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

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1. Introduction

Carbon nanotubes (CNTs) are gaining much attention for device application, especially bio-sensing [1]. The main advantage of CNTs for this application is a very high sensitivity due to the large surface to volume ratio of a CNT. The use of a high-κ dielectric as a gate insulator for a CNTFET is valid 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 non-volatile memory [2]. CNTs can be introduced onto HfO_2 using dispersion techniques, but CNT growth by CVD would be more compatible with mainstream Si technology. However, CVD growth of CNTs on HfO_2 appears to be very difficult and to our knowledge no work has been reported so far.

In this paper, a CNT growth process on HfO_2 is reported 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.

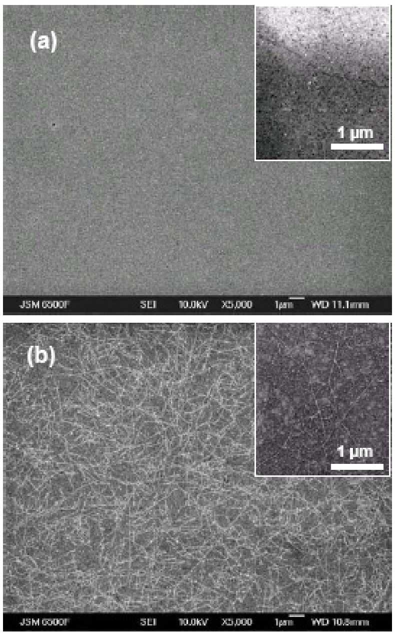

Fig. 1. SEM images after CNT growth on HfO_2 substrates using (a) Fe nanoparticles only and (b) a combination of Ge and Fe nanoparticles. CNT area densities are 0.15 and 6.2 µm length/µm^2 respectively.

2. 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. A 30nm SiO_2 layer was then deposited by 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 CVD 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 nanoparticles 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 laser lithography and lift-off. The use of Al instead of the more common Pd can both reduce the cost and improve the yield, as Pd has poor adhesion to HfO_2. 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.

3. 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

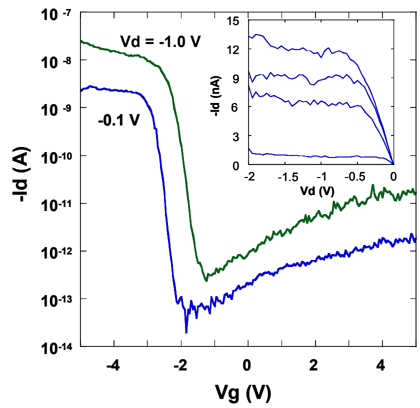

Fig. 2. I-V characteristics of an Al contacted CNTFET with channel length Lg = 2.0 µm after H_2 anneal. Sub-threshold characteristics for Vd = -0.1 and -1.0 V and output characteristics for Vg = -1.0, -1.5, -2.0, -2.5 V.

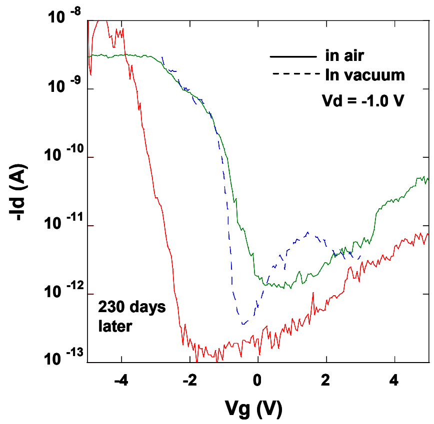

Fig. 3. The sub-threshold characteristics of an Al contacted CNTFET (Lg = 2.0 μm) with a SiO_2/HfO_2 gate insulator were measured under several conditions including just after H_2 anneal, in vacuum of 1×10^{-6} Torr, and in ambient air after 230 days.

heights between 1.3 and 2.9 nm. This result agrees well with previous results by Min *et al* [3]. Fig. 1 shows FE-SEM images after CNT growth for samples using Fe nanoparticles only (a) and a 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. 1(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.

The diameter of the SWNTs is estimated at about 1.5-2.0 nm from the RBM peaks of Raman spectra, though thicker SWNTs may also be present due to the cut-off of our Raman notch filter.

Fig. 2 shows one of the best electrical characteristics of CNTFETs measured in ambient air and it can be clearly seen to 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 saturation (V_d > -0.5 V) and good saturation (V_d < -0.5 V). The results in Fig. 2 are rather surprising, since earlier research on CNTFETs with Al S/D electrodes showed n-FET behavior [4], [5]. 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 O_2 can transform CNTs into p-type conductivity and the removal of O_2 by annealing in vacuum can transform CNTs to n-type conductivity [6].

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. 3). 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 the adsorption of oxide. 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 sub-threshold slope and linear output characteristics below saturation in Fig. 2 suggest that the Al S/D contacts have a low Schottky barrier height after H_2 anneal. The most likely explanation for the formation of low Schottky barrier height S/D contacts after H_2 anneal is the adsorption of H_2, which could modify the electronic structure of the SWNT due to the stable covalent C-H bonding [7], [8]. In particular, the H_2 could decrease the electron affinity of the SWNTs, tending to produce p-FET behavior. An alternative possibility is that Al could dope the S/D of the SWNT p-type, as has been reported for boron [9]. However, we have no evidence to support the latter explanation.

4. Conclusions

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 indicate that the CNTFETs are suitable for application as nano-sensors.

Acknowledgements

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