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INFLUENCE OF HIGH VACUUM ANNEALING TREATMENT ON SOME PROPERTIES OF CARBON NANOTUBES

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Carbon nanotubes (CNTs) were synthesized using a chemical vapour deposition (CVD) method. The properties of CNTs before and after vacuum annealing treatment were studied using scanning electron microscopy (SEM), scanning tunneling microscopy/spectroscopy (STM/STS) and thermogravimetric analysis (TG). Field emission characteristics of the raw and vacuum heated (up to 650ºC) carbon nanotube films (CNTFs) were measured in a diode system. Emissive properties of the CNTFs depend on an annealing process during which structural changes in the nanotube walls take place. The structural changes, related to saturation of dangling bonds, influence a rate of oxidation process and also improve the emissive field properties.

Keywords: *carbon nanotubes, electron field emission, structural defects, thermogravimetry, topological defects*

Introduction

CNTs [1] exhibit unusual structures and properties [2–6] e.g., a high Young's modulus along the tube, electronic conductivity that varies from metallic to insulating, very large aspect ratio (length to diameter), an extremely small radius and hollow channel, high specific surface area and chemical stability. The unique chemical, physical, mechanical and electrical characteristics make them useful in many practical applications e.g., as electron field emission sources [7–9], scanning probes [10, 11], chemical force sensors [12], nanoelectronic components [13], nanocomposites [6, 14] and gas storage materials [15]. Some properties of CNTs can change during annealing treatment under a vacuum at relatively low temperature. Such a process can affect local defects in the tube walls [16]. It is known that topological defects beside the chirality and tube diameter play an important role in determining electrical properties [17].

In the present work, we show how a high vacuum annealing process (10 Pa, 650°C, 8 h) of CNTs influences their defects, a rate of their oxidation and field emissive properties. CNTs were obtained using a thermal chemical vapour deposition (CVD) method with a xylene–ferrocene mixture (C_8H_{10}–$Fe(C_5H_5)_2$) as a source of carbon and catalyst. The morphology of carbon nanotube films (CNTFs) was examined using a scanning electron microscope (SEM). Scanning tunneling microscopy and spectroscopy (STM and STS, respectively) measurements were used to investigate electronic properties of the tubes and their topological and structural defects. Thermogravimetric analysis (TG) performed in air atmosphere was applied to show changes in behaviour of the CNTs after a high vacuum annealing process in comparison with the raw material. In addition, the electron field emission characteristics of the two CNT samples: a – the raw material and b – heated up to 650ºC under a vacuum of 10 Pa, are discussed. The emissive properties are analyzed by Fowler–Nordheim (F–N) model [18]. This model could describe field emission (FE) from carbon nanotubes although it was originally developed for flat metallic surfaces.

Experimental

CNTs were synthesized using a CVD injection method, similar to that reported by Andrews *et al*. [19]. The injection process allows controlling the ratio of catalyst to carbon. Our experimental set-up has been described elsewhere [20]. A solution of 10 mass% ferrocene in xylene was injected at a rate of 3 $cm^3\ h^{-1}$ into a reactor, placed in a two-stage furnace. In the first section (180–200ºC) the solution evaporated and then the vapour was transported by argon to the second section (650ºC), where it was decomposed. Argon flow rate was maintained at 40 $dm^3\ h^{-1}$. Carbon product was deposited on the reactor walls and also on the inserted quartz substrates. The substrates were covered previously with indium–tin oxide in order to use them directly as the cathodes in field emission measurements.

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The diameter, length and the degree of alignment of CNTs in the deposits were characterized by SEM (Leo 1530). STM/STS measurements were performed at ambient conditions using Omicron GmbH STM/AFM microscope. The STM tip was made of 90% Pt–10% Ir alloy wire. For the STM investigation around 1 mg of CNT deposit was subject to ultrasonic treatment for 3 h in 1,2-dichloroethane ($C_2H_4Cl_2$). Few droplets of the solution were placed on highly oriented pyrolytic graphite (HOPG) surface and dried in air. The sample was investigated in a constant current STM mode. The tunneling current was set at 0.15–1.2 nA and a bias voltage 0.2–1.5 V. Each of the current–voltage (I–V) characteristics was recorded for both polarities in the ±1.5 V range. The normalized tunneling differential conductance $(dI/dV)/(I/V)$–(V) was calculated numerically from the experimental $I(V)$ plots.

