Synthesis and characterization of vertically aligned multiwall carbon nanotubes (VA-MWCNTs) coated with silver thin films

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Due to the unique circumstances and characteristics of carbon nanotubes and properties of silver, Ag/MWCNT can be a good promising hybrid metal containing material in the field of composites. To this end, we synthesized Vertical Aligned Multi-walled Carbon nanotubes (VA-MWCNT) using plasma enhanced chemical vapour deposition (PECVD) on silicon wafer through a thin nickel catalyst layer at a temperature of 650 °C. Silver Nano layers were deposited on the surfaces of VA-MWCNTs via DC-magnetron sputtering with thicknesses of 20, 35, 60, 85 and 100 nm. Formation of silver layers on the surfaces of carbon nanotubes can attribute to different fundamental to industrial applications such as increasing antibacterial activity and biosensors. Influence of different growth conditions on the structure and composition of these layers were investigated by field emission scanning electron microscope (FESEM) and atomic force microscope (AFM) and X-ray diffraction, respectively.

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1. Introduction

Nanotechnology deals to design, manipulate, construction, production and application of structures of the order of 100 nm or less. Structures, such as nanoparticles, quantum dots, quantum wires, nanofibers and nanocomposites have found many applications [1]. Carbon nanotubes with their one-dimensional structures, due to the special characteristics of electronic, mechanical, catalytic, have been proposed for various applications [2]. Silver properties like good reflectivity, good electrical conductivity and antibacterial activity can sit on carbon nanotubes and enhance their properties [3-4]. One of the favorite topics is production of hybrid materials based on multiwall carbon nanotubes (MWCNTs) with various metal-containing nanoparticles or coatings deposited specially such as silver on their surface. These materials are promising sources for new reinforced composites with metal matrices as well as for construction of new catalytic and sensor devices.

Recently, nanoparticles of gold, platinum and silver have been added onto multi-walled carbon nanotubes using different methods such as chemical oxidation, electrostatic deposition or physical adsorption [5]. Formation of silver layer on the surface of carbon nanotubes can be followed for a variety of applications such as molecular gas absorption [6], improved field emission properties [7], enhancement of antibacterial activity [8] and biosensors [9].

On the other hand, one of the favorite topics is production of hybrid materials based on multiwall carbon nanotubes (MWCNTs) with various metal-containing nanoparticles or coatings deposited specially such as silver on their surface. These materials are promising sources for new reinforced composites with metal matrices as well as for construction of new catalytic and sensor devices. Fabrication of one dimensional Ag/multiwall carbon nanotubes nano-composite using the electroless silver plating process has been reported [10]. In this study, silver was deposited by direct current sputtering onto multiwall carbon nanotubes. Also, the main goal of the study is to finding the best condition for preparation of vertically aligned carbon nanotubes coated with silver and study silver matrices composites, the role of reinforcement component in the augmentation of conductivity. In this study, a layer of silver was deposited by direct current sputtering onto carbon nanotubes.

2. Experimental details

2.1. Preparation of samples

In the first step, Si substrates were washed and cleaned ultrasonically by alcohol and acetone. Then, they were cleaned by standard RCA method for removing the surface contaminants (washing with a solution containing ammonia, hydrogen peroxide and deionized water with a

1:1:5 Volume ratios). Finally, they were rinsed in deionized water and were blow-dried by air.

In the next step, a thin layer of nickel was deposited by electron beam evaporation on the substrate surface. The conditions are given in Table 1.

