Fe/Ge Catalyzed Carbon Nanotube Growth on HfO_2 for Nano-Sensor Applications

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Abstract—A carbon nanotube (CNT) growth process on HfO_2 is reported for the first time for application in nano-sensors. The process uses a combination of Ge nanoparticles and ferric nitrate dispersion and achieves an increase in CNT density from 0.15 to 6.2 μm length/μm^2 compared with the use of ferric nitrate dispersion alone. The growth process is validated by the fabrication of back-gate CNT field-effect transistors (CNTFETs) using Al source/drain (S/D) contacts and a H_2 anneal at 400 °C. The transistors exhibit p-FET behavior with an I_{on}/I_{off} ratio of 10^5 and a steep sub-threshold slope of 130 mV/dec. These results are rather surprising, as earlier research in the literature on CNTFETs with Al S/D electrodes showed n-FET behavior. The p-FET behavior is shown to be due to the H_2 anneal, which we ascribe to the smaller electron affinity of hydrogenised CNTs. Measurements of the temperature dependence of the drain current show low Schottky barrier height Al S/D contacts after a H_2 anneal, which tends to confirm this explanation.

I. Introduction

Recently, carbon nanotubes (CNTs) are gaining much attention for bio-sensing [1] because they offer the prospect real-time, label-free sensing for point-of-care diagnosis. The main advantage of CNTs for this application is a very high sensitivity due to the large surface to volume ratio of a carbon nanotube. The use of a high-κ dielectric as a gate insulator for a CNT field-effect transistor (CNTFET) is of interest because it delivers improved performance due to an increased I_{on}/I_{off} ratio. CNTFETs with a HfO_2 gate dielectric have also recently been researched for application in high-speed CNT memories and a strong hysteresis effect has been observed [2]. CNTs can be introduced onto HfO_2 using dispersion techniques, but CNT growth by chemical vapor deposition (CVD) would be more compatible with mainstream silicon technology. However, CVD growth of CNTs on HfO_2 appears to be very difficult and to our knowledge no work has been reported on this topic to date.

In this paper, a CNT growth process on HfO_2 is reported for the first time and this growth process is used to produce back gate CNTFETs with Al source/drain (S/D) contacts. The novel growth process uses a combination of Ge nanoparticles and ferric nitrate dispersion to achieve a dramatic increase in CNT yield compared with the use of ferric nitrate dispersion alone. Electrical measurements on completed CNTFETs show p-FET behavior, an excellent I_{on}/I_{off} ratio of 10^5, and a steep sub-threshold slope of 130 mV/dec.

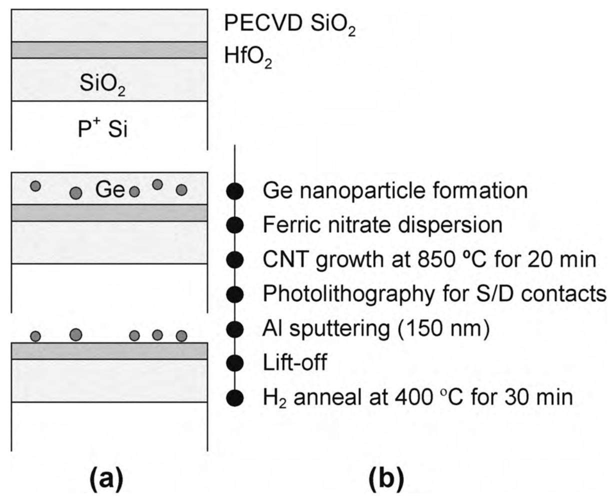

Fig. 1. (a) Schematic cross-section illustrations of the Ge nanoparticle fabrication process. (b) Main CNTFET fabrication process flow after Ge nanoparticle formation.

II. Experimental

A p^+ Si substrate (0.005 Ω·cm) was employed as a back gate and a passivating SiO_2 layer was thermally grown, followed by the deposition of a HfO_2 layer by atomic-layer deposition, as shown in Fig.1. A 30nm SiO_2 layer was then deposited by plasma enhanced chemical vapor deposition (PECVD) on top of the HfO_2 and densified at 950 °C. The SiO_2 layer was then implanted with 5×10^{15} cm^{-2}, 20 keV Ge and annealed in N_2 at 600 °C for 40 min to create Ge nanoparticles. The SiO_2 layer was then removed using a HF vapor etch to expose the Ge nanoparticles on top of the HfO_2 layer. Then the HfO_2 substrate was dipped in ferric nitrate solution for 1 min and rinsed with hexane. The CNT growth was performed using chemical vapor deposition in a hot-wall reactor at atmospheric pressure. CNTs were grown at 850 °C for 20 min using a mixture of methane (1000 sccm) and H_2 (300 sccm) immediately after a pre-anneal in H_2 (1000 sccm) at 900 °C. For comparison, CNT growth on HfO_2 without Ge particles was also carried out.

