Growth of vertically aligned multiwalled carbon nanotubes forests on metal alloy Ni-Nb-N with low content of catalyst

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Abstract. This research shows the possibility of carbon nanotubes (CNTs) formation on the surface of low nickel (~ 10 at.%) Ni-Nb-N amorphous metal alloy film by CVD method at 550 °C of the gas mixture based on acetylene. The structure of CNT were studied by transmission and scanning-electron microscopy, energy-dispersive X-ray and the Raman spectroscopy.

1. Introduction

A recent report by ITRS (International Technology Roadmap for Semiconductors) [1] predicts that by 2023 the use of the semiconductor interconnects based on Cu and W will reach it's physical limit in terms of reliability, dimensions, electrical and thermal conductivity. Scaling of VLSI technology increases the interconnect resistance in 5-10 times as compared with the volume value associated with the scattering at the grain boundaries and surfaces [2]. As a result of increased interconnect lines resistance and the number of transistors per unit area will increase the power dissipation, which is a serious problem for modern VLSI technology and future 3d integrated circuits [3].We should not forget about the fact that the production of interconnects of smaller size and higher aspect ratio is a complicated and time-consuming task [4].

One alternative material for semiconductor interconnects is carbon nanotubes are [5] due to their high thermal conductivity [6], low resistance value [7] and the ability to withstand high current densities (up to 10^{12} A/cm^2).

For the synthesis of carbon nanotubes using laser ablation techniques, arc discharge, chemical vapor deposition (CVD) and variations thereof [8,9]. The most preferred method of synthesis of CNTs, embedded in the VLSI technology, considered PECVD-method which allows to obtain the uniform arrays of CNT with desired density on the surface of the solid phase in a suitable temperature range for VLSI technologies [10]. This method is implemented in the presence of catalysts such as Fe, Co, Ni and alloys thereof [11]. Often the catalyst metal is supported by layers of other catalytic metals and oxides (Al_2O_3, SiO_2, MgO), that allows you to control the parameters of the nanotube arrays, up to the cultivation of single-walled nanotubes. [12] There are also reports on the use of these catalysts, alloys with other metals, in which, however, the content of the catalyst is always predominant [13].

In this study we demonstrated CNT growth at 550°C, using a thin Ni-Nb alloy film containing Ni (~ 10 at.%) with addition of nitrogen as a catalyst. The use of Ni-Nb-N alloy as a catalyst will produce reproducible and controlled CNT synthesis on thin catalytic films with different thicknesses, as well as to carry out dry etching operation without the danger of etching of a thin layer of catalyst.

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2. Experimental

In work were used Si substrate (100) orientation, coated with SiO_2 layer. The substrates were standard KARO washing solution (H_2SO_4: H_2O_2 = 1:1), followed by rinsing in deionized water and dried in isopropanol vapor.

Formation of a thin layer of Ni-Nb-N alloy was produced on a heated substrate in an atmosphere of Ar + N_2 by magnetron sputtering using a composite target Nb-Ni. The residual pressure in the chamber was about 1×10^{-5} Torr, working gas pressure - 5×10^{-3} Torr.

The CNTs synthesis was carried out by PECVD on the «Plasmalab System 100» made by «Oxford Instruments». CNT formation process occurs in the gas mixture of C_2H_2 + NH_3 at 550°C substrate temperature and a pressure of 3 Torr. CNT growth process occurred within 2 minutes.

CNTs samples were investigated with a scanning electron microscope (SEM) Helios NanoLab 650i, transmission electron microscope (TEM) Tecnai G2 20 S Twin, equipped with EDAX attachment for EDS, by FEI, and Raman spectroscopy on the LabRAM HR Evolution by «Horiba Scientific», with the laser wavelength 514.5 nm.

3. Results and discussion

Investigation by SEM Energy Dispersive X-Ray Analysis (EDX) showed that the film composition of the initial alloy (at.%) was $Ni_{10}Nb_{30}N_{40}O_{20}$.

