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# EFFECT OF Au THICKNESS ON PREPARATION OF CARBON NANOSTRUCTURE BY USING NANOSTRUCTURED ZnO AS A TEMPLATE

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## ABSTRACT

Different thickness of Au was prepared as a catalyst to deposit ZnO nanostructure on Au-coated surfaces by sol-gel method. The ZnO nanostructure will be used as template to deposit carbon nanostructure by using thermal chemical vapor deposition (TCVD) method. The carbon material has been successfully grown by using ZnO nanostructure material as template. Rod-like ZnO appeared with sphere-like carbonaceous material on the surface of the template. The as-prepared material has been characterized with X-ray diffraction (XRD), scanning electron microscopy (FESEM) and Fourier transmission infrared (FTIR). The XRD peaks of the products were indexed to ZnO materials, but exhibited different relative intensities for the (002) diffraction peak. ZnO play a role as a template for the growth of the carbonaceous material and they can link ZnO particles together as a complex fabrication. This discovery is useful for nano-electronic applications.

## INTRODUCTION

Nanostructured materials have thus stimulated a great deal of research and development with regard to their mechanical, thermal, and electrical properties. In recent years, nanosize semiconductors have attracted much attention, due to their special electrical and optical characteristics in fabricating nanoscaled electronic and optoelectronic devices. Among them, one-dimensional (1D) nanostructures such as nanotubes [1], nanowires [2], nanorods [3], nanobelts [4], nanocables [5], and nanoribbons [6] have stimulated considerable interest for scientific research due to their importance in fundamental physics studies and their potential applications in nanoelectronics, nanomechanics, and flat panel displays.

Zinc oxide (ZnO) is of much interest because of its attractive optical properties based on its wide band gap of 3.37 eV and exciton binding energy of 60 meV, which is larger than the thermal energy at room temperature. In this regard, ZnO is regarded as a promising photonic material for UV/blue devices, such as short-wavelength light emitting diodes and laser diodes. A particularly striking recent observation is that of lasing action in micron-sized rods [2,7]. ZnO has been prepared by a number of methods such as the reaction of zinc salt with base [8], chemical bath deposition [9],

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thermal decomposition [10], hydrothermal synthesis [11], sol–gel methods [12], template methods including the use of alumina membranes [13], and vapor phase transport [2].

One-dimensional (1-D) semiconductor nanostructure is of interest since it offers highly unique and interesting optical, electrical, mechanical and thermochemical properties for nanodevice applications like light-emitting devices [14] and chemical sensors [15].

In this work, we deposited carbon nanostructure on ZnO template with different thickness of Au. Au is commonly used as catalyst for growth of 1D nanowire ZnO [2].The carbon deposited by thermal chemical vapor deposition method using palm oil as the starting material. We explore the effect of selected thickness of Au has on the crystallite orientation of ZnO by employing considered as the catalyst for the growth of carbon nanostructured material.

## METHODOLOGY

*Preparation of ZnO nanostructured thin film with different Au thickness*

$Zn(NO_3)_2.6H_2O$ was used as a starting material for nanostructured ZnO preparation. $Zn(NO_3)_2.6H_2O$ was mixed with stabilizer, HMTA and dissolved in deionized water. The solution was heated at 60°C with stirring for 2 hours, aged for 24 hours at room temperature with continuous stirring. A thin film of Au was sputter deposited onto the substrates (silicon substrates p-type) at 20 mA for 30, 60, 90 and 120 sec (Emitech K550x Sputter Coater). Coated substrates were annealed at 500°C for 30 min to ensure robust adherence of Au on the substrate. The substrates were immersed vertically in the prepared solution of ZnO for 15 hours at 80°C in dry oven. The substrates were then spanned at 3000 rpm for 20s and were heated at 150°C for 1 hour. Annealing process was then done at a chosen temperature of 600°C for 1 hour to obtain the respective oxides.