Back gate CNTFETs were fabricated with Al S/D contacts. Al was deposited by sputtering and the S/D electrodes were formed using direct write optical lithography and lift-off. The use of Al instead of the more common Pd can both reduce the

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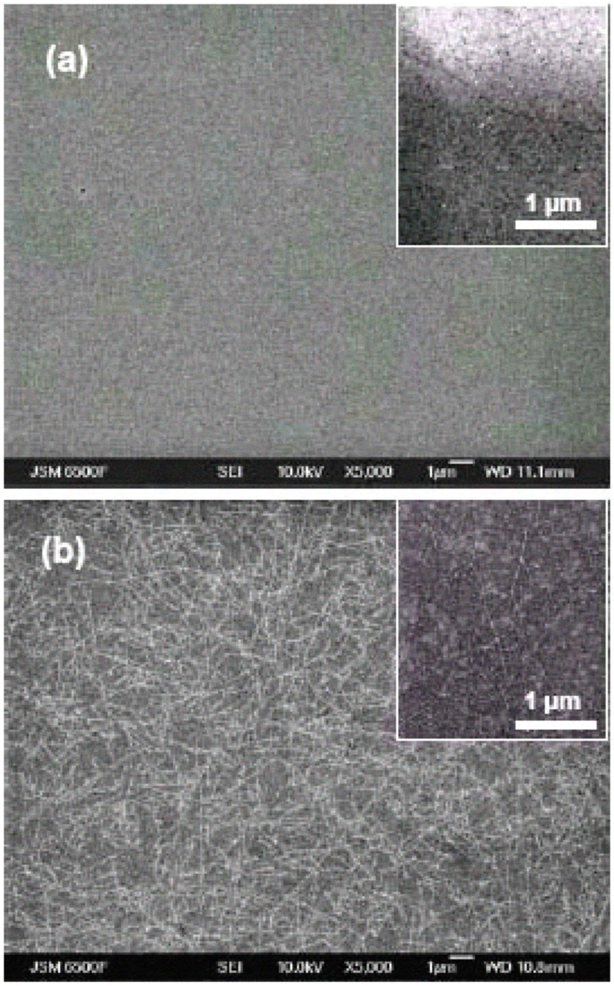

Fig. 2. SEM images after CNT growth on HfO_2 substrates using (a) Fe nanoparticles only and (b) a combination of Ge and Fe nanoparticles. CNT area densities are 0.15 and 6.2 µm length/µm^2 respectively.

cost and improve the yield, as Pd has poor adhesion to oxides. The gap between the S/D electrodes was 2.0 µm and the width was 5.0 µm After Al patterning, the devices were annealed in H_2 at 400 °C for 30 min. The area densities of CNTs were evaluated using FE-SEM images and ImageJ was used to determine the total contour length of CNTs [3]. Ten SEM images taken from the same sample were used for quantitative analysis, with overlapping regions being discarded. Raman spectra were obtained using a Renishaw micro-Raman system with He-Ne ($\lambda_{excitation}$ =632.8 nm) laser excitation with power of 12 mW.

III. Results and Discussion

The Ge nanoparticles were evaluated by means of atomic force microscopy. These results showed a high density of particles (460 ± 30 particles/µm^2), with particle heights between 1.3 and 2.9 nm. This result agrees well with previous results by Min *et al* [4]. Fig. 2 shows FE-SEM images after CNT growth for samples using Fe nanoparticles only (a) and a

