CVD-growth of MWCNT arrays on Me-Ct-N-(O) thin films

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Abstract. The formation of carbon nanotubes (CNTs) arrays by chemical vapor deposition on Me-Ct-N-(O) catalyst alloys, where Ct is a catalytic metal from the group Ni, Co, Fe, Pd; Me is transition metal of IV-VII of the Periodic Table of Elements, with low content of catalyst has been investigated. It is shown that CNTs effectively grow, if the alloy contains Ti, V, Cr, Zr, Hf, Nb and Ta. The structure of CNT were studied by transmission and scanning-electron microscopy, energy-dispersive X-ray and the Raman spectroscopy.

1. Introduction

Over the quarter century since the discovery of CNTs, their unique chemical, physical and mechanical properties have been well studied [1,2]. Due to these properties, CNTs are one of the most promising materials for use in various fields of science and technology [3-5].

Electric arc discharge, laser ablation of graphite and CVD are the most common methods of CNT synthesis[2]. From the viewpoint of reproducibility and growth process control, the chemical vapor deposition method is most suitable for formation of CNT array on substrate surface. This method implements the CNT growth process in the presence of catalysts such as Fe, Co, Ni, Pd and their alloys with each other, where the cluster size determines the parameters of the tube [6, 7]. It is known that the parameters of nanotube arrays may be controlled via the support of the catalytic metal by oxides of non-catalytic elements Al2O3, SiO2, MgO [8, 9]. The authors [10,11] have reported about the use of the alloys of these catalysts with other metals, wherein the catalyst content is predominant. Yue Hu et al. in [12] have demonstrated an interesting method of catalyst preparation for the growth of single-walled CNTs. However, the method of preparation of such catalyst is rather complicated. In [13] it was shown that the array of multiwall carbon nanotubes can be formed on a thin film of catalyst-containing Nb-Ni-N-(O) amorphous alloy with low (~10 at.%) content of Ni. Distinctive feature of this process is that it can be performed on Nb-Ni-N-(O) alloy films of varying thickness, which makes it technically attractive.

In the present study we demonstrated that a similar process can be carried out on a number of alloys of catalyst with other transition metals V-VII of the Periodic Table of Elements. This process is dependent on a wide range of factors that allows you to control the parameters of CNT arrays, such as height, density and diameter.
2. Experimental

In this work were used (100) Si substrate, coated with SiO₂ layer. The substrates were washed in standard CARO solution (H₂SO₄:H₂O₂ = 1:1), and then rinsed in deionized water and dried in isopropanol vapor.

In alloy composition Me-Ct-N the element Ct was selected from the group Ni, Co, Fe, and Pd; element Me – from the group Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, W and Re. Alloy layers with thickness from 10 to 500 nm with a catalytic metal content of 6–40 at.% and different nitrogen content were deposited on an unheated substrate by magnetron sputtering of a composite target Ct-Me in the atmosphere of argon or mixture of argon and nitrogen at a residual pressure in the chamber of $1 \times 10^{-5}$ Torr and a working gas pressure of $5 \times 10^{-3}$ Torr. Nitrogen content in the gas mixture Ar+N₂ varied in the range 0–10 vol.%. CNTs were grown by CVD using Oxford PlasmaLab System 100 plasma etcher. CNT growth was carried out in CVD mode without plasma in the flow of acetylene with the addition of ammonia. Reactive gas flow for all the samples was constant. We varied the following parameters: synthesis temperature (in the range 400–750°C), synthesis time and the time of holding the sample at temperature of synthesis prior to supplying reactive gas.

CNTs samples were investigated using dual-beam scanning electron microscope FEI Helios NanoLab 650 i, transmission electron microscope FEI Tecnai G² 20 S-Twin, equipped with EDAX energy dispersive X-ray spectrometer and HAADF detector, Horiba Scientific Lab RAM HR Evolution Raman spectrometer equipped with lasers with wavelength of 514.5 nm and 633 nm.

3. Results and discussion

Figure 1 shows the SEM image of CNTs grown on 20 nm thick film of the Zr-Co-N- (O) alloy. It should be noted that the array looks like rather dense forest of CNTs, about 9 μm in height.

![Figure 1. The morphology of CNT sample grown on Zr-Co-N-(O) alloy film at 600°C.](image)

We found that CNT diameter depends on the metal Me, one of the components in the alloy. The thinnest CNTs were obtained on the alloys containing zirconium, while the thickest were synthesized on the vanadium alloy. It should be noted that CNT growth was not observed on W-Ni-N-(O), Re-Ni-N-(O), and Ta-Pd-N-(O) alloys. Instead free-shape carbon buildups were synthesized as shown in Figure 2. Size of free-shape buildups ranged from 50 to 200 nm.
Figure 2. The morphology of free-shape carbon buildups sample grown on W-Ni-N-(O) alloy film at 650°C.

In the Raman spectrum of CNTs shown in Figure 2, D (1345 cm$^{-1}$), G (1580 cm$^{-1}$) and 2D (2700 cm$^{-1}$) peaks are present. The separation of D and G peaks and the ratio $I_D/I_G \approx 0.90$, indicate both good quality, and the presence of defects in the CNTs structure [14]. In turn, the presence of intense 2D (or G') peak in spectrum indicates sufficient quality of carbon structure [15]. For other CNTs obtained on Me-Ct-N-(O) alloys, the positions and separation of the peaks in Raman spectra are substantially the same; minor changes were observed only in $I_D/I_G$ ratio.

Figure 3. Raman spectra of CNT grown on a thin film of V-Ni-N-(O) alloy thickness of 20 nm at 600°C.
Figure 4 shows the results of investigation of nanotubes by transmission electron microscopy. On the high-resolution image we can see that the nanotubes are multiwall. Some of them have inclusions in the internal channels of CNTs. EDX spectrum of the inclusion is also shown in Fig. 4. From the spectrum we can conclude that this inclusions are the particles of the catalytic metal Ni.

Figure 4. Energy dispersive X-ray spectrum of a single CNT with metallic inclusions (right). High-resolution TEM image of the object, where location of the analysis is marked by a circle. (left).

4. Conclusions

In commonly used methods of growth of carbon nanotubes, the catalyst particles are formed on the surface of a solid body through evaporation of extremely small amount of catalyst. This method is difficult to incorporate into integrated technology where the devices are formed on substrates of large diameters, since even slight variations of thickness cause substantial change of size and the number of clusters and therefore leads to the formation of CNTs differing in diameter and a height at different substrate areas.

The attractiveness of proposed process of CNT growth on the films of catalytic metal alloys with metals IV-VII of the Periodic Table of Elements is a broad set of factors for process control that allows you to manage the parameters of the nanotube arrays, such as height, density and diameter. Our experiments have shown that CNT growth is possible on thin alloy films of various thickness and conductivity. All this enables embedding of this process into integrated technology.

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