MWCNTs - Ni-Cu NPs @ a-C:H thin films: Study of relation between the average diameters of CNTs with optical density and topological characterizations

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Research Article

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Abstract

In this paper, Ni-Cu NPs @ a-C:H thin films with different content of cooper by co-deposition of RF-sputtering and RF-plasma enhanced chemical vapor deposition (RF-PECVD) were prepared from acetylene gas and Ni and Cu targets. The prepared samples as catalysts for growing multi-wall carbon nanotubes (MWCNTs) were used from liquid petroleum gas (LPG) by thermal chemical vapor deposition (TCVD) at 825 °C. The films deposited with 5% Cu have minimum value the average diameter of CNTs and were about 100 nm. The fractal dimensions and structural characteristics as well as optical density of Ni-Cu NPs thin films have been investigated. AFM images can estimate the lateral size of the nanoparticles on the films surface. These values for Ni NPs without Cu NPs @ a-C:H thin film and with Cu NPs thin film contenting 5%, 40%, 75% Cu are obtained about 7.2, 5.34, 6.04 and 11.16 nm respectively. The optical density ($D_{opt}$) of thin films was obtained from the relation $D_{opt} = \alpha t$. Films deposited with 75% Cu have maximum value of optical density specially in high energy. The spectral density power of all layers reflects the reverse flow changes, especially in the high spatial frequency region, indicating the presence of fractal components in prominent topographies. Films deposited with 75% Cu have minimum value of fractal dimension. The diagram of the Bearing Area proportion the height shows the percentage of cavities and single-layers. It can be seen that the single-layer content of all films were about 95%.

1. Introduction

Carbon nanotubes (CNTs) have attracted much attention due to their exceptional optical, electrical and mechanical properties and attractive potential applications [1–4]. There are three main ways to grow CNTs: arc discharge [5], laser ablation [6] and chemical vapor deposition (CVD) [2, 7, 8]. Among different methods, the CVD technique has attracted much attention owing to its advantages including lower cost, high purity, high yield and selective growth of CNTs. In the CVD method, the characteristics of CNTs such as surface density, morphology, crystallization and diameter distribution are significantly affected by the synthesis parameters ranging from growth temperature, hydrocarbon source, pressure and type of substrate to the catalyst characteristics including its morphology, composition and the technique of catalyst preparation [9–15]. Transition metals such as Ni, Fe, Co and their alloys or compounds have been widely used as the catalysts [15]. There are different physical or chemical approaches for catalyst preparation such as sol–gel, reverse micelle, electron gun evaporation, ion beam sputtering and thermal evaporation [16–20]. One important aspect to take into account is the substrate onto which the CNTs are grown. For these utilizations, electrically conductive materials are needed, acting as electrodes, where high currents are injected by CNTs, and are mostly limited by the contact resistance [21]. Metals like copper (Cu) for such applications are preferred, because of the high thermal and electrical conductivity, combined with a low economical cost [22]. The direct growth of CNT on Cu would provide good electrical contact to the CNT [23]. At the same time, the growth of carbon nanotubes directly on metallic substrates also resolves the problem of adhesion of nanotubes layers [24]. We have studied Ni nanoparticle catalyzed growth of multi-walled carbon nanotubes (MWCNTs) on Cu substrate. Morphology and electrical and optical properties of Cu nanoparticles thin layer is affected by Cu content and each of them
is effective parameter on growth of MWCNTs based on Ni nanoparticles catalyst [25]. Nickel-copper nanoparticles (Ni-Cu NPs) have attracted attention due to their potential application in magneto-optical recording, spintronic and data storage devices, interconnects, and their giant magnetoresistance (GMR) [26].