Investigation by TEM showed the thin alloy film is in an amorphous state, as shown in Figure 1a. This fact confirms the diffraction pattern of the film, having the form of a diffuse halo (inset figure 1a) [14]. It should be noted that at a temperature synthesis of CNTs film is completely crystallized and diffraction pattern takes the form of rings [15]. Crystallization of the thin film layer is accompanied by the appearance of two kinds of catalyst particles of different average size on the substrate surface. As can be seen in Figure 1b average size of large and smaller clusters is about 40 nm and 6 nm, respectively. These two types of catalyst particles, enriched with nickel, are the initiators of the subsequent CNT growth (Figure 1c) [16].

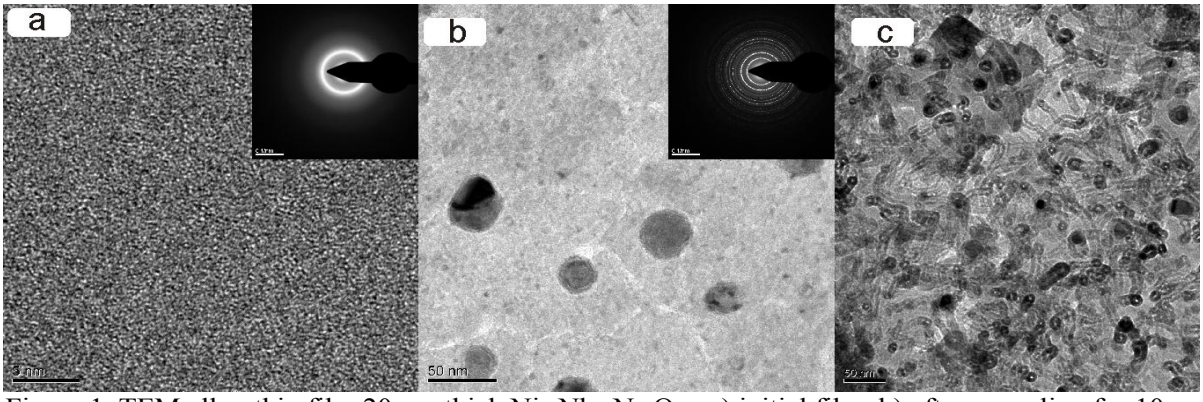


Figure 1. TEM alloy thin film 20 nm thick $Ni_{10}Nb_{30}N_{40}O_{20}$: a) initial film; b) after annealing for 10 minutes at 550°C; c) after the process of synthesis of CNTs at 550°C for 7 seconds.

Figure 2 shows a SEM-picture of a CNT array grown on 20 nm thick film of $Ni_{10}Nb_{30}N_{40}O_{20}$ at substrate temperature of 550ºC in the course of 2 min. Analysis of images revealed that there are two kinds of array with different heights and diameters of tubes. CNTs arrays have a height of about 2.6 and 12 μm (Figure 2). The average diameter of the nanotubes: small array ~20nm; high array ~60 nm.

