Electrical properties of carbon nanotubes synthesis by double furnace thermal-CVD technique at different temperatures on porous silicon template

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Abstract. Multiwalled Carbon Nanotubes (MWCNs) were synthesized using double-furnace thermal chemical vapor deposition technique at 700 - 900 °C on porous silicon nanostructure (PSiNs). Palm oil used as a carbon natural source, ferrocene as a catalyst and nitrogen gas as a carrier gas. The precursor were vaporized at 475 °C carried by nitrogen gas which flow at constant rate 150 sccm/min. Carbon nanotubes characterized by using Raman Spectroscopy and field emission scanning electron microscopy (FESEM) to check its structure and crystallites before tested with I-V probe. Au contact used as a metal contact deposited on CNTs layer. Carbon nanotubes (CNTs) with uniform diameter were found grown on porous silicon for each temperature used. Based on micro-Raman spectroscopy result, the peak of carbon nanotubes (around 1 300 to 1 600 nm) was detected. The I-V characteristic of CNTs deposited had different profile when deposited at different temperature.

1. Introduction
A carbon nanotube is a carbon in tube-shape material and having a diameter in nanometer scale. This carbon consist a hollow cylindrical-shape molecules with graphitized walls [1]. Carbon nanotubes (CNTs) attracted a lot of attention in wide researches’ application today especially in electronics application such as sensor [2], field emission [3], hydrogen storage [4] etc. CNTs also are a good material in term of thermal stability and mechanical properties. Electrical characteristics studied of important material to measure the capability of material in electronic field application. It can be explained in term of resistance, conductance and capacitance measurement. Generally, CNTs divided in two types: single-walled (SWCNTs) and multi-walled (MWCNTs). The SWCNTs are consists a simple nanostructure with single rolled layer (concentric tubes) of graphite, while the MWCNTs are consist multiple rolled layers of graphite (various SWCNTs). The SWCNTs can be either semiconducting or metallic materials because its depend on the chiral vector \( (n, m) \); where \( n \) and \( m \) are integer) [5, 6]. Different with SWCNTs, the MWCNTs could be form by combination of metallic and semiconducting nanotubes element [7].
In this work, porous silicon nanostructures were used as a substrate to grow carbon nanotubes. Porous silicon is Si substrates after partial electrochemical etching in hydrofluoric acid (HF) based material. Porous silicon nanostructures (PSiNs) ideal substrate for grow self-oriented nanotubes on large surfaces and CNTs produced was better than on plain Si [8]. Carbon nanotubes (CNTs) generally can be synthesized by using a few techniques, likes arc discharge [9], laser ablation [10], chemical vapor deposition [3] and others. The selection method is important in order to produce CNTs with predictable and reproducible properties. In addition, the controllable CNTs diameter and chirality would allow the exploitation in electrical, thermal and mechanical properties in various applications. In this work, thermal-CVD method was choose because CNTs can be synthesized at lower temperatures (500-900 °C) [3] and it is a simply method. CNTs synthesized at different deposition temperatures on porous silicon to study the effect of structures and morphology of CNTs to their electrical properties because each parameter will affect nanomaterial properties. This work found that the structural of CNTs affected by temperature and I-V curve show the relationship between structural and electrical properties of CNTs.

2. Experiment detail

2.1 Electrochemical Etching Process
Firstly, porous silicon nanostructures (PSiNs) was prepared by using electrochemical etching method using p-type Si wafer [100] with 0.4-2 Ω cm resistivity and 330 ± 40 μm thickness. A square dimension was cleaved and placed in cell using a piece of aluminum foil as a back contact. The etching process was set up at $t = 20$ minute and $J = 20$ mA/cm$^2$. Ethanoic hydrofluoric acid (HF) 48% and absolute ethanol (C$_2$H$_5$OH) at ratio 1:1 with illumination by halogen lamp was used as a based solution in etching process. After porous form on silicon, it was rinsed by DI water and dried using nitrogen gas. The surface topography of PSiNs was investigated by using FESEM.

