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Air-stable $n$-type carbon nanotube field-effect transistors with $\text{Si}_3\text{N}_4$ passivation films fabricated by catalytic chemical vapor deposition

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Air-stable $n$-type carbon nanotube field-effect transistors (CNTFETs) were fabricated, with $\text{Si}_3\text{N}_4$ passivation films formed by catalytic chemical vapor deposition (Cat-CVD). Electrical measurements reveal that the $p$-type characteristics of CNTFETs are converted to $n$-type after fabricating $\text{Si}_3\text{N}_4$ passivation films at 270 °C. This indicates that adsorbed oxygen on the CNT sidewalls was removed during the formation process of the $\text{Si}_3\text{N}_4$ passivation films. In addition, the source-drain current of the $n$-type CNTFETs does not change over time under vacuum, or in air. Consequently, the $n$-type CNTFETs are completely protected by the $\text{Si}_3\text{N}_4$ passivation film from further effects of ambient gases. Therefore, Cat-CVD is one of the best candidates to fabricate $\text{Si}_3\text{N}_4$ passivation films on CNTFETs. © 2005 American Institute of Physics. [DOI: 10.1063/1.1886898]

Carbon nanotubes (CNTs) have attracted much attention, due to their unique mechanical, chemical, and electronic properties. They are quasi one-dimensional conductors with properties such as a high current carrying capability. CNTs may exhibit either semiconducting or metallic behavior, and this is dependent on the chirality of the CNT. Semiconducting CNTs can operate as the active element in field-effect transistors, in particular, for highly sensitive biosensors. CNTFETs built from as-grown tubes are normally found to be unipolar $p$-type, i.e., no electron current flows even at large positive gate biases. However, the capability to produce $n$-type transistors is technologically important, because it allows the fabrication of CNT-based accessory logic devices and circuits. Recent experiments have reported that the conversion from $p$- to $n$-type CNTFETs can be made by simply annealing the device in vacuum, or in an inert gas. Annealing in vacuum removes adsorbed oxygen, so that the $p$-type characteristics of the CNTFETs are converted to $n$-type. However, by exposing the $n$-type CNTFETs to air, the $n$-type CNTFETs return to $p$-type FETs. Therefore, in order to fabricate air-stable $n$-type CNTFETs, it is necessary to completely remove the adsorbed oxygen on the CNTs sidewalls, and then to protect the CNTFET device from further effects of ambient gases.

Plasma-enhanced chemical vapor deposition has been a widely used technique to obtain high quality passivation films. However, passivation films are fabricated by collision between energetic electrons and molecules of source gases, resulting in the introduction of defects to the CNTs by the plasma. In recent work on CNTFETs, Lu et al. used polymer electrolytes as the top gate, and succeeded in greatly improving the device performance and controlling the device behavior using concepts different to the above method. However, polymer materials may not be durable and thermally stable. Moreover, it may be difficult to precisely control the thickness of these materials.

In this letter, we have investigated the fabrication and electrical characteristics of CNTFETs where CNT channels are passivated with $\text{Si}_3\text{N}_4$ films by catalytic chemical vapor deposition (Cat-CVD). The Cat-CVD method is a technique, in which catalytic cracking reactions within a heated catalyzer placed near the substrate, decompose deposition gases so that the passivation film is deposited at the surface temperature of the substrate, below 300 °C, without the aid of plasma or photochemical excitation. Using this method, defects in the CNTs are expected to be rarely induced, because of the low temperature of the deposition. Therefore, the Cat-CVD method can be useful for forming passivation films on nanotube devices. In this study, the CNTFETs, with $\text{Si}_3\text{N}_4$ passivation films fabricated at 270 °C by this method, show air-stable $n$-type characteristics.