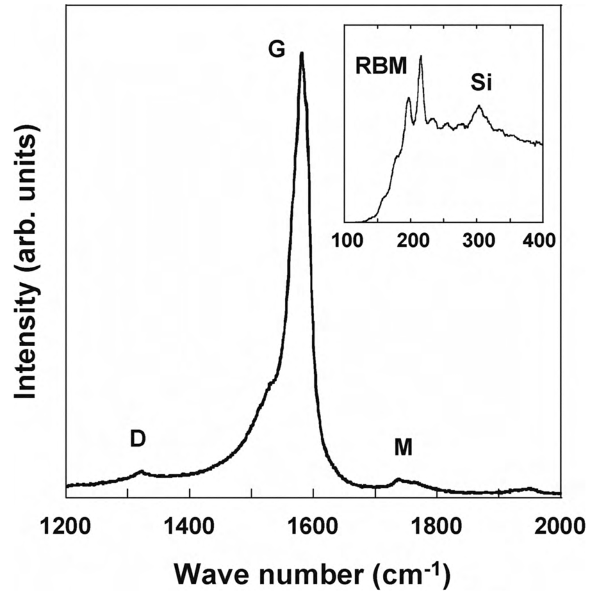

Fig. 3. Raman spectra of CNTs grown from a combination of Ge and Fe nanoparticles on HfO_2 substrate. The inset shows radial breathing mode (RBM), indicating that SWNTs are present,

combination of Ge and Fe nanoparticles (b). For Fe nanoparticles only, very few CNTs are present and only isolated CNTs are occasionally seen as shown in inset of Fig.2(a). The area density of CNTs was estimated as 0.15 µm length/µm^2. In contrast, the presence of the Ge nanoparticles dramatically aids CNT growth, giving an area density of 6.2 µm length/µm^2. These results suggest that selective CNT growth is possible by means of Ge ion implantation with photo resist mask patterns. The improvement of the CNT yield using Ge nanoparticles is consistent with the work of Segura *et al.* [5], who showed that Ge could suppress agglomeration of metal particles during annealing.

The CNTs grown from combined Fe/Ge nanoparticles were characterized by micro Raman spectroscopy (Fig. 3). All samples clearly showed the radial breathing mode (RBM) and M-band, indicating that single-walled CNTs (SWNTs) are present. The Raman intensity ratio (I_D/I_G) of D-band to G-band was less than 0.1, indicating that synthesized SWNTs have a low defect density. The diameter of the SWNTs is estimated at about 1.5-2.0 nm from the RBM peaks, though thicker SWNTs may also be present due to the cut-off of our Raman notch filter.

Fig. 4 shows an FE-SEM image of a back gate CNTFET with a SiO_2/HfO_2 gate insulator and Al S/D contacts. The SWNTs bridge the 2.0 µm gap between the Al S/D electrodes. We have successfully fabricated in total more than 80 functional devices.

Fig. 5 shows one of the best electrical characteristics of CNTFETs measured in ambient air and it can be clearly seen that the devices exhibit p-FET behavior. The sub-threshold characteristics show an excellent I_{on}/I_{off} ratio of 10^5 and a reasonably steep sub-threshold slope of 130 mV/dec. The output characteristic shows linear characteristics below

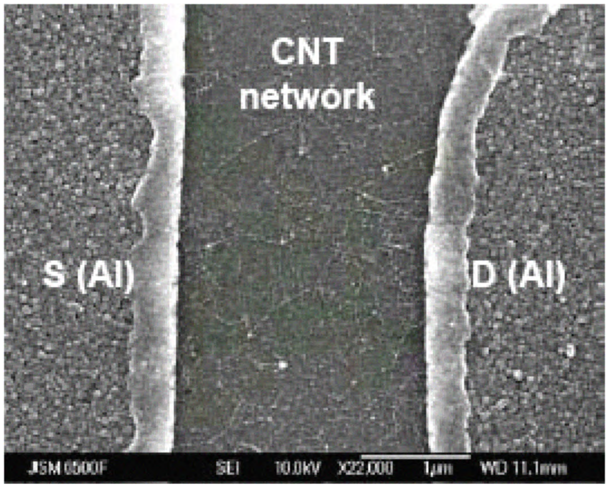

Fig. 4. SEM image illustrating the CNT distribution between and Al source (S) and drain (D) contacts of the CNTFET.

saturation ($|V_d| < 0.5$ V) and good saturation ($|V_d| > 0.5$ V).

The results in Fig. 5 are rather surprising, since earlier research on CNTFETs with Al S/D electrodes showed n-FET behavior [6], [7]. Furthermore, we would expect ambipolar or n-FET behavior from the work function for Al (4.2 eV) and the electron affinity of CNTs (4.0 eV). It is well known that the absorbed oxygen can transform CNTs into p-type conductivity and the removal of oxygen by annealing in vacuum can transform CNTs to n-type conductivity [8].

