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MORPHOLOGY AND ELECTRON FIELD EMISSION FROM CARBON NANOTUBES PREPARED BY ALCOHOL CATALYTIC CHEMICAL VAPOUR DEPOSITION

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In this paper we report on the morphology and field emission from nanotubes prepared by AC CVD (Alcohol Catalytic Chemical Vapour Deposition) technique. Samples were prepared by growing of carbon nanotubes (CNTs) on Ni and Fe supporting wires. The vapours of alcohol were used as a source of carbon atoms. A heat from halogen bulbs boosted the growth up. Raman spectroscopy was used for the detection of the presence of nanotubes. The morphology of created nanotubes was investigated by high resolution scanning electron microscopy. Cold electron emission properties (emission current density *vs.* electric field characteristics) in dependence on the material of wires and the alcohol vapour pressure have been determined from I-V measurements.

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1 Introduction

In the last two decades of the previous century a lot of articles have been published devoted to carbon technologies. Before the year 1970 only two of carbon allotrope modifications were known. These were graphite and diamond. Then, after discovering fullerenes and investigating their interesting properties (biochemical activity, photo-induced electron transfer, gas occlusion, superconductivity), many researchers started their formation by various technologies. In the last decade of the century, when S. Iijima [1] found nanotubes, a further boom in this branch has been noticed. It was found that carbon nanotubes could be used in electronic devices because of very easy electron emission. Of course, other interesting properties were found for application also in medicine, biology or as fuel cells. Saito et al. [2] reported in 2000 an application of CNTs to electron sources for lighting elements. Also, Bonard et al. [3] demonstrated that nanotubes

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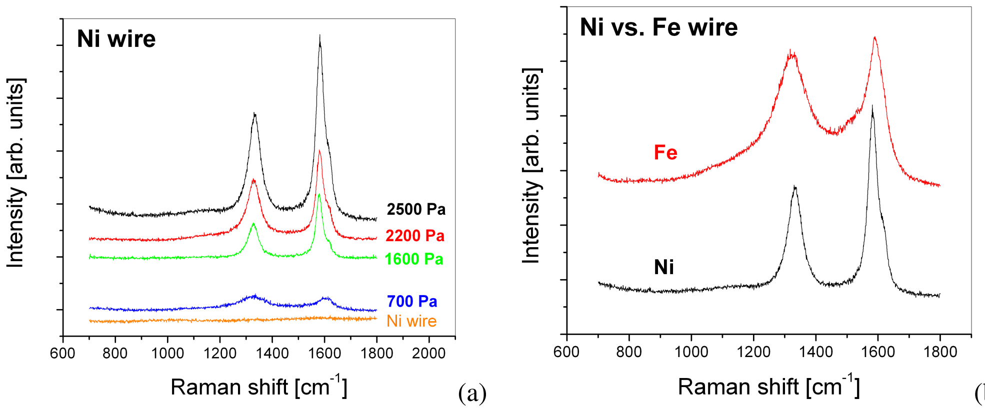

Fig. 1. Raman spectra of samples (a) Ni wire in dependence on pressure, and (b) Ni and Fe wires.

deposited on a cylindrical element could be used as cold electron emitters in a cylindrical field emission diode. The excellent emission properties of the cathode allow realization of a mercury-free luminescent tube. Nowadays, the growth of carbon nanotubes on planar substrates is well described [4] but deposition of carbon nanotubes on non-planar surfaces like cylindrical elements is less usual.

In our laboratory, the diamond technology trends were partially captured at the end of the nineties. We grew diamond layers on various substrate materials by hot filament chemical vapour deposition (HF CVD). Rather good results were reached in production of diamond layers on such substrates as W, Mo, Cu, Si, and WC/Co. After that we pointed our interest to electron emission properties of the diamond surface [5]. In this paper we present the morphology and field emission of the carbon nanotubes films obtained by alcohol catalytic CVD. Carbon nanotubes were directly deposited on Ni and Fe wires.