Table 1. Nickel catalyst layer deposition conditions

Temperature (°C)	120
Layer thickness (nm)	9
Substrate	Si

After this stage, carbon nanotubes were grown on the surface of the catalyst nickel layer of 9nm thickness by the DC-PECVD facility SensIran PE-802 model. The presence of nanometric sites on the surface of catalyst layer is necessary for growing carbon nanotubes. The samples were placed in the quartz tube and it was evacuated up to 5×10^{-4} Torr via a two-stage rotary and a turbo mechanical pumps. By the heating system, the temperature of the samples reached to120˚C and was kept constant for 15 minutes with a 20 sccm blowing of hydrogen gas, up to nanoscale Ni islands to form. At this time, by turning on the hydrogen DC plasma (30 mA current and 500 Volt), for a 5 minutes time interval in a temperature of 650˚C, nickel atoms continues to find Kinetic Energy to merge with each other and entering into the amorphous nickel layer and changing it to a crystalline structure. For the synthesis of multi-walled carbon nanotube, we used this technique which generally has been used [11]. Under the appropriate conditions of temperature and plasma, nanometric islands were formed. In the final stage, acetylene gas (C_2H_2) with a flow of 4.5 sccm was introduced into the system, as the carbon source. In this case, the current and voltage was set at 32 mA and 600 V and CNT growth time was set at 15 and 30 minutes, respectively. In the last step, the silver deposition was done using DC sputtering facility. Silver with high purity was the target for deposition. The experimental condition of this process is given in Table 2.

Table 2. Experimental conditions of silver deposition.

Base Pressure (mbar)	6.2×10^{-5}
Working pressure (mbar)	5×10^{-2}
Current (mA)	14
Voltage (V)	60
Deposition Temperature °C	35
Target to substrate Distance (cm)	8
Deposition Thicknesses (nm)	35 – 100
Gas	Argon

2.2. Characterization of samples

Surface morphology of the resulted carbon nanotubes was investigated by field emission scanning electron microscope (FESEM) operated at 20-30 kV before and after the deposition of different thicknesses of silver thin films.

The composition, phase formation and crystallinity of the samples were analysed by XRD X'Pert Pro MRD model in grazing mode, cu kα radiation source. Phase analysis was done by X'Pert High score plus software.

The structural study was characterized by the atomic force microscope Model DS-95-50E, manufactured by DME Company operating in non-contact mode.

3. Results and discussion

The FESEM images of CNTs in different growth times of 15 and 30 minutes are shown in Figs. 1- 2.

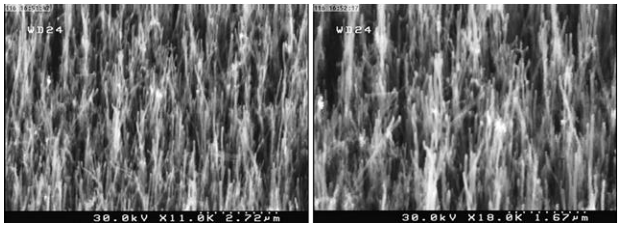

Fig. 1. FESEM images of carbon nanotubes (30 min growth times).

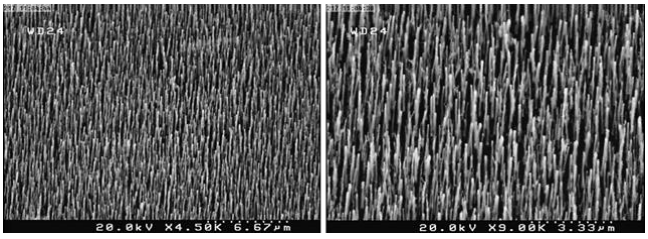

Fig. 2. FESEM images of carbon nanotubes (15 min growth times).

As can be seen from Fig. 1, the nanotubes have more opportunity to growth and thus have a greater height. It's the height of nanotubes attached to each other at various points. In these circumstances, there is a greater density of nanotubes. In the shorter nanotube growth time, the tubes with lower density and lower elevation are independent of each other. In order to study the changes on the structure of the nanotubes and the best view of these changes, the less favorable growing time is more suitable. In shorter time (Fig. 2) nanotubes have been grown with lower density and height and are independent of each other. So to study structural changes on CNTs, shorter time is optimal. FESEM images of samples after deposition of silver shown in Fig. 3 and Fig. 4.

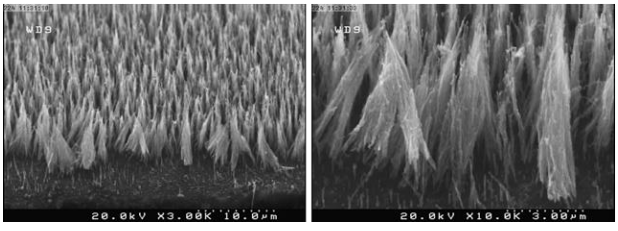

Fig. 3. FESEM images of carbon nanotubes with 30 min growth time and 20 nm silver deposition.