To investigate whether type conversion occurs in our CNTFETs, sub-threshold characteristics were measured just after H_2 anneal at 400 °C and after 30 hours in a vacuum of 1×10^{-6} Torr at room temperature to exclude the effect of water and oxygen. We also measured the same device after 230 days in air at room temperature (Fig. 6). The device still shows p-FET behavior in vacuum and it can therefore be concluded that the p-FET behavior is not due to absorbed oxygen. The threshold voltage shift of 2 V after 230 days in air is attributed to oxidation. These results clearly indicate that the fabricated devices are suitable for nano-sensors.

Measurements of sub-threshold characteristics were also made before H_2 anneal and the device exhibited weak ambipolar characteristics, a poor value of I_{on}/I_{off} ratio and a very low value of I_{on}. It can therefore be concluded that the p-FET behavior is caused by the H_2 anneal.

The steep values of sub-threshold slope and linear output characteristics below saturation in Fig. 5 suggest that the Al S/D contacts have a low Schottky barrier height after H_2 anneal. To test this possibility, we have measured the temperature dependence of the sub-threshold characteristics using the same device in Fig. 6. Fig. 7 shows an increase in drain current with decreasing temperature from 300 to 250 K and a decrease at lower temperatures. A similar trend has been reported on Pd contacted CNTFETs [9] and was attributed to a low Schottky barrier height S/D contact. The most likely explanation for the formation of low Schottky barrier height S/D contacts during the H_2 anneal is the adsorption of H_2, which could modify the

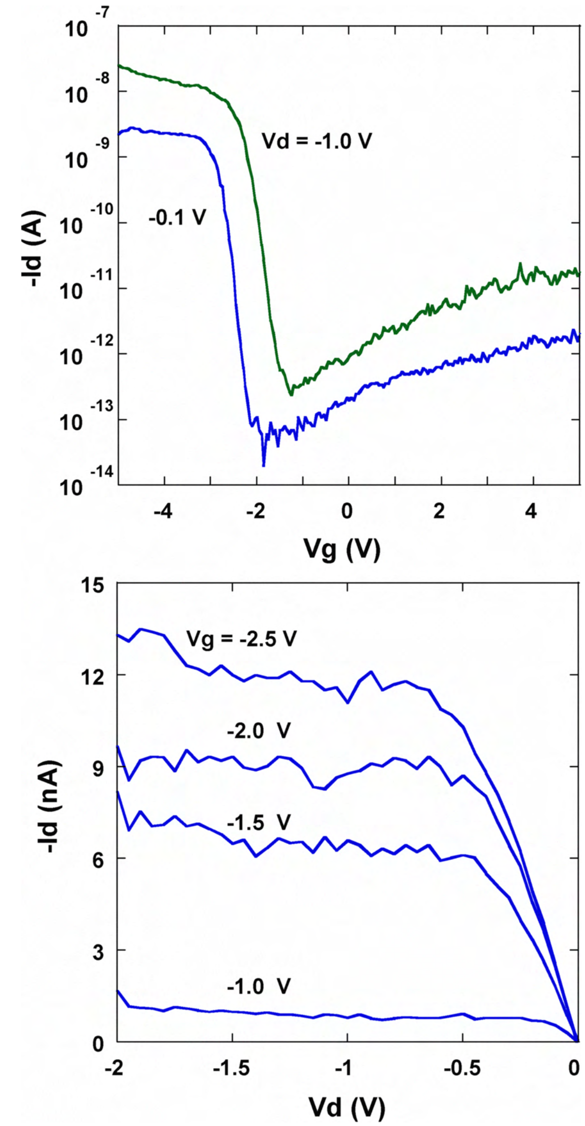

Fig. 5. I-V characteristics of an Al contacted CNTFET with channel length Lg = 2.0 µm after H_2 anneal. (a) Sub-threshold characteristics for Vd = -0.1 and -1.0 V and (b) Output characteristics for Vg = -1.0, -1.5, -2.0, -2.5 V.

electronic structure due to the stable covalent C-H bonding [10], [11]. In particular, the H_2 could decrease the electron affinity of the CNTs, tending to produce p-FET behavior. An alternative possibility is that Al could dope the S/D of the CNT p-type, as has been observed for boron [12]. However, we have no evidence to support this explanation.

In order to investigate the suitability of the CNTFETs for memory applications, hysteresis in the sub-threshold characteristics was measured at Vd = -1.0 V and results are shown in Fig. 8. A strong hysteresis is seen, with an I_{on}/I_{off} ratio of 10^2 and a memory window of 4 V. The hysteresis effect of CNTFETs is attributed to absorbed molecules such as water [13] and more recently *Rinkio et al.* have shown that a high-k dielectric gate CNTFET has strong hysteresis due to the charge trapping levels in the high-κ dielectric [2].

