Synthesis of a Novel Structure Carbon Nanocoils and Their Application in Photo Diode Devices

Mohammed Ibrahim Mohamed
Chemical Engineering Department / University of Technology/ Iraq Baghdad
email:mohab1964@yahoo.com

Abstract. In this paper, the novel structure of carbon nanocoils were synthesized successfully by catalytic thermal decomposition of acetylene in CVD reactor under inert atmospheric pressure. Fe as a catalyst coated alumina beads used as substrate, both were placed inside a cylindrical shape stainless steel mesh SSC and located at the mid of CVD reactor. Preliminary study of application of prepared carbon nanocoil in synthesis of photodiode showed that the photodiode has a good rectification and the forward current obeys to tunneling-recombination model.

Keywords: Carbon nanocoil, Stainless steel mesh, SEM, Catalyst, Photodetector.

1. INTRODUCTION
The coiled Carbon nanotube CNTs is a kind of quasi one-dimensional CNTs-based nanostructures with a certain spiral angle (Liu Lizhao,2013). An important feature of the carbon nanocoil models is the periodic incorporation of pentagons and heptagons in the hexagonal network (Amelinckx,1994., Zhang,1994). Due to the spring-like geometry, the coiled CNTs possess fascinating mechanical properties, which are known as super elastic properties. This super elasticity allows the coiled CNTs to act as electromechanical, electromagnetic, and chemical sensors (Coluci,2008). In addition, the coiled CNTs have been used commercially to fabricate flat panel field emission display, microwave absorbers and cosmetics (Liu Lizhao,2013). The coiled CNTs synthesized experimentally are usually formed by the bundle of single-walled CNTs and have large ring diameters. Therefore, fabricsations of the single-walled coil CNTs of controllable ring diameters are great challenges.

Coil, helical or spring micro and nano feature have been synthesized by the thermal decomposition of hydrocarbons either with single catalysts such as Ni, Co, and Fe or mixed catalysts or alloys such as Sn-Fe and Fe-Ni-ITO (Yang,2005,2008, Zhan,2000). Systematically understanding of the growth mechanism of carbon nano or micro coil is difficult, since the synthesis of either one is hardly reproducible and experimental parameters dependent(Kuzuya,2002). The aim of this work is to synthesis of coiled carbon nanotube using CVD technique and testing their performance in photodiode devices.

2. EXPERIMENTAL
2.1 Preparation of Catalyst
The catalyst precursor prepared by mixing 0.1 M ferric nitrate aqueous solution (Fe(NO₃)₃·9H₂O) with alumina particles of average diameter of 2mm for 24h. Then the beads of alumina after coated with a thin film of ferrite solution was dried in oven at 120 °C for a day to remove water and was further treated in tubular furnace at 550 °C for 2h under hydrogen environment to reduce the ferrite into iron. 2g of Fe-catalyst was then placed inside a cylindrical shape (200mm long x 20mm diameter) stainless steel mesh container (SSC). Both ends of SSC was closed before transfer to place inside the mid of CVD reactor.

2.2 Synthesis of Carbon NanoCoils CNCs
The experimental setup of (CVD) reactor which was used for fabrication of (CNTs) in this work is shown schematically in figure (1).

The reactor consists of tubular furnace in which quartz tube of 900mm in length and 30mm in diameter was inserting. Pure argon (99.99% purity) is used as an inert gas. The hydrocarbon gas C₂H₂ (99.99) is used as a source of carbon in preparation of CNTs. The catalyst was placed inside a stainless steel mesh and both was inserted through the reactor and located at the middle of the quartz tube.

The furnace was heated up to 750 °C at rate of 10°C, and Nanocoil is then grown by admitting 0.5 sccm of C₂H₂ and 5 sccm of argon for 1hr under atmospheric pressure. Then the reactor is switched off and allowed to cool under inert atmosphere. The (CNTs) then was collected and subject for further treatment for purification.
CNTs yield $y \text{(mg/mg)}$ deposited on the catalyst after reaction was roughly estimated using the following Eq. 1:

$$y(\text{mg/mg}) = \frac{C_0(\text{mg})}{B(\text{mg})} \quad \ldots \ldots \quad (1)$$

where $C_0$ is the weight (using 4-digit electronic balance) of as prepared product sample (mg) and $B$ is the weight of the catalyst precursor (mg).