2. Experimental Details

Ni-Cu NPs on the amorphous hydrogenated carbon (a-C:H) thin films with different Cu concentration were prepared by a capacitance coupled radio frequency - plasma enhanced chemical vapor deposition (RF-PECVD) system with 13.56 MHz power supply. The reactor consists of two electrodes with different area size. The smaller electrode was copper plate as a powered electrode. The other electrode was grounded via the body of the stainless steel chamber. The deposition was performed at room temperature on the glass and silicon substrates on this electrode. The chamber was evacuated to a base pressure of about $10^{-5}$ mbar prior to the deposition and then was raised to desired ambient pressure with acetylene gas. The deposition was done in two trends, constant RF power and constant initial pressure trends. In the first trend, the power was kept at 200W and the initial gas pressure was set at different pressures from 0.03 to 0.05 mbar. Samples by different content of Cu were prepared in this trend with initial pressure of 0.05, 0.04, 0.035 and 0.03 mbar. In the second trend, the initial pressure was set at 0.03 mbar and the power was kept at 200, 220, 230 and 240 W for samples, respectively. The deposition time of all samples was 10 min and thickness of films was about 100 nm. We obtained the Rutherford Back Scattering (RBS) spectra of the samples by protons with energy 2 MeV. The thickness and atomic content of the films were obtained from RBS data by SIMN-RA software simulation. SIMN-RA is software for the simulation of backscattering spectra for ion beam analysis with MeV ions. Three steps must be performed for calculation of backscattering spectrum. In a first step the experimental situation (incident ions, geometry) has to be defined, then the target must be created, and in the third step the cross-sections used for the calculation have to be chosen. AFM in non-contact mode was used to obtain the surface topography of the films and the average size of nanoparticles. The optical properties of the samples were obtained from their UV–Visible spectra. The Surface Plasmon Resonance absorption peak was obtained by a double beam UV–Visible spectrometer in the range of 300–800 nm.

3. Results And Discussion

The SEM images of CNTs grown on Ni NPs without CuNPs @ a-C:H thin film and with Cu NPs @ a-C:H thin film contenting 5%, 40%, 75% Cu are shown in Figs. 1(a-d), respectively. By adding Cu NPs thin film the density of the CNTs is greatly enhanced. Furthermore, the average diameter of the grown CNTs increases by increasing of Cu content of thin film. The average diameter of the grown CNTs on the Ni-Cu@a-C:H with Cu content of 5%, 40% and 75% Cu are obtained about 100, 120 and 160 nm respectively. Figure.1(e) shows SEM image of carbon onion made on the Cu NPs @ a-C:H thin film without Ni NPs. As it is clear from this figure, MWCNTs are not formed on the Cu NPs @ a-C:H and one can conclude that Cu by itself has no catalyst property in production of CNTs growth as was reported in reference [27].
Ni-Cu NPs @ a-C:H catalyst lm were determined by RBS spectra, AFM images, UV-Visible spectroscopy. Cu, Ni, O, C and Si contents of the samples were obtained from RBS spectra. Figure 2 shows RBS spectra for Ni NPs with Cu NPs @ a-C:H thin layer contenting 5%, 40% and 75% Cu as a function of the incident ions energy. The small step at 850 KeV is related to C nuclei. The steps at 650 and 1050 KeV is due to O and Si nuclei of amorphous SiO2 substrate respectively. The peak between 1450 and 1550 KeV is attributed to Cu and Ni nuclei. The results of SIMN-RA software simulation of RBS spectra indicated that the different thin film with 5%, 40% and 75% Cu and their thickness is about 89, 124 and 113 nm respectively [28]. The XRD profile show that the prepared Ni NPs and Cu NPs have fcc crystal structure.