2.2 Chemical Vapor Deposition (CVD) Method
The carbon nanotubes synthesized by using double-furnace CVD method [11] set up like in figure 1. 5% wt of ferrocene which used as catalyst mixed in palm oil and placed in alumina boat in a double furnace (Furnace 1). PSiN, which used as a template, place on alumina boat in the quartz tube at the centre of Furnace 2. Rubber stopper used at the end of quartz tube to avoid the carbon gases react with oxygen and produce carbon dioxide. Nitrogen gases was used as a gas carrier flow at constant flow rate 150 sccm/min from end of quartz at Furnace 1 to Furnace 2. The Furnace 1 was heated to 475 °C and 700-900 °C at Furnace 2. The deposition time set at 1 hour and followed with annealing process for 30 min. The characteristics of CNTs on porous silicon analyzed by using FESEM (JOEL), micro Raman spectroscopy (Horiba Jobin Yvon, LabRam HR800) and I-V probe.

![Diagram](image)

**Figure 1.** Double furnace thermal-chemical vapor deposition (TCVD) set-up to produced CNTs.
3. Result and Discussion

Field emission scanning electron microscope (FESEM-JOEL) was used to investigate the surface structure of porous silicon nanostructures (PSiNs) and CNTs. Figure 2(a) show the FESEM image of PSiNs surface structures prepared by electrochemical etching obtain at $J = 20$ mA/cm$^2$ and $t = 20$ minutes view by at magnification 50k. FESEM results show micrometer-size of pore form on the surface of p-type silicon with the columnar pores is not regular. These pores know as nano pores because, the size of pore produced were between 15 ~ 30 nm and its represent by a dark area (small figure) in the figure 2(a).

We were successful deposited multiwall carbon nanotubes (CNTs) on porous silicon by using double furnace thermal-CVD at different deposition temperatures. Figure 2 show CNTs on porous silicon grow viewed using magnification 1k and 100k. We can see that the density of CNTs grow on Si substrate increase respectively with temperatures. At lower temperature (figure 2(b)), less CNTs produced because the thermal energy at furnace 2 not suitable for carbon source and catalyst activity to form a CNTs.

![Figure 2](image_url)

**Figure 2.** The FESEM image of (a) PSiNs surface produced by electrochemical etching process and multi-wall CNTs grow on porous silicon substrate at temperatures various temperatures; (b) 700, (c) 750, (d) 800, (e) 850 and (f) 900 °C.
When temperatures increase, dense CNTs synthesized on PSiN substrate. Smooth nanotubes produced at temperature 750 - 900 °C. Temperature at 750 °C is good parameter to synthesized good quality of CNTs because small diameter and smooth tubes produced (figure 2(c)). It can be supported by Raman result in figure 3. Besides that, uniform nanotubes in bundle success synthesized at this temperature. Based on FESEM image, we also can observed that the diameter of tube change with temperatures. The CNTs have large diameter in the range 75-90 nm at temperatures 850 °C (in figure 2(e)). CNTs produced at 900 °C had a small diameter, but more amorphous carbon produced. The multi-walled carbon nanotubes have diameters of 15-30 nm indicated in figure 4(f). The type of CNTs grown on porous detected by using Raman spectroscopy (figure 5).

Raman spectroscopy used to measure Raman scattering spectra of nanotubes which are important for CNTs characteristics [12]. Figure 4 shows the Micro-Raman spectra for the CNTs grown on porous silicon substrate at temperature 700 – 900 °C. The spectrum is dominated by two peaks (D and G) located at 1530 cm⁻¹ (D line) and 1570 - 1650 cm⁻¹ (G line). In the high frequency spectra, a G-band representing crystalline graphitic carbon and D-band indicates lattice distortions in the curve graphene sheets, tube ends, etc [13]. The carbon G and D peaks for the samples at that position substantiate that are multi-walled (MWCNT) type were synthesized [14]. No lower frequency RBM peaks which lies from 100 to 400 cm⁻¹ can be attributed single-walled CNTs (SWCNT) detected on this sample.