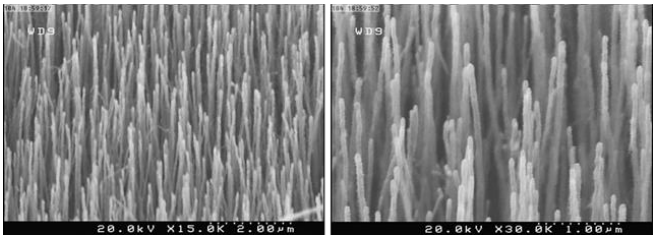

Fig. 4. FESEM images of carbon nanotubes with 15 min growth time and 60 nm silver deposition.

Fig. 5 gives the atomic force microscope phase of the same sample (Fig. 4). Using phase images obtained from the microscope, we can get information about the elements and find that how they are distributed over the surface. The red dots represent silver, green dots represent the carbon and blue spots indicate the presence of nickel.

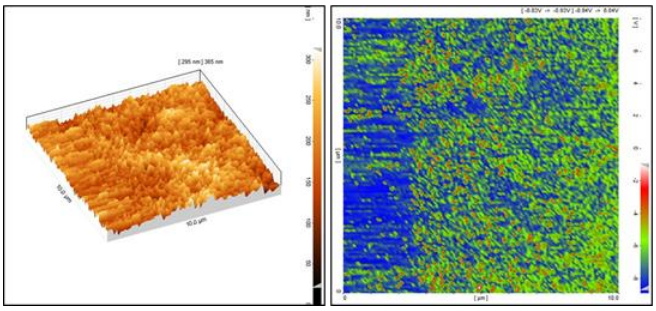

Fig. 5. Atomic force microscope Topography (left) and Phase (right) images of the sample with 60 nm silver deposition.

According to FESEM images, the sample with 60 nm deposition of silver has a better order and aggregation in respect to other samples. Thus, the result of XRD was more eligible. Fig. 6, shows the XRD pattern for this sample.

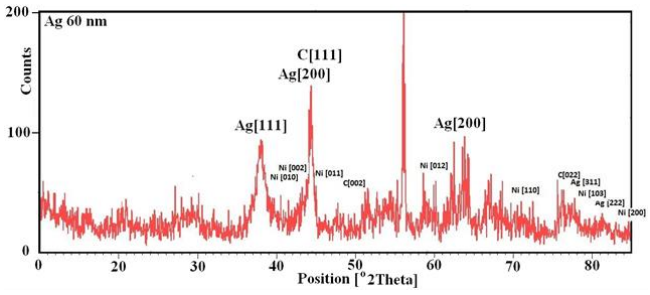

Fig. 6. XRD pattern of the sample with 60 nm silver deposition.

As can be seen in Fig. 6, the peaks are all belong to Silver (Ag), Carbon (C) and Nickel (Ni) and no chemical composition has been detected. The peaks at angles 38.1°,44.4°, 64.2°, 77.5° and 81.5° are belong to silver with cubic crystal structure and those at angles of 44.3°,51.6° and 75.9° belong to carbon with the same crystal structure, whereas the peaks at angles 39.1°, 41.5°, 44.5°, 58.4°, 70.9°, 78° and 84.2° are respect to nickel with hexagonal crystal structure. The preferred orientation for both carbon and silver is (111) direction and represents that silver is in line with carbon nanotubes.

4. Conclusions

In the stages of growth and deposition, we found that deposition process and thickness of catalyst layer has a great effect on the growth and distribution of carbon nanotubes over the surface. Also, in smaller growth time, the tubes distribute over the surface with lower density, but completely vertical. In this case tubular structure is preserved and their structure and morphology is more suitable. Silver deposition rate must be pretty slow to sit uniformly on nanotubes. As we have seen higher deposition rates causes the nanotubes to join together and gets them away from the vertical mode. As a result, we cannot investigate the effects of silver embedded onto the nanotubes. XRD is an evidence for phase identification, gives the crystalline structure and directions of nanostructure ingredients and we can see that no chemical composition has been recorded in the samples. The atomic force microscopy phase image is a further evidence for the presence of silver.

Acknowledgments

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