2 Method and experimental details

For the growth of CNTs we used a similar method as presented in the article of Maruyama et al. [6]. A conventional CVD apparatus uses heat from a furnace to activate gas molecules. In our case halogen bulbs replace the furnace and we do not use a quartz tube. This allows varying the temperature very quickly. Our experiments were focused on the influence of the alcohol vapour pressure and the material of the substrates upon the morphology and electron emission properties of carbon nanotubes. The deposition temperature was maintained at 700 $^\circ$C. Ni or Fe wires were used as substrates. Before the deposition the supporting wires were ultrasonically cleaned in acetone. After deposition four different analytical techniques were used to characterize the samples: Raman spectroscopy, cold electron emission characteristics measurement, SEM and TEM. Raman spectroscopy was performed in a conventional micro-Raman spectrometer ISA Labram (Jobin Yvon/Spex/Dilor, Horiba Group) equipped with a He-Ne laser (632.817 nm line) in backscattering geometry. For measuring the cold electron emission characteristics we used a cylindrical coaxial electrode configuration [7]. The morphology of CNTs was investigated by

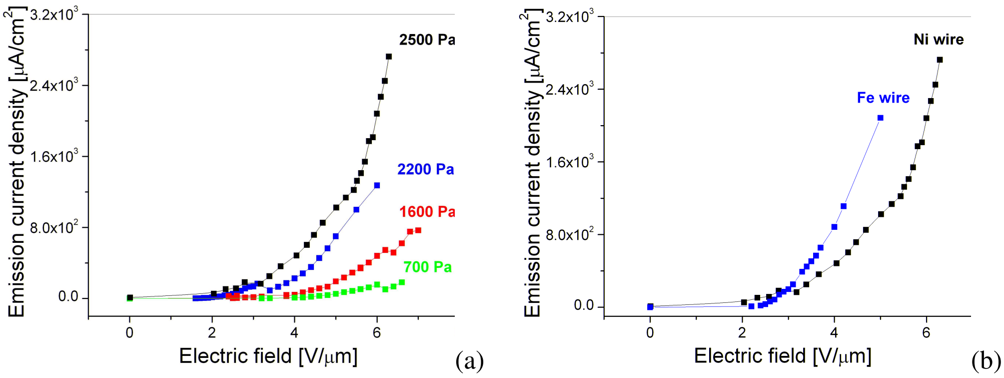

Fig. 2. Cold electron emission measurements of (a) nanotubes deposited on Ni at different pressures, and (b) comparison of cold electron emission of nanotubes grown on Ni and Fe wires.

the high-resolution scanning electron microscope LEO 1550 using in-lens detector of secondary electrons.

3 Results and discussion

Figure 1(a) shows Raman spectra of samples prepared at different pressures. Raman spectra of all samples contain two sharp peaks located at $\sim$ 1330 cm^{-1} (D band, D line) and around 1590 cm^{-1} (G band). Both of the peaks are typical for graphite, as well as for multi-walled and single-walled carbon nanotubes [8]. The D band has been known in graphite for 30 years and it has been shown that the peak is induced by disorder. The D line is attributed to the presence of amorphous carbonaceous products, disordered carbon or defects in graphite sheets [9]. In Fig. 1(b) a comparison is shown of Raman spectra for Ni and Fe samples prepared under the same deposition conditions. Raman spectra of the samples contain also two sharp peaks. We can see that D and G peaks for Ni sample are sharper and the ratio between G and D is much lower.

The I-V characteristics were measured under vacuum pressure less than 4×10^{-6} Pa. The measured I-V characteristics were then recalculated to draw $F - i$ (the electric field intensity F vs. emission current density i) curves. The $F - i$ characteristics of nanotubes deposited on Ni wires at different alcohol pressures are depicted in Fig. 2(a). The highest current densities were reached for the sample deposited at the highest alcohol pressure of 2500 Pa. The reached emission current density i was 2.7 mA/cm^2 at an electric field intensity of 6 V/μm. As a nice result we also consider the open voltage in the range of 2 to 3 V/μm. Presented results are significantly better in comparison with our previous obtained on samples covered by diamond layers. The decrease in deposition pressure resulted in a lower current density and also pure CNTs growth, which is seen from Fig. 3(c). $F - i$ characteristics for Ni and Fe substrates are compared in Fig. 2(b). As can be seen, the open voltage is similar for both substrates, but higher current densities are observed for the Fe wires at the same electric field. We have also measured the electron emission stability and we observed slight short-term current instabilities during the measurement of samples. There were no significant changes (in percent values only) in the electron emission from the samples during observation lasted for 340 minutes.