The raw and annealed samples (a and b, respectively) were characterized by TG (DuPont Instruments TGA 951). TG measurements were carried out at 10°C min^{-1} heating rate under static air atmosphere, using a platinum boat.

Field emission characteristics $I(E)$ (where I – electron current intensity and E – electric field) of both a and b samples were measured at room temperature in diode system described elsewhere [21].

Results and discussion

SEM investigation

A SEM image of the raw CNTs, deposited on a quartz substrate, is shown in Fig. 1. As we can see they are curved and entangled. The shape of CNTs results from the defects of their walls. Such defects like bent or terminated graphene sheets have been observed in our previous TEM investigations [22]. It was proved also that nanotubes synthesized by decomposition of a xylene–ferrocene mixture were multi-walled with poorly ordered graphene sheets, contaminated by Fe particles.

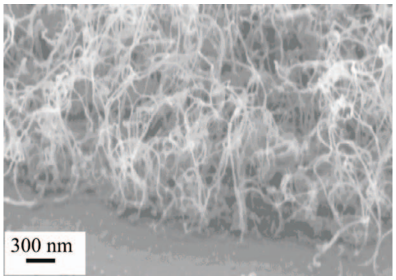

Fig. 1 SEM image of the raw CNTs, deposited on a quartz substrate, covered previously with indium–tin oxide layer

STM/STS studies

STM studies indicate that the surface of the catalytically grown nanotubes is rough and can be related to topological defects [23] (the presence of pentagons or heptagons in the hexagonal lattice) and structural defects [24] (the absence of hexagons in the hexagonal lattice leading to open ends of nanotubes or pits on their surface with a zigzag or an armchair configuration) in the tube walls. As shown in Fig. 2, the diameter of the selected nanotube from the raw carbon product changes along the tube. The two sites marked by arrows in the figure on the left have approximate diameters of 39 and 44 nm, estimated from the STM z-profile shown in the figure on the right.

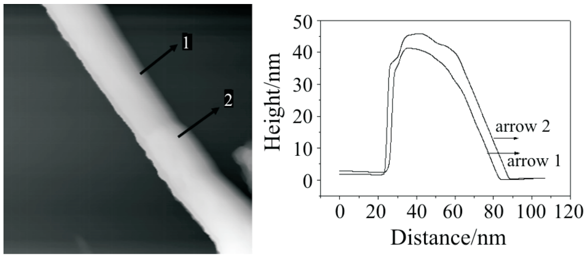

Fig. 2 left – STM image, 300×300 nm, of a CNT selected from the raw deposit and right – STM z-profiles measured in sites, marked by arrows

The defects influence the electron local density of state (LDOS) of CNTs, therefore we used STS to investigate the synthesized carbon material. According to the model proposed by Tersoff and Hamann [25], $dI/dV(V)$ is a measure of the LDOS in the region close to the Fermi energy.

The normalized local differential conductivity plots $(dI/dV)/(I/V)$–(V) measured on the tube surface at various points (curves 2–4), compared with those of the HOPG substrate (curve 1), are shown in Fig. 3. For the sake of clarity the curves are shifted vertically and a horizontal line under each curve indicates the zero level. The non-zero value of $(dI/dV)/(I/V)$ at the sample bias voltage $V=0$ indicates a metallic electrical conductance. Curve 1 recorded over the HOPG surface with poorly visible features localized at ~–0.65 and +0.8 eV, i.e. below and above the Fermi energy respectively, is typical of pure graphite [26]. The normalized conductance curves recorded over the raw nanotubes differ significantly from those registered over the HOPG. It suggests that the CNT walls are locally defected. The representative spectroscopic plot of sample a (curve 2) recorded over the defect on the tube surface is characterized by the maximum located at ~–0.1 eV (below the Fermi energy). As was previously discussed [24, 27], this additional surface state (RS – localized resonant state) close to the Fermi level appears on the defective HOPG and is related to