In order to purify the produced CNTs, 0.5 gm of CNTs was put in a ceramic boat and then inserted inside the furnace at 450°C for two hours to oxidize the amorphous carbon. The CNTs were then dipped in 250 ml acidic solution (sulfuric acid and Nitric acid with a ratio (3:1) and stirred for 1 hour at 90 °C. The CNTs was then removed from acidic solution using a centrifuge (Unimedica 800 centrifuge, China) at 3000 rpm for 10 minute. The remaining CNTs were washed with deionized water and then centrifuged for another 10 minute at 3000 rpm. This process was repeated 3-4 times until the pH of the solution becomes 7. The CNTs were then dried in an oven at 90°C for 2 hours.

2.3 Preparation of CNCs/Si Photodiode

0.8mg CNTs as prepared, 30ml ethanol (99.99%) and 0.016mg of citric acid were mixed carefully with continuous stirring for 24h. Piece of Si(111) wafer each has 1cm² area and resistivity of 1-3Ωcm after cleaned by acetone are cover with a thin film of carbon nanocoil solution using drop casting technique and spinning homogenizer. The specimens were then treated at 450 °C for 2h under inert atmosphere in tube furnace. For each sample ohmic contacts (electrodes) were made on both front and back sides by deposition of Al thick films. Photovoltaic measurements were carried out using a white light. I-V and the characteristics of photodiode was investigated. Spectral responsively of photodetector was measured using monochromator after calibration with silicon.

3. RESULTS

A spring shape nanocoil prepared by catalytic thermal CVD is shown in SEM micrograph of figure 2a and 2b. The nanocoils grown at reaction temperature 750°C for 1hr on Fe/Al2O3 catalyst with acetylene/Ar ratio of (0.1). A coil with outer diameter $D_0=2um$, Coil inner diameter $D_i=330nm$ tubular diameter$D_t=230nm$, coil pitch $\lambda=0.415um$ and coil length $L=34um$ has been obtained. Since $D_i=3/4D_0$ and in such case shear modulus of around2.5Gpa was estimated as reported by Chen et al.

![CVD System for Synthesis of CNTs](image)
XRD pattern Fig. 3 shows two peaks reflecting the line (002) at 2theta 26.4 and the line (100) at 2 theta 43.3 which corresponding to the crystalline structure of carbon nanocoils. Small peak at 2theta 46.0 which corresponding to Fe catalyst (400) reflection. No other peaks have been observed which confirm the crystallinity of the sample and the majority of CNTs. This result was confirmed by chemical analysis of product using EDX as in Fig. 4 which shows a very well defined presence of carbon (94%) with small amount of Fe catalyst (3.95%).

Our preliminary study on application of prepared carbon nanocoil in photodiode shows significant results. The characteristics of photodiodes prepared by drop casting of carbon nanocoil on Si-Wafer have been measured.
Our preliminary study on application of prepared carbon nanocoil in photodiode shows significant results. The characteristics of photodiodes prepared by drop casting of carbon nanocoil on Si-Wafer have been measured. Figure 5 shows the dark and illuminated I-V characteristic of C NTs/Si photodiode in the reverse direction. The photodiode showed good rectification and the forward current obeys to tunneling-recombination model. No breakdown was noticed at low voltage. The ideality factor of photodiode was found to be 3. The reverse current increases after illuminated with white light which give an indication of good photoresponse as depicted in Fig. 5. The spectral responsivity of photodetector is given in Fig. 6; the result confirmed that the photodetector is response to visible and near IR regions. There are two response peaks, the first peak located at 400nm due to absorption edge of carbon and the second peak was located at 800nm due to absorption of light in silicon substrate. The maximum responsivity was around 0.3A/W at 800nm. This value is much better than those reported recently. The band gap $E_g$ of CNT was measured using visible spectrophotometer in the spectral region of 400-900nm. Fig UV.7 Shows the variation of $(\alpha h\nu)^2$ with photon energy $(h\nu)$, the band gap estimated by extrapolating of curve to the $h\nu = 0$ points according to the following Eq. 2:

$$ah\nu = A(h\nu - E_g)^{0.5} \quad (2)$$

Where $\alpha$ is the absorption coefficient, $A$ is constant, $h\nu$ is the photon energy. The results revealed that the band gap of CNT is around 3.8eV. No difference in the value of band gap was observed for carbon nanocoil.
4. CONCLUSIONS

On the bases of the experimental work described in text. The main conclusions can be summarized as follows:

1. Carbon nanocoil are successfully synthesized by catalytic CVD method using acetylene as a carbon source and Iron film coated on alumina beads placed inside SSC.

2. Using SSC, increase the CNTs yield by a factor of 2 which was attributed to increase in catalyst surface area due to convert elements of SSC substrate into carbide at high temperature.

3. Preliminary study on application of prepared carbon nanocoil in synthesis of photodiode showed that the photodiode has a good rectification and the forward current obeys to tunneling-recombination model.
REFERENCES