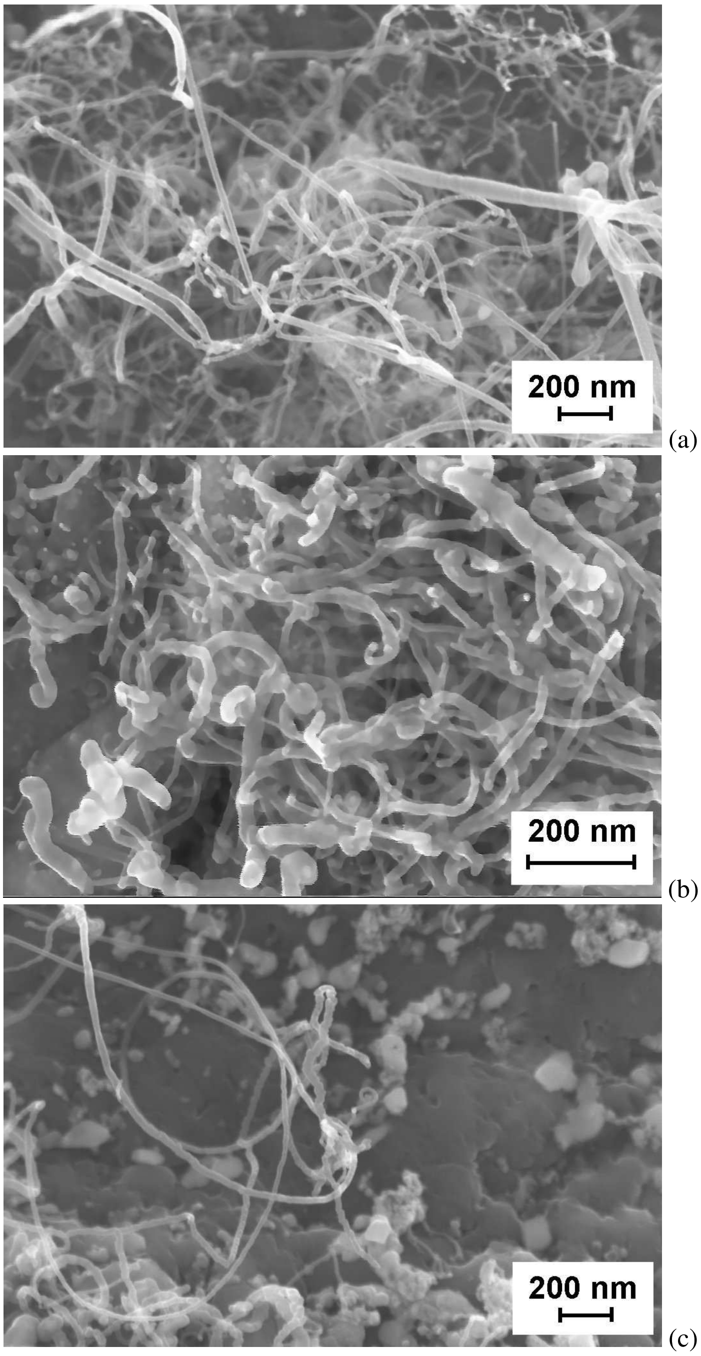

Fig. 3. SEM micrographs of carbon nanotubes (a) grown on Ni wire at 2500 Pa, (b) grown on Fe wire at 2500 Pa, (c) grown on Ni wires at 1600 Pa.

SEM micrographs of carbon nanotubes deposited on Ni and Fe wires at the same conditions are compared in Fig. 3(a) and 3(b). CNTs are randomly aligned and have different lengths and outer diameters. As can seen, the CNTs grown on Fe wire are shorter and more twisted than the CNTs on Ni wire. Additional TEM analysis of samples has only confirmed that CNTs grown on wires are hollow and multi-walled (MWCNT).

4 Conclusions

Under conditions kept in our reactor it is possible to coat Fe and Ni filaments by a film of carbon nanotubes. The film has good electron emitting properties. We observed that the type and emission properties of carbon nanotubes depend on the substrate material. Also, decreasing the deposition pressure resulted in a pure growth of CNTs and in a lower emission current density.

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