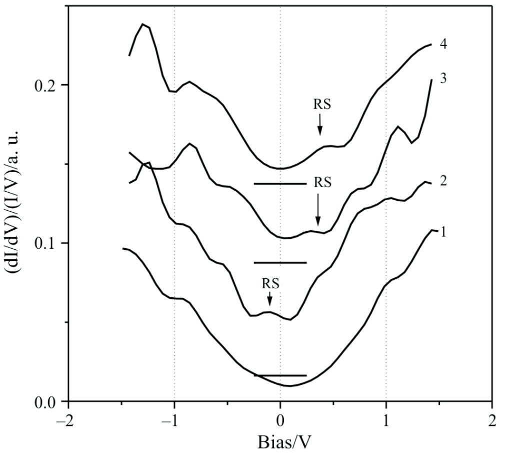

Fig. 3 Normalized local differential conductivity plots measured at various points of nanotubes surface (curves 2–4) and HOPG substrate (curve 1). The curve 2 is recorded over the defect of the raw nanotube, the curve 3 is registered over the end of the nanotube, the curve 4 is recorded over the defect of the annealed nanotube far from the tube's end

a zigzag configuration of hexagons forming the pit or the terrace edge. Our results suggest that the raw nanotubes have defects originating from dangling bonds at terminated graphene sheets.

It is worth noticing that $(\mathrm{d}I/\mathrm{d}V)/(I/V)$–$(V)$ curves with the additional maximum localized at ~0.3 eV above the Fermi energy were also found in sample a, but was somewhat rare. The maximum at ~0.3 eV (RS) close to the Fermi level could be ascribed to pentagon ring defects in the hexagonal network because such a maximum was registered in the spectroscopic plot (curve 3) mainly when the STM tip was over the tube end. It is known that pentagon rings are necessary to form closed CNT ends, therefore we conclude that the local resonant state at ~0.3 eV can be related to pentagon rings. The representative spectroscopic plot of sample b (curve 4) recorded over the tube surface far from the CNT end is similar to curve 3. Therefore we can suppose that pentagon rings are present on the surface of the annealed nanotubes.

On the basis of the STS results we conclude that the high vacuum annealing process could cause structural changes in the tube surface. Dangling bond defects (structural defects), observed predominantly in the raw material (sample a), could be substituted for other defects like topological ones (pentagon rings) mainly registered in the annealed CNTs (sample b), thus dangling bonds were saturated forming rings. It seems possible, as was shown previously [16] that the defective SWCNTs with dangling bonds coalesce forming MWCNTs to saturate the carbon bonds.

The influence of thermal treatment on properties of CNTs can be observed by thermogravimetric analysis and electron emission studies.

TG analysis

TG and DTG curves of both a and b samples are shown in Fig. 4. During heating in air carbon can be burnt out and iron (Fe originating from ferrocene in synthesis) can be oxidized. The experiment demonstrates that the raw material burns at a lower temperature and the onset of oxidation is shifted from 453 to 470°C for the annealed CNTs. The maximum rate of oxidation (DTG peak) occurs at about 620°C for both samples and above this temperature, the oxidation curves are not identical. X-ray diffraction measurements of the residue after the oxidation process showed that the raw carbon nanotubes were burnt out completely, leaving on the platinum boat, only Fe_2O_3 (15 mass% of the initial mass) while sample b converted into a mixture of Fe_2O_3 (15 mass% of the initial mass) and rhombohedral graphite (20 mass% of the initial mass).