The AFM images of nanoparticles on the surface (20 nm × 20 nm) of the thin films are shown in Figures 3(a–d) respectively. Atomic Force Microscopes (AFM) are a group of scanning probe microscopes that, in addition to being able to be imaged in a non-vacuum environment, can also take biological and non-inductive samples. These images can estimate the lateral size of the thin films on the sample surface. The AFM values of CNTs grown on Ni NPs without Cu NPs thin film and with Cu NPs thin film contenting 5%, 40%, 75% Cu are obtained about 7.2, 5.34, 6.04 and 11.16 nm respectively. The lateral size changes of nanoparticles on the surface of the thin films are shown in Figure 4, where the lateral size of the nanoparticles is estimated using the AFM image. For Ni-Cu NPs thin films Most of the lateral changes are related to sample 75% Cu, which has a large leap, while it is changing for samples 5% and 40% Cu with low slope. The nanoparticles are almost spherical in shape and deforms from spherical state with increasing Cu content. Also, the lateral size changes of nanoparticles are increased on the surface of thin films and increase with increasing Cu content.

The optical density, \( D_{\text{opt}} \) or the absorbance is proportional to both the concentration of the absorbing material and the thickness of film samples. The optical density \( D_{\text{opt}} \) of thin films can be obtained from the following simple equation: 
\[
D_{\text{opt}} = \alpha t \]
where \( t \) is the thickness of the thin film which was calculated using DEKTAK 3 profilometer method and \( \alpha \) is the absorption coefficient obtained from Lambert's equation: 
\[
\alpha = 2.303 \frac{A}{t},
\]
where A is the absorbent of the films [31]. Figure 5 illustrates the variation of the optical density \( D_{\text{opt}} \) with the incident photon energy, \( h\nu \) (eV) for Ni NPs without Cu NPs @ a-C:H thin film and Ni-Cu NPs @ a-C:H thin films with different Cu content. By adding Cu NPs thin film, the optical density for the prepared MWCNTs using Ni NPs with Cu NPs @ a-C:H containing 5%, 40%, 75% Cu enhanced with a monotonous slope. For Ni NPs without Cu NPs @ a-C:H thin film the optical density is constant between 1.5 and 2.25 eV and increases with a slope very slow after 2.25 eV.

Figures 6(a–d) show the height changes of nanoparticles on the surface relative to the axis for the prepared MWCNTs using Ni NPs without Cu NPs @ a-C:H thin layer, Ni NPs with Cu NPs @ a-C:H containing 5%, 40%, 75% Cu respectively. Since the scanning size on the surface of the layers is about 1 \( \mu \text{m} \times 1 \mu \text{m} \) by the AFM, so the maximum numerical value on the X-axis is 1 \( \mu \text{m} \). The height changes on the surface of the layers indicate that the layers have a phase change for typical sample Ni-Cu NPs @ a-C:H with 75% Cu compared to other samples, so that the layers have a phase change of about 6 nm and indicate that the layers in this case are, firstly, very smooth and, secondly, can have a phase change.
The Power Spectral Density (PSD) points of samples are extracted from 1 µ × 1 µ AFM images of Fig. 3. It can be seen that all the PSD points include of a high spatial frequency region. According to the Dynamical Scaling Theory, for a system of lateral size L, the relation P(k) and frequency k be written as:

\[ P(k) \propto k^{-\beta} \]

where \( \beta \) is calculated as the slope of the log-log in PSD of high spatial frequency. The fractal dimension of \( D_f \) by solving the \( \beta \) slope of the log-log graph is obtained: \( D_f = 4 - \beta / 2 \). Figures 7 show the spectral density change of the spatial frequency layers for the prepared MWCNTs using Ni NPs without Cu NPs @ a-C:H thin layer, Ni NPs with Cu NPs @ a-C:H containing 5%, 40%, 75% Cu respectively. The spectral density power of all layers reflect the reverse flow changes, especially in the high spatial frequency region, indicating the presence of fractal components in prominent topographies. Thus, the power spectrum method is sensitive to the size of the data set, frequency, and specific domain. This value determines the relative values of surface irregularities at different distance scales. By increasing of Cu content of Ni-Cu NPs @ a-C:H thin films, the slope of the spectral density power performance decreases, which may be due to the increase in the lateral size of the nanoparticles. The fractal dimension values of the thin films are shown in Figure 8. It is obvious that the fractal dimension values depend on the amount of Cu content. The fractal dimension values of CNTs grown on Ni NPs without Cu NPs thin film and with Cu NPs thin film containing 5%, 40%, 75% Cu are estimated about 5.6, 5.62, 5.7 and 5.53 nm respectively. Therefore, by adding of Cu NPs @ a-C:H with different contents up to 40% Cu the fractal dimension of the CNTs were enhanced and then over 40% Cu they decrease.