From figure 4 it was observed that the intensity of G-peak is greater than D-peak with sharp peak indicated that good graphitization in nanotubes successes synthesis and the graphitization increase by temperature observed. The G-peaks intensity highest at deposition temperature 750°C observed, that means good graphitization of CNTs produced at this temperature. At 700 °C, 750 °C and 850 °C, the D- and G-peak observed at 1350 cm⁻¹ and 1580 cm⁻¹. At temperature 800 °C (Fig. 3(c)), D- and G-peak shifted to higher wave number (1416 cm⁻¹ and 1642 cm⁻¹). This shifted happen maybe cause by defects in the tube [15].

![Figure 3](image-url)

**Figure 3.** Raman spectra of MWCNTs on PSiNs substrate deposited at different temperatures.

In CNTs sample, the relative intensity of the D band with respect to the G band can be used to measure the concentration of defect [16]. When $I_D/I_G$ ratio low, the CNTs with graphite structures were produced more compare to defect structures. Table 1 below show the $I_D/I_G$ ratio of CNTs deposited on Si substrate. At 750 °C, the high graphite structures produced compare to other samples because the relative intensity $I_D$ to $I_G$ is lowest.
Table 1. $I_D/I_G$ ratio of CNTs deposited at different temperatures.

| Deposition Temperature (°C) | $I_D/I_G$   |
|-----------------------------|------------|
| 700                         | 0.9705     |
| 750                         | 0.7079     |
| 800                         | 0.9516     |
| 850                         | 0.9352     |
| 900                         | 0.9812     |

$I-V$ characteristics of CNTs samples come by using 2-point probe $I-V$ testing. Au contact used as a metal contact sputter on CNTs layer about 60 nm to reduce the contact resistant between CNTs layer and $I-V$ probe. Figure 4 show the $I-V$ characteristics samples of CNTs samples after 3V potential applied on its. All samples show Ohmic profile with linear line produced when graph current versus voltage plotted. This can be concluded that Au performs a good contact with CNTs layer because the barrier is so low. The current flow is high even though low potential applied (0-5V) during the testing for all sample especially sample prepared at 750 °C. This can reduce the applied potential in device application.

![Figure 4. $I-V$ characteristics of CNTs samples.](image)

Figure 5. $I-V$ characteristics of CNTs were synthesized on PSiNs at different temperatures.

The resistance dramatically drops by temperature showed in Table 2. Commonly, the conductivity of nanomaterial depends on crystallinity and doping or impurities in nanomaterial. For CNTs, another factor can influence that property is diameter of tube. From table 2 below, we can see that the conducting of CNTs increase when temperature depositing increase. This is due to the diameter and graphene structures of CNTs were synthesized. CNTs synthesized at temperature 850 °C possess large tubes diameter, so the number of wall ($N_{wall}$) in tube is large because based on literature $N_{wall}$ increases at larger CNT diameter [17]. The high conductivity of align CNTs produced effected by graphene structures existence more compare with defect. These help the carrier moving easily through graphitic interfacial layer [18] because lower barrier resistance.

Table 2. The resistance of CNTs deposited at different temperatures.

| Deposition temperature (°C) | Resistance (Ω) |
|-----------------------------|---------------|
| 700                         | 250.00        |
4. Conclusion

We have successfully synthesized multi-walled carbon nanotubes by thermal chemical vapor deposition on porous silicon nanostructures substrate made by electrochemical etching method. CNTs produced on porous silicon substrate proved that it can be used with semiconductor devices to fabricate integrated circuits (IC). I-V characteristics of CNTs affected by structures and quality produced. CNTs synthesized on porous silicon at temperature $750^\circ$C possess more graphite structures and fewer defects. It was directly influence the electrical property. Conductivity of CNTs increases when the diameter of nanotubes increases.

5. References

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