Journal of ELECTRICAL ENGINEERING, VOL. 54, NO. 5-6, 2003, 166–167

REVIEWS - LETTERS - REPORTS

CARBON STRUCTURE (NANOTUBE) ELECTRON EMITTERS GROWN AT STU

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The article presents the first results on carbon structure (nanotubes) formation at the Department of Microelectronics, Slovak University of Technology (STU). The structures were grown on an iron wire in a vacuum furnace heated by halogen bulbs by ACCVD (Alcohol Catalytic CVD) process. The properties of the created structures were investigated by measuring the field effect electron emission and by Raman spectroscopy.

Keywords: nanotubes, nanoropes, Raman spectroscopy, fullerenes, CVD

1 INTRODUCTION

In the last two decades of the previous century a lot of articles appeared devoted to carbon technologies. Before the year 1970 only two of carbon allotrope modifications were known: graphite and diamond. Then, after discovery of fullerenes and their interesting properties (biochemical activity, photo-induced electron transfer, gas occlusion, superconductivity) many researchers have started their formation by various technologies. In the last decade of the century, after S. Iijima discovered nanotubes, a next boom in this branche 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 their application also in medicine, biology or as fuel cells. At the Microelectronics Department of the Slovak University of Technology, research in carbon and diamond technologies has been made since the end of the ninetieths [1]. Diamond and diamond layers were grown on various substrate materials. We have achieved good results with diamond layers grown on such substrates as W, Mo, Cu, Si, and WC/Co [2]. Some experiments were made also with glass and sapphire substrates [3]. After some time we focused our interest on electron emission properties of carbon and diamond surface [4]. In this paper we deal with formation and characterization of the first, as we believe, carbon nanotubes.

2 EXPERIMENTAL

We used a similar apparatus like that used in the article of Maruyama et al [5]. The small difference of the described apparatus was that we have replaced the furnace used in the cited paper by halogen bulbs. It enables us to vary the temperature and samples very quickly. As samples we used filaments of Fe. Their characterizations were performed by two different types of techniques. The first one was Raman spectroscopy. It was performed by a conventional micro-Raman spectrometer (ISA Labram equipment Jobin Yvon/Spex/Dilor, Horiba Group) equipped with a 632.817 nm line from a He-Ne laser in backscattering geometry. A 100 microscope objective was used to focus the laser onto a spot of approximately 1 μm in diameter and to collect the scattered light, which then passed through the spectrometer onto a CCD detector. Furthermore, a confocal hole diameter of 200 μm, a spectrograph entrance slit of 150 μm, and 1800 grooves/mm diffraction grating were employed.

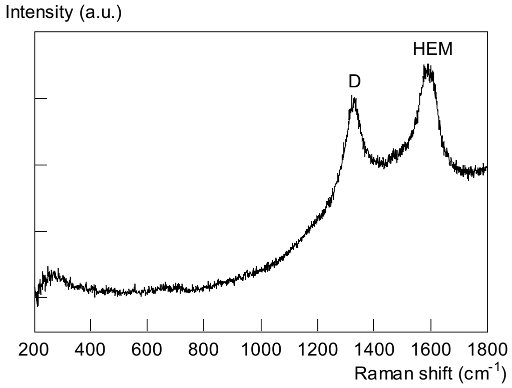

Fig. 1. Raman spectrum of Fe filament surface

The Raman spectrum of single carbon nanotubes contains three distinct features, the radial breathing mode around 200 cm^{-1}, the D mode, a disorder induced Raman peak, and the high-energy modes (HEM) between 1500 and 1600 cm^{-1} [7]. The Raman spectrum in Fig. 1 contains two dominant broad peaks, one around 1330 cm^{-1}, know as D mode, and the second one at around 1590 cm^{-1}, known as HEM. The two broad peaks are typical for graphite and multiwall and single walled car-

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ISSN 1335-3632 © 2003 FEI STU

bon nanotubes as well. The D mode has been known in graphite for 30 years and was shown that the mode peak was induced by disorder. The frequency of the D mode is shifted with the energy of the exciting laser and a similar shift as in graphite is found in multiwall and single walled carbon nanotubes as well [6]. The HEM mode in carbon nanotubes occurring in the 1500-1605 cm^{-1} range is basically derived from the Raman-allowed optical mode E_{2g} of the 2D graphene Brillouin zone into the 1D nanotube Brillouin zone, noting that only modes with A, E_1 and E_2 symmetry are Raman active for single wall carbon nanotubes [7]. The Raman spectrum in Fig. 1 shows no evidence of the presence of single walled nanotubes but the created structures (if wire-like) should be multiwall nanotubes. As the second technique, measurements of $I-V$ curves were performed. We use a cylindrical coaxial electrode configuration [8]. The $I-V$ characteristics were measured under pressure better than 410^{-6} Pa. The measured $I-V$ characteristics were recalculated to $E-I$ (electric field - current density) values. In Fig. 2, three lines are shown. The first, marked as "nt" belongs to a sample with carbon nanotubes. Lines D_1 and D_2 belong to samples with diamond layers, reported in [9]. During the measurement of sample "nt" we found current instabilities. It indicated that under current loading some process in the layer goes on. These changes were irreversible. As a nice result we consider the thresh-hold voltage less than of 2 V/μm.

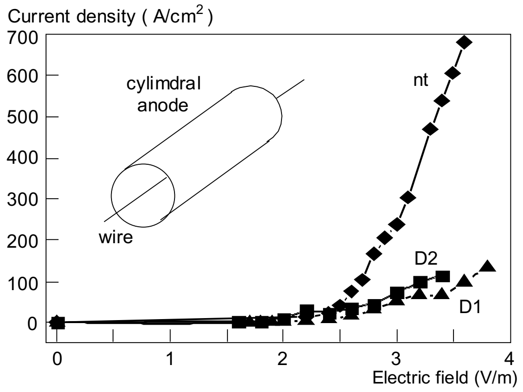

Fig. 2. Field emission $E-I$ curves of filaments

3 CONCLUSION AND PLANS TO THE FUTURE

Under certain conditions kept in our apparatus it was possible to cover Fe filaments by carbon layers (fullerenes) with suitable electron emitting properties. We believe that these are carbon nanotubes. Now we will try to confirm our statement. This can be done by high resolution TEM. If this result will be positive then we will try to make electron emitters on a Si plane. For this planar configuration new measuring equipment is needed.

Acknowledgement

The authors would like to thank Mr. J. Král for technical assistance. This work has been supported by the Grant Agency of the Slovak Republic via Grants No.1/9044/02 and No.1/0275/03.

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Received 25 May 2003

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