*Deposition of carbon nanostructured material on ZnO nanostructured template*

Carbon nanostructure materials were deposited in a horizontal 2 furnace system by a thermal chemical vapor deposition method. Palm oil was chosen as the starting material because of the natural hydrocarbon source. Before switching on any of the furnaces, argon gas was purged for a few minutes for complete removal of air from the reaction chamber. The flow rate of the carrier gas (argon) was set at 30 ml/min. The second furnace was switched ‘on’ and kept at 850$^{o}$C for ~ 30 minutes. After this, the first furnace, which had the precursor palm oil, was switched ‘on’ and kept at 450$^{o}$C. The vapors from palm oil were driven by the carrier gas to the second furnace where ZnO nanostructure template. The carbonaceous vapor of the palm oil while passing over template breaks leading to formation of carbonaceous material on the ZnO nanostructure template. The materials were collected and characterized using scanning electron microscopy (JEOL JSM-636 OLA), X-ray diffraction (RIGAKU D-max) and Fourier Transmission Infrared (Perkin-Elmer Spectrum One 4035).

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## RESULTS AND DISCUSSION

Upon the deposition of carbonaceous materials on the ZnO nanostructure template, the resulting material showed the presence of interesting nanostructure. XRD analysis measurements were employed to investigate the composition of the synthesized materials as shown in Fig. 1.

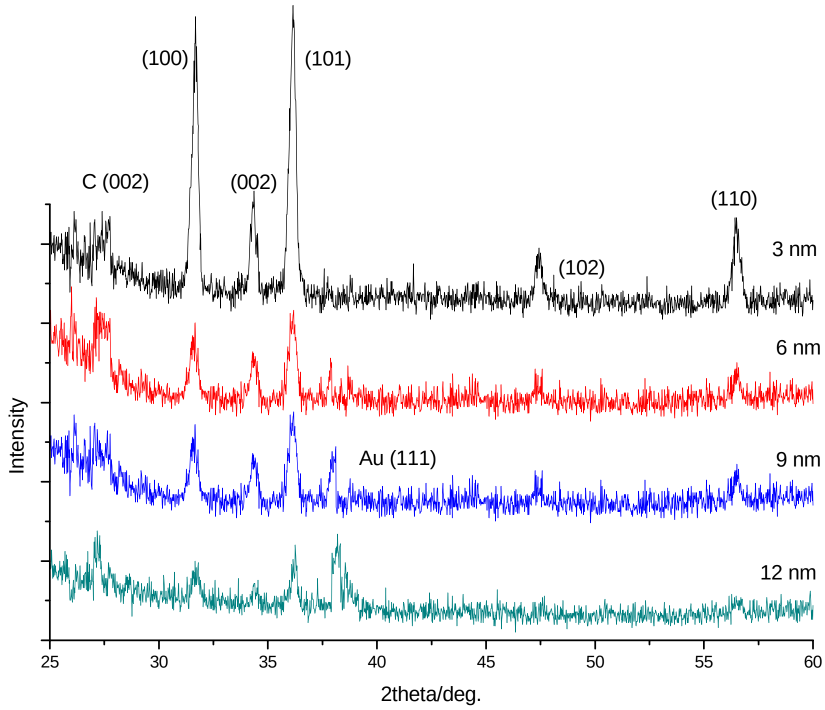


Figure 1: XRD patterns of carbon nanostructure material grown on ZnO template in different thickness of Au coated on Si substrate

The XRD peaks of the composite correspond well with the reported values of ZnO (JCPDS 36-1451). The diffraction angles at $2\theta$ = 31.84°, 34.58°, 36.36°, 47.36° and 56.64° can be assigned to (100), (002), (101), (102) and (110) planes of ZnO, respectively. The peaks are consistent with the standard pattern for hexagonal ZnO. The peak at 26.06° is attributed to the characteristic peaks of carbon structure or graphite (002) which confirmed the existence of carbonaceous material [16]. Au (111) peak also appear at 38.12° with proportional intensity to thickness. At 3 nm Au thickness, we observed sharp intense peaks of ZnO nanostructure but the intensity is lower at 6, 9 and 12 nm Au thickness. This is due to higher existence of carbon structure on the surface of the ZnO nanostructure template. The direct evidence of the formation of carbon nanostructure on the surface of ZnO nanostructure template is given by SEM in Figure 2.