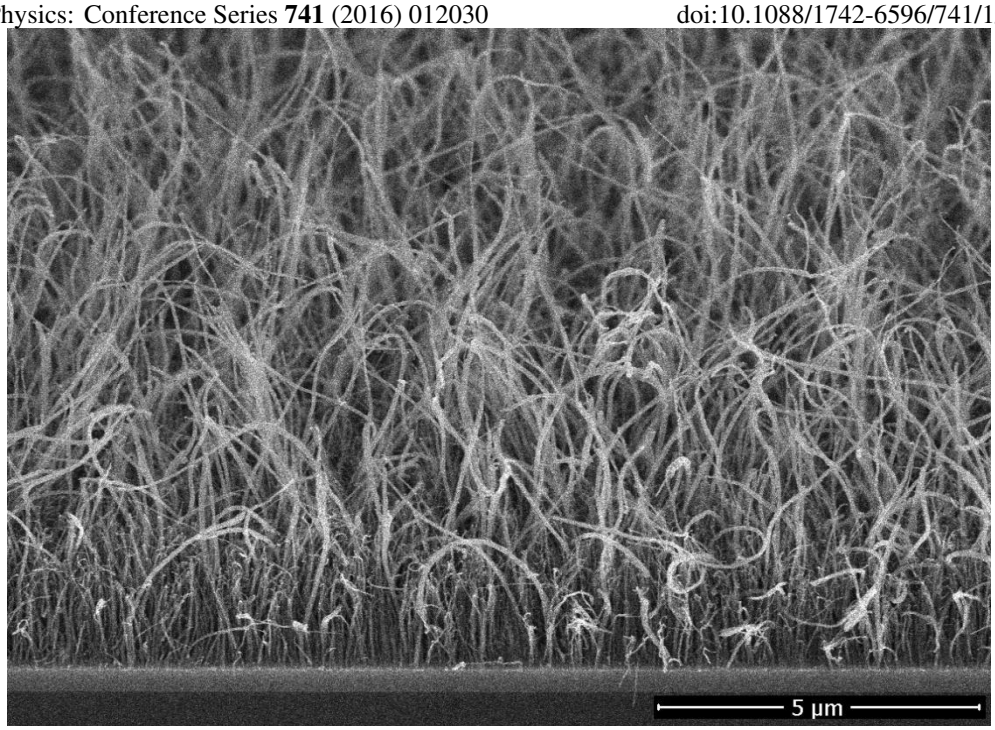


Figure 2. The morphology of CNT sample grown on $Ni_{10}Nb_{30}N_{40}O_{20}$ alloy film at 550°C.

The Raman spectrum of CNTs (Figure 3) shows a well-separated peak D-1350 cm^{-1} and G-peak at 1580 cm^{-1} whose intensity ratio is 0.97, indicating a high quality of the structure [17]. At the same time close the ratio I_D / I_G to one indicates the presence of a large number of defects in the sample of CNTs that TEM microscopy confirms the presence of crystalline structure disorders. Raman-spectrum shows the presence of a sufficiently intense 2D (or G ') peak at 2700 cm^{-1} inherent in high-quality material based on graphite [18].

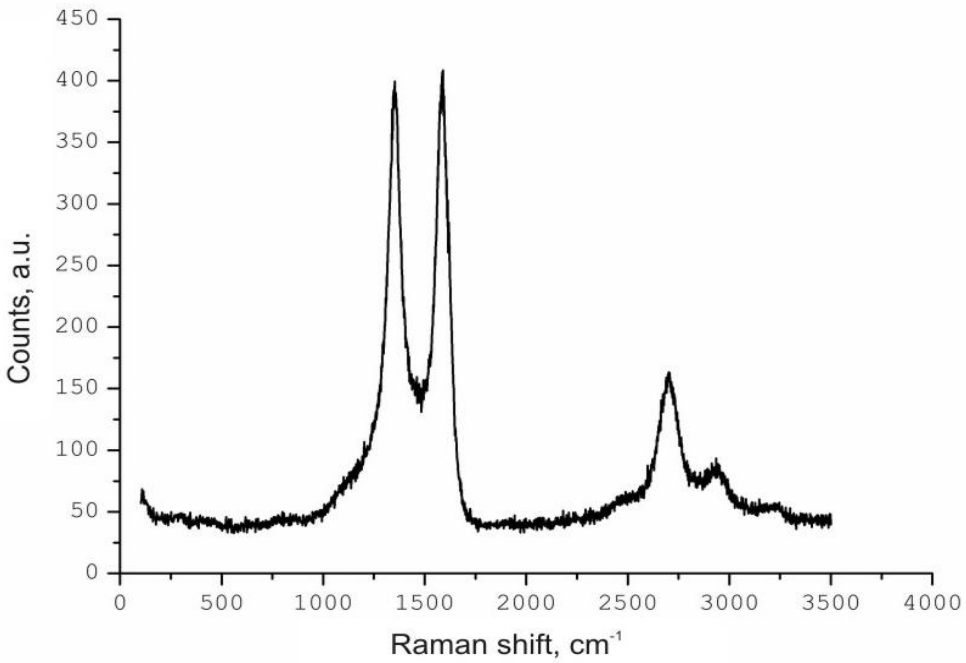


Figure 3. Raman spectra of CNT grown on a thin film of $Ni_{10}Nb_{30}N_{40}O_{20}$ alloy thickness of 20 nm at 550°C.