Figure 1 shows a schematic structure of the CNTFET with a $\text{Si}_3\text{N}_4$ passivation film. A $p$-type Si wafer with thermally oxidized SiO$_2$ (150 nm) was used as a substrate. First, a metal catalyst consisting of a double layer of Fe (2 nm) over Mo (10 nm) was patterned on the substrate using conventional photolithography and metal liftoff processes. Next, the CNTs were synthesized by thermal chemical vapor depo-
sition (CVD) at 900 °C for 10 min, using C2H4OH as a source gas. At the high temperature of 900 °C, thin Fe film forms nanoparticles, and the CNTs start to grow from the Fe particles, so that the position of the CNTs is controlled by the patterned Fe catalyst.12,13 Following this, Ti/Au electrodes were formed, both on the patterned catalysts and on the backside of the substrate. The gap distance for the source and drain was 5 μm. Finally, Si3N4 films (50 nm) were formed on the CNTFET devices by Cat-CVD. For the formation of Si3N4 passivation films, a mixture of SiH4 and NH3 was used as a source gas, with flow rates of 7.6 and 300 sccm for SiH4 and NH3, respectively. The surface temperature of the substrate was 270 °C, measured by a thermocouple when depositing Si3N4 films on the CNTFET devices. The refractive index of the films was estimated to be 1.994, indicating that the fabricated Si3N4 passivation film consists of an approximately stoichiometric composition of an ideal Si3N4 film. In this experiment, the drain current (ID) versus drain-source bias (VDS) and the drain current versus gate-source bias (VGS) characteristics of the CNTFETs at room temperature were measured using a semiconductor parameter analyzer.

Figures 2(a) and 2(b) show the liner ID–V DS characteristics in vacuum for the fabricated CNTFETs, without and with Si3N4 passivation films, using gate biases as parameters, respectively. For this measurement, V GS was changed from −5 to 5 V with a 1 V step. For the CNTFETs without Si3N4 passivation films, as shown in Fig. 2(a), the ID increases with increase in V GS toward the negative direction, indicating that the carriers in the channel are holes (p type). Good pinchoff characteristics with a threshold voltage of −2 V were obtained. On the other hand, for CNTFETs with Si3N4 passivation films, as shown in Fig. 2(b), the ID increases with increase in V GS toward the positive direction, indicating that the carriers in the channel are electrons (n type). These results reveal that p-type CNTFETs were converted to n-type FETs after application of Si3N4 passivation films fabricated by Cat-CVD.

As already mentioned, CNTFETs usually exhibit unipolar p-type characteristics, resulting from adsorbed oxygen on the CNT sidewalls. The effect of the adsorbed oxygen on the electrical properties of a nanotube device has previously been observed.8,14 First, adsorbed oxygen on the CNT sidewalls functions as holes in the CNT channels. Second, the presence of adsorbed oxygen at the metal–CNT interfaces has an effect on the height of the Schottky barriers. In this study, before the Si3N4 passivation films were deposited on CNTFETs, the sample was annealed at a temperature of 270 °C for several minutes in vacuum, resulting in the removal of adsorbed oxygen during the process of Si3N4 passivation films by Cat-CVD. After the adsorbed oxygen is removed, holes do not exist in the CNT channels, and/or, electrons can be easily injected into the CNT channels since the barrier height for holes becomes too high. Therefore, the carriers in the CNT channels are electrons (n type).

Figure 3 shows ID (linear and logarithmic scales) — V GS characteristics of CNTFETs with Si3N4 passivation films at V DS=1 V. This result reveals that good pinchoff characteristics with a threshold voltage of −2 V are obtained. Moreover, ID does not increase with increase in V GS toward the negative direction, as shown in Fig. 3 (logarithmic scale). This indicates that the carriers in the channel are not a combination of holes and electrons (an ambipolar conduction)3,8,15 but only electrons (n type), i.e., complete conversion to n-type conduction. In addition, the n-type CNTFETs, with Si3N4 passivation films fabricated at 270 °C by Cat-CVD, have current flow of 80 nA at V GS=5 V. This suggests that defects in the CNTs, after fabricating Si3N4 passivation films, are scarcely induced, because of the low temperature of deposition. These results indicate that the Cat-CVD method is useful for forming passivation films on CNT devices without inducing any defects. Consequently, n-type CNTFETs have been successfully fabricated by this method.