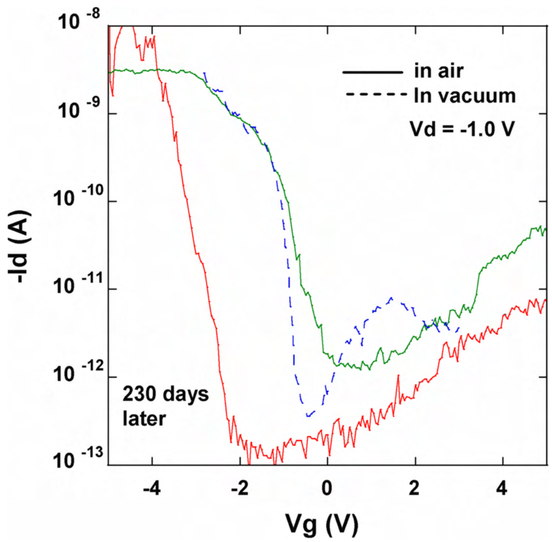

Fig. 6. The sub-threshold characteristics of an Al contacted CNTFET (*Lg* = 2.0 µm) with a SiO_2/HfO_2 gate insulator were measured under several conditions including just after H_2 anneal., in vacuum of 1×10^{-6} Torr, and in ambient air after 230 days.

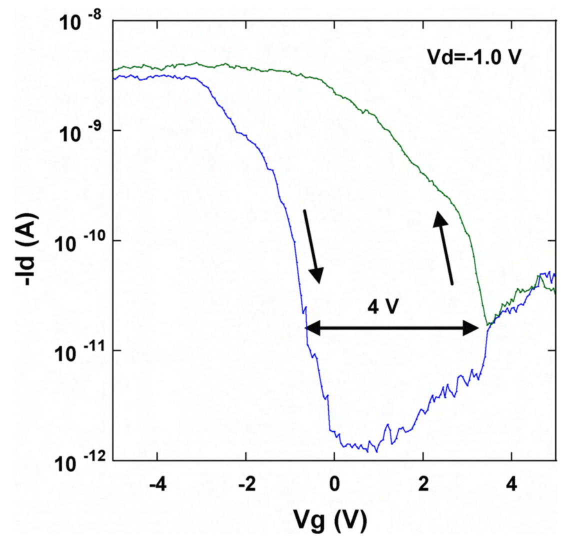

Fig. 8. A hysteresis of *Id-Vg* characteristics of the same device in Fig. 6.

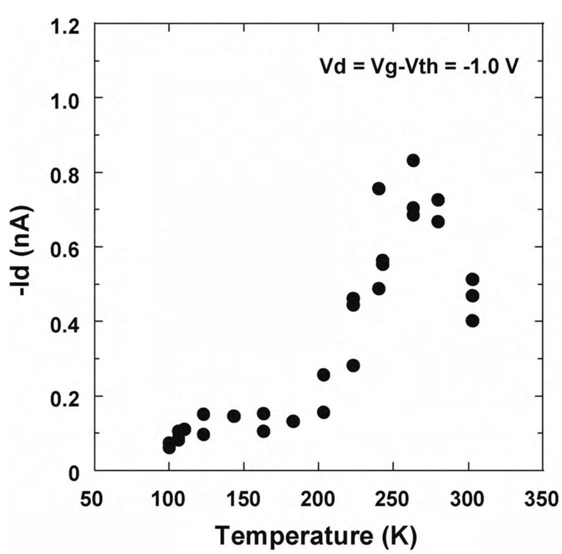

Fig. 7. Temperature dependence of the drain current (*Id*) at *V d* = *Vg-Vth* = -1.0 V for the same device in Fig. 6.

IV. Conclusion

We have developed a novel CNT growth process on HfO_2 using a combination of Ge nanoparticles and ferric nitrate dispersion. The synthesized CNTs were successfully applied to fabricate back gate CNTFETs with Al S/D contacts for application in nano-sensors. The CNTFETs have an excellent on/off current ratio of 10^5 and a steep sub-threshold slope of 130 mV/dec. The sub-threshold characteristics including threshold voltage shift after exposure in air and after hysteresis loop measurements indicate that the CNTFETs are suitable for application as both nano-sensors and non-volatile memory.

Acknowledgment

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