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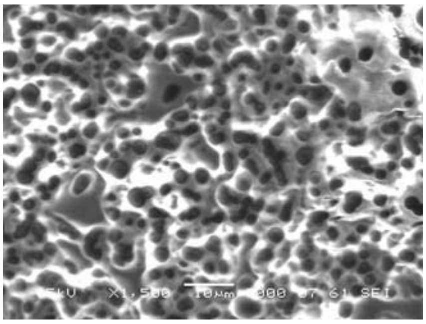
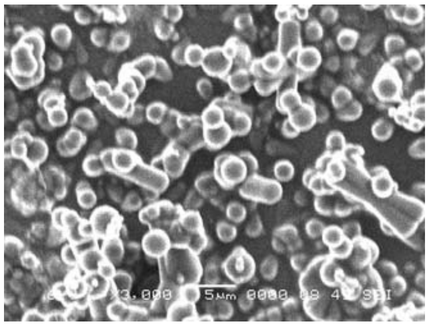
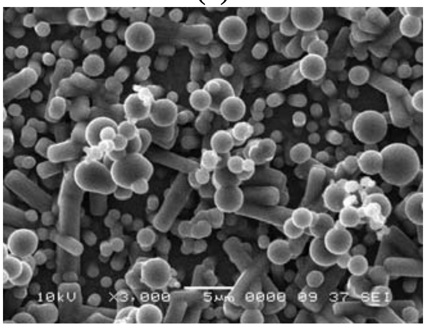


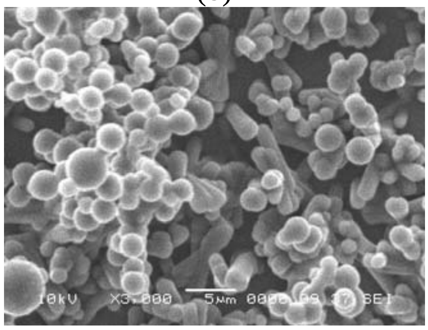
(a)



(b)




(c)



(d)

Figure 2: SEM micrographs of carbon nanostructure grown on ZnO nanostructure template in different Au thicknesses of (a) 3 nm (b) 6 nm (c) 9 nm (d) 12 nm.

It can be observed that the carbonaceous structure uniformly grow on the surface on ZnO nanostructure material at 850$^{o}$C. From Figure 2(a) a black sphere-like carbonaceous structure clearly visible on the surface of the ZnO template. Most of the carbonaceous materials are uniform with diameters ranging from 550 nm to 900 nm. The morphology of the ZnO nanostructure template consists of elongated particles; with rod-like structure. It can be observed that most of carbon material exists individually or agglomerate with each other covering on top of the ZnO template. From the SEM micrographs, the density of the carbonaceous material increased when the ZnO nanostructure template Au thickness is higher. The density result is consistent with the SEM micrographs (Figure 2 (a) -2 (d)), in which the carbonaceous nanostructure is denser when the Au thickness is higher. Here, we found that Au thickness does play a role as a catalyst in the growth of carbonaceous nanostructure as obviously seen from the XRD data.

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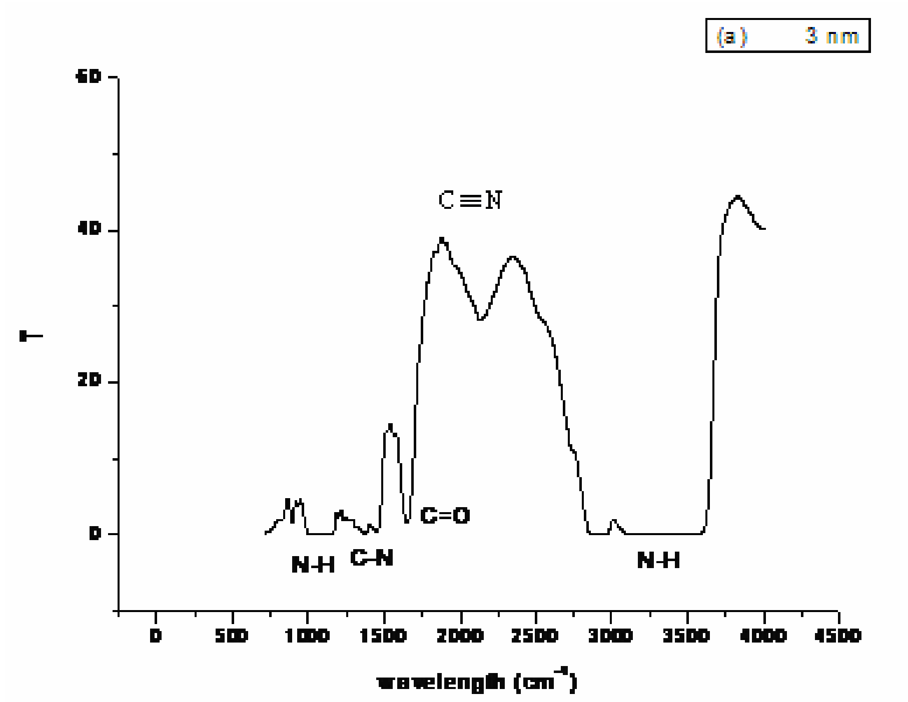