In the study of individual nanotubes by TEM, it was found that the CNTs are multiwall (inset in Figure 4). It can be seen that the outer diameter of the nanotubes about 20 nm, an inner diameter of ~ 7 nm. It is important to note that the TEM revealed the presence of metal inclusion in the internal channels of the CNT. In these particles revealed the presence of Ni and C, which demonstrates Figure 4, which shows the spectrum of metal cluster within a single tube. The presence of copper peaks in the spectrum related to a noise signal from the sample holder (copper grid).

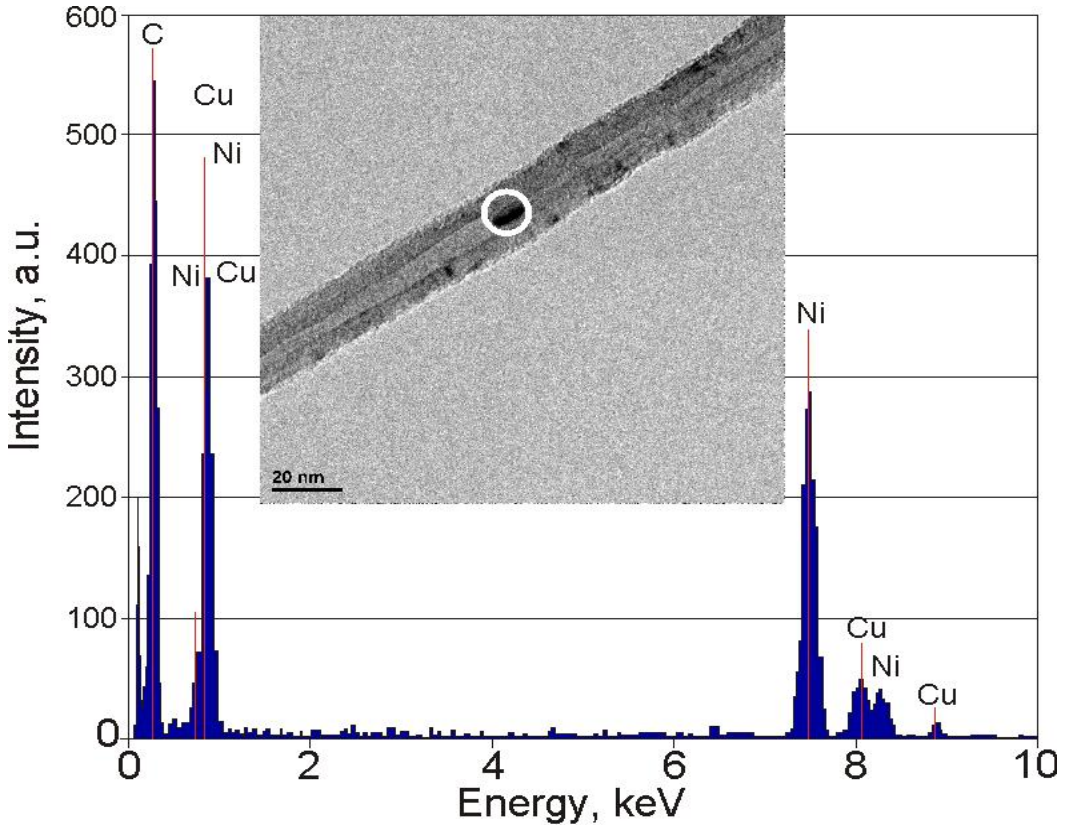


Figure 4. Energy dispersive X-ray spectrum of a single CNT with metallic inclusions. The inset shows a high-resolution TEM image of the object. The location of the analysis is marked by a circle.

4. Conclusions

In this paper demonstrated of CNTs growth by PECVD at 550°C using a catalyst thin film of $Ni_{10}Nb_{30}N_{40}O_{20}$ alloy. It is shown that in one cycle of CVD on the alloy $Ni_{10}Nb_{30}N_{40}O_{20}$ synthesized concurrently two kinds of vertical arrays of CNTs with different average diameter and the height of the tubes. Synthesis of CNTs arrays with different height and diameter due to the presence on the substrate surface the small(~6 nm) and big (~40 nm) clusters of Ni that TEM investigation confirmed. The investigations demonstrated the possibility of using the alloy $Ni_{10}Nb_{30}N_{40}O_{20}$ in integrated circuit technology as a catalyst film for nanotubes synthesis.

Acknowledgments

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