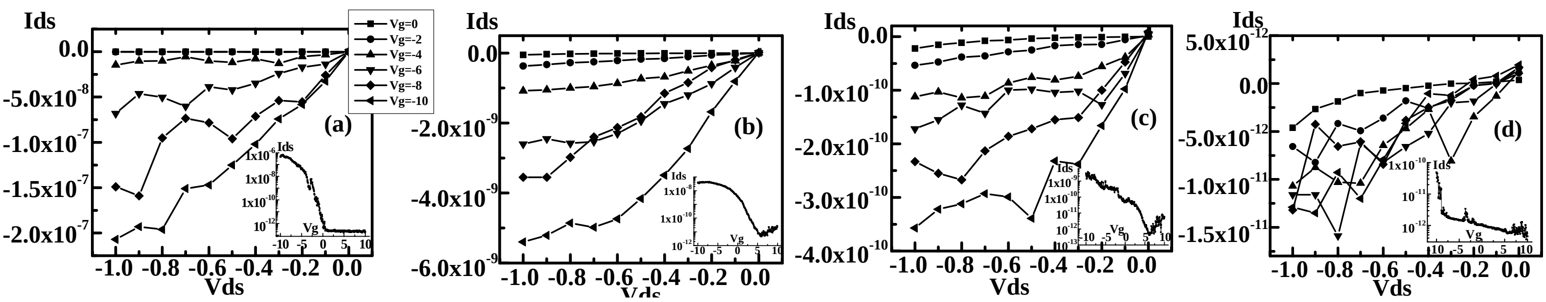

Fig. 3. Ids-Vds characteristics of (a) an as-grown p-type semiconducting CNT-FETs, (b) after the first Ar plasma treatment under 20W/20W/1sec condition. (c) after the 2nd Ar plasma treatment, and (d) After the 3rd Ar plasma treatment. Insets show the corresponding transfer characteristics. The as-grown p-type characteristics are preserved after plasma treatments.

TABLE I. Summary of experimental conditions and the percentage of metallic CNTs and semicinducting CNT-FETs

	RF power: Top/Bottom/ DC bias	Substrate / Chamber wall Temp.	Process Gas	Process Time	Before Plasma treatment		After plasma treatment		Electrical OPEN after Plasma
					M-type[a]	S-type[b]	M-type	S-type	
Experiment I	180W/160W /No record	60 °C/60 °C	Ar(80sccm)/ Cl_2/BCl_3	45 sec	65%	35%	0%	0%	100%
Experiment II	180W/160W /No record	60 °C/60 °C	Ar (80 sccm)	45 sec	60.6%	39.4%	0%	0%	100%
Experiment III	60W/55W /-107V	60 °C/60 °C	Ar (80 sccm)	30 sec	56.5%	43.5%	1st : 1.6% 2nd: 0.4%	1st : 0.4% 2nd: 0 %	1st : 98% 2nd : 99.6%
Experiment IV	60W/55W /-107V	60 °C/60 °C	Ar (80 sccm)	1 sec	73%	27%	1st : 3%	1st :18.2%	1st : 78.8%
Experiment V	20W/20W /-37V	60 °C/60 °C	Ar (80 sccm)	1sec	60.8%	39.2%	1st : 13% 2nd : 8% 3rd : 8%	1st : 83% 2nd: 75% 3rd : 68%	1st : 4% 2nd: 17% 3rd: 24%

[a]M-type stands for metallic-type CNT [b]S-type stands for semiconducting-type CNT-FET