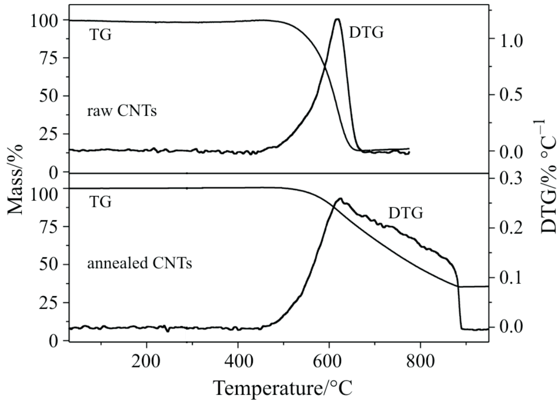

Fig. 4 TG and DTG curves (in air) of the raw CNTs (sample a) and after a high vacuum annealed CNTs (sample b)

Such different behaviour in the samples could be caused by structural defects, existing to a greater extent in the raw CNTs (dangling bonds can initiate oxidation of tubes at the lower temperature onset) and also by the structural changes occurring in the annealed nanotubes, leading to the improvement of their crystallinity and to generation of more stable structures. Therefore the tubes from the vacuum annealed material probably burn incompletely.

The observed effects cannot be related to the purification of CNTs. After synthesis carbon deposits were annealed for 2 h at 650°C under argon atmosphere; this is sufficient to obtain the purified carbon nanotubes devoid of the remnants of decomposed hydrocarbons.

Field emission measurements

The current (I) *vs*. electric field (E) characteristics of the raw and annealed samples are shown in Fig. 5. The annealed CNTs start to emit at lower electric field

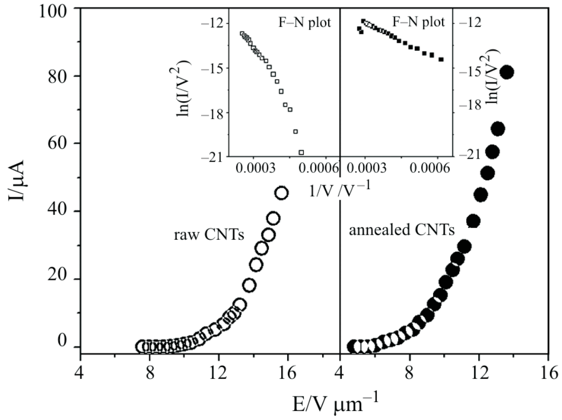

Fig. 5 *I–E* characteristics with F–N plots (insets) of the raw CNTs and after a high vacuum annealing process, samples a and b, respectively

and also show higher final current intensity than the raw material. According to the F–N theory the field emission current I is a function (1) of: an applied electric field E ($E=V/d$, d is a distance of the counter-electrode), a local work function of the emission tip Φ (Φ=5 eV for multiwalled carbon nanotubes) and a field enhancement factor β. The factor β [28] is a strictly geometrical parameter and depends on the tip geometry (curvature, chirality, diameter and defects) and radius of the emitter and also on its surroundings.

$$I \propto (E^2/\Phi)\exp(-\Phi^{3/2}/E\beta) \qquad (1)$$

The slope of the F–N plot ($\ln(I/E^2)$ *vs.* $1/E$ – insets in Fig. 5) are smaller for the annealed sample in comparison with the raw CNTs, pointing to the larger field enhancement factor β of the material b (the parameters d and Φ for a and b samples are unchanged). Registered effects indicate that the annealed CNTs are better emitters; this is probably caused by an amplified local electric field (larger factor β) following from the increase in density of emitting sites. This increase in density of emitting sites in the annealed carbon material suggests that electron emission occurs not only through ends of nanotubes but also out of their walls, in which structural defects (dangling bonds) were saturated forming the closed rings (topological defects).

Conclusions

The catalytic thermal decomposition of hydrocarbons enables synthesizing carbon nanotube films (CNTFs) on substrates used directly as cold cathodes in electronic devices. STM/STS measurements reveal the presence of structural and topological defects on the tubes surface observed as localized resonant states, additionally occurring near the Fermi energy. A high vacuum annealing process of CNTFs can cause structural changes of the tubes. Dangling bond defects (structural defects observed mainly in the raw sample) could be substituted for other defects like topological ones. These changes related to saturation of dangling bonds influence the rate of the oxidation process and also improve the emissive field properties. The CNTFs after a high vacuum annealing process are more effective as field emission cathodes than the raw films. Results of our observations should be taken into account during the design of CNT electronic devices.

Acknowledgements

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