The effect of various environments on the characteristics of CNTFETs with Si3N4 passivation films was then investigated. ID–V GS curves were measured for the CNTFETs without Si3N4 passivation films in vacuum for 1 and 12 h, and also CNTFETs with Si3N4 passivation films in vacuum for 1 and 12 h, or in air. Figures 4(a) and 4(b) show ID–V GS characteristics of the fabricated CNTFETs without and with Si3N4 passivation films at V GS=1 V, respectively. For the CNTFETs without Si3N4 passivation films, the ID slowly decreases over time in vacuum (for 1 and 12 h), as shown in Fig. 4(a). This result reveals a decrease of 10% in ID

![Figure 2](image2.png)

![Figure 3](image3.png)
nels are passivated with Si$_3$N$_4$ films by Cat-CVD. After fabrication of CNTFETs have been investigated, where the CNT channels with Si$_3$N$_4$ passivation films formed by the Cat-CVD method have been successfully fabricated. -type CNTFETs with Si$_3$N$_4$ passivation films change in various environments. On the other hand, for CNTFETs with Si$_3$N$_4$ passivation films, passivation films are completely protected from further effects of ambient gases by Si$_3$N$_4$ passivation films. Fabrication of air-stable $n$-type CNTFETs with Si$_3$N$_4$ passivation films formed by Cat-CVD has been achieved. In addition, Si$_3$N$_4$ is thermally stable and has a higher dielectric constant than SiO$_2$. Furthermore, the thickness of the Si$_3$N$_4$ passivation films can be precisely controlled on a nanometer scale using the Cat-CVD method. Therefore, it will be possible to fabricate CNTFETs with top gate structures of Si$_3$N$_4$ passivation films in the near future. This suggests that CNT-based devices may realize complementary logic devices and circuits.

The authors are grateful to Toshikazu Niki of Ishikawa Seisakusho, Ltd. for helping with the fabrication of passivation films by Cat-CVD.

$V_{GS} = -5$ V, which is consistent with the characteristics of $p$-type CNTFETs, given in Ref. 16. In the report, water molecules, which are weakly adsorbed on CNT sidewalls, are removed by vacuum. This affects the characteristics of the CNTFETs, so that holes, which are the carriers in the channel, decrease. The electrical measurements in Fig. 4(a) indicate that the characteristics of the CNTFETs without Si$_3$N$_4$ passivation films change in various environments. On the other hand, for CNTFETs with Si$_3$N$_4$ passivation films, $I_D$ does not vary over time in vacuum (for 1 and 11 h) or in air, as shown in Fig. 4(b). The above results clearly indicate that the CNTFET devices are completely protected from further effect of ambient gases by Si$_3$N$_4$ passivation films. Air-stable $n$-type CNTFETs with Si$_3$N$_4$ passivation films formed by the Cat-CVD method have been successfully fabricated.

In summary, the fabrication and electrical characteristics of CNTFETs have been investigated, where the CNT channels are passivated with Si$_3$N$_4$ films by Cat-CVD. After fabricating Si$_3$N$_4$ passivation films at 270 °C, electrical measurements reveal that $p$-type characteristics of CNTFETs are converted to $n$-type FETs, resulting from removal of adsorbed oxygen on the CNT sidewalls during formation process of Si$_3$N$_4$ passivation films by Cat-CVD. Moreover, it is found that the $n$-type CNTFETs are completely protected from further effects of ambient gases by Si$_3$N$_4$ passivation films. Fabrication of air-stable $n$-type CNTFETs with Si$_3$N$_4$ passivation films formed by Cat-CVD has been achieved. In addition, Si$_3$N$_4$ is thermally stable and has a higher dielectric constant than SiO$_2$. Furthermore, the thickness of the Si$_3$N$_4$ passivation films can be precisely controlled on a nanometer scale using the Cat-CVD method. Therefore, it will be possible to fabricate CNTFETs with top gate structures of Si$_3$N$_4$ passivation films in the near future. This suggests that CNT-based devices may realize complementary logic devices and circuits.

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![Graph](https://example.com/graph.png)

**FIG. 4.** (Color online) (a) $I_D$–$V_{GS}$ characteristics of a $p$-type CNTFET without Si$_3$N$_4$ passivation films preserved in vacuum for 1 h (red triangles) and 12 h (blue circles), and (b) $I_D$–$V_{GS}$ characteristics of the $n$-type CNTFET with Si$_3$N$_4$ passivation films preserved in vacuum for 1 h (red triangles), 11 h (blue circles), and in air (black squares).

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