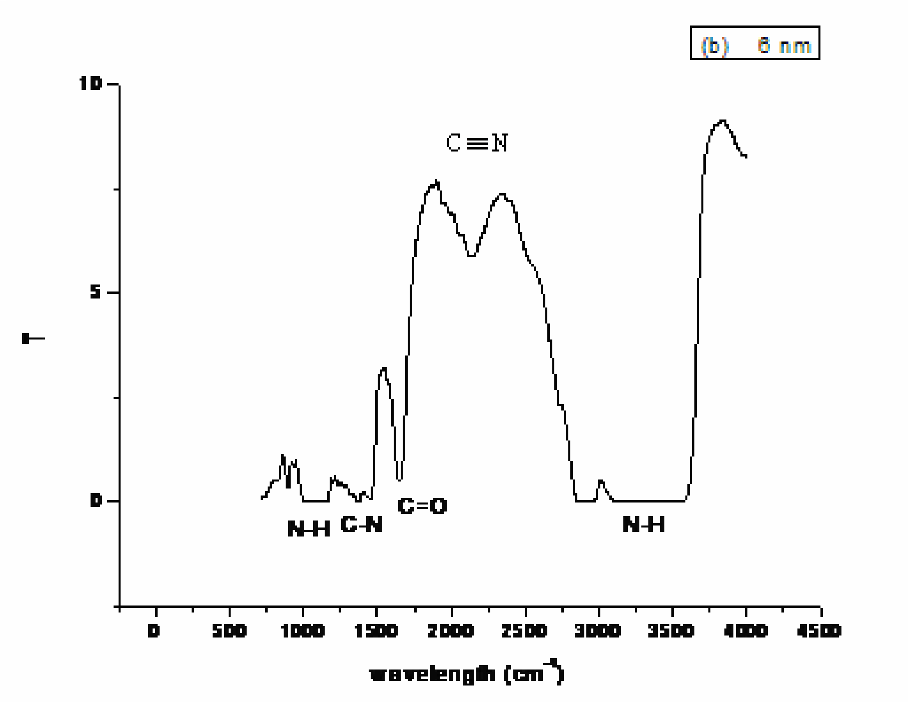


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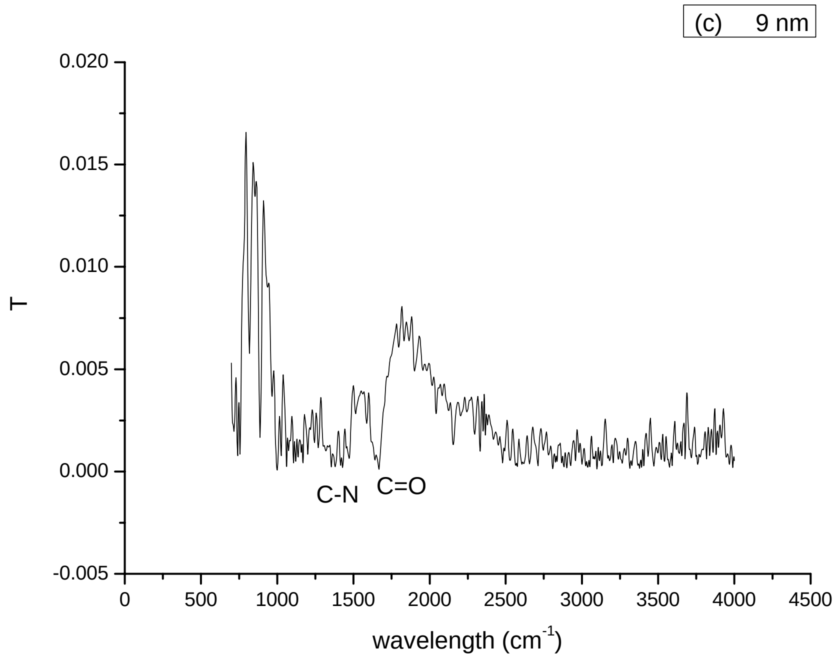