Figure 9 shows the bearing area versus height of thin films. It actually shows the amount of cavity (bottom curve) and single-layer (top curve) of the nanoparticles. For the prepared MWCNTs using Ni NPs without Cu NPs @ a-C:H thin film and Ni-Cu NPs @ a-C:H thin films with different Cu content, the cover coefficient of zero (cavity) is less than 10% and the single-layer content is about 95%, which is 90% isolated (between the cavity and the single-layer). The address layer did not have much effect on the amount of cavity and single-layer.

4. Conclusions

We found that the Cu NPs @ a-C: thin layer play an important role in the growth of MWCNTs based on Ni NPs catalyst. The density of the grown MWCNTs is greatly enhanced and the average diameter of the grown MWCNTs increases by increasing of Cu content of thin layer. AFM images can estimate the lateral size of the nanoparticles on the sample surface. The nanoparticles are almost spherical in shape and deforms from spherical state with increasing Cu content. Also, the lateral size changes of nanoparticles are increased on the surface of thin films and increase with increasing Cu content. By increasing of Cu content of Ni-Cu NPs @ a-C:H thin films, the slope of the spectral density power performance decreases, which may be due to the increase in the lateral size of the nanoparticles. The height changes on the surface of the layers show that the layers have a phase change about 6 nm for typical sample Ni-Cu NPs @ a-C:H with 75% Cu. By adding Cu NPs thin film, the optical density for the prepared MWCNTs using Ni NPs with Cu NPs @ a-C:H containing 5%, 40%, 75% Cu enhanced with a monotonous slope. The fractal dimension values of CNTs grown on Ni NPs without Cu NPs thin film and with Cu NPs thin film...
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Figures
Figure 1

SEM images of the prepared MWCNTs using (a) Ni NPs without Cu NPs @ a-C:H thin film, (b) Ni NPs with Cu NPs @ a-C:H containing 5% Cu, (c) 40% Cu, (d) 75% Cu, (e) prepared carbon onion particles using Cu NPs @ a-C:H without Ni NPs.
Figure 2

RBS spectra of Ni-Cu NPs @ a-C:H with 5% Cu, 40% Cu and 75 % Cu.
Figure 3

AFM images of nanoparticles on the surface of (a) Ni NPs without Cu NPs @ a-C:H thin film, (b) Ni NPs with Cu NPs @ a-C:H containing 5% Cu, (c) 40% Cu, (d) 75% Cu.
Figure 4

Changes in lateral size of nanoparticles on the surface of Ni NPs without Cu NPs @ a-C:H thin film and Ni-Cu NPs @ a-C:H thin films with different Cu content.
Figure 5

Optical density versus Energy for Ni NPs without Cu NPs @ a-C:H thin film and Ni-Cu NPs @ a-C:H thin films with different Cu content.
Figure 6

Z-height changes of nanoparticles on the surface by axis for the prepared MWCNTs using Ni NPs without Cu NPs @ a-C:H thin film and Ni-Cu NPs @ a-C:H thin films with different Cu content.
Figure 7

Power spectral density variation versus frequency k of Ni NPs without Cu NPs @ a-C:H thin film and Ni-Cu NPs@ a-C:H thin films with different Cu content.
Figure 8

Fractal dimensions of Ni NPs without Cu NPs @ a-C:H thin film and Ni-Cu NPs @ a-C:H thin films with different Cu content.
Figure 9

The bearing area versus height of Ni NPs without Cu NPs @ a-C:H thin film and Ni-Cu NPs @ a-C:H thin films with different Cu content.