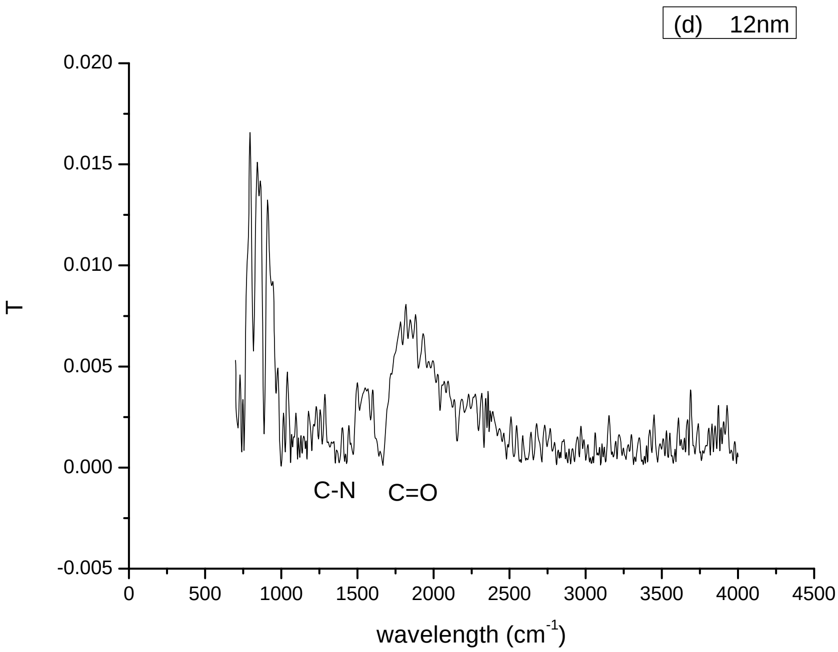


Figure 3: FTIR patterns of carbon nanostructure grown on ZnO nanostructure template on different thickness of Au coated on Si substrate

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For further confirming the chemical functional group of the as-synthesized materials, we measured the IR spectra of the carbon nanostructure grown on ZnO template in different thickness of Au as shown in Figure 3. A band at 1720 $cm^{-1}$ which is due to the stretch mode of carboxyl groups can be observed in the IR spectrum of the acidic solution from sol-gel process for preparation of ZnO template. This indicates that carboxylic acid groups formed on the surface of the ZnO template. The appearance of new bands in the range of 3600-3100 $cm^{-1}$, 900-1350 $cm^{-1}$ attributed to the N-H stretching vibration, and 1250-1000 $cm^{-1}$ assigned to C-N stretching vibration in the IR spectrum of the intermediate product, gives an unambiguous evidence of the $Zn(NH_3)_4^{2+}$ attaching to the carbonaceous material. Lower intensity at 2136 $cm^{-1}$ also visible in 3 nm and 6 nm attributed to $C\equiv N$. However, at higher Au thickness (9 and 12 nm) the $C\equiv N$ disappeared due to agglomeration of carbonaceous material on the ZnO template. The presence of N atoms is due to the stabilizer used in sol-gel process; hexamethylenetetraamine, $C_6H_{12}N_4$, (HMTA), (to chelate the $Zn^{2+}$ ions). In the IR spectrum of carbonaceous material, the band at 1720 $cm^{-1}$ attributed to carboxyl groups which may be produced by the partially decomposition of the CONH-$Zn(NH_3)_{2+}^{3}$ groups in intermediate products were observed. Au thickness at 9 nm and 12 nm (Fig. 3c and d) gave significant decrease on the growth, probably due to poor chemical reactivity at the surface and could also be due to enhanced lattice mismatch and higher strain between the nuclei and growth. Hence, it will effect the growth of carbon nanostructure on the ZnO template.

## CONCLUSION

A simple and effective method has been developed to grow carbon nanostructure on ZnO nanostructure template with different thickness of catalyst (Au). From the SEM micrographs, rod-like ZnO appeared with sphere-like carbonaceous material on the surface of the template. The density of carbonaceous material increased on the surface of the ZnO template as the thickness of Au increased. This is confirmed with the XRD results where the carbon peak appear in all the samples but the intensity of nanostructured ZnO (100), (002), (101) were significant and planes of (102) and (110) were fainter if the Au thickness is higher. This is due to the agglomeration of carbonaceous material on the template. From the IR result, zinc-ammonium complex ion covalently attached to the carbonaceous material on the ZnO nanostructure template through the C-N bonds.

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