The influence of activation and growth time on the geometry and structural perfection of multi-walled carbon nanotubes

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Abstract. We studied the influence of the activation time on the phase composition and geometric parameters of catalytic centers (CC). We found, that the treatment of substrate in an ammonia atmosphere allows to restore oxidized nickel. The activation time and the presence of ammonia plasma do not affect the phase composition of catalyst, but has a significant effect on the geometric dimensions of catalytic centers. Also we studied the influence of growth time on the geometry and structure of vertically aligned carbon nanotubes (VACNT). When the growth time ranged from 5 to 15 min we observed the formation of new walls, which resulted in an increase of the outer diameter. Within the range of 15 to 30 minutes, however, there was a decrease in the diameter of carbon nanotubes, which is associated with the disturbance of structural perfection and disorientation of carbon nanotubes caused by wall undercutting in the plasma.

1. Introduction

The unique properties of VACNT provide extended opportunities for their use as functional elements of emission nanoelectronics devices [1], memory cells [2, 3] and interconnections [4]. The key factors for the wide use of CNTs in these devices are high aspect ratio [5] and the metallic nature of their conductivity [6]. Thus there is definitely a clear need for research in process conditions to grow VACNT with controlled geometry, structure and properties.

It is well known that plasma enhanced chemical vapor deposition (PECVD) is considered to be the most promising method of CNT formation [7, 8], which allows to grow aligned CNTs on substrates with catalytic centers [3]. The processes of deposition of the catalyst film and the growth of CNTs are usually carried out on different equipment. This leads to the oxidation of the catalyst film upon contact with the atmosphere. Hence, the necessary step in the CNTs production is the activation, i.e. the restoration of the oxidized catalyst film with a hydrogen or ammonia atmosphere in PECVD process. But the influence of the activation parameters on the structure and geometrical dimensions of CC has not been studied sufficiently and requires further research.

We should note that a large number of interrelated parameters of PECVD (such as temperature, pressure, flow and type of process gas, catalyst film material, etc.) have a significant impact on VACNT
growth processes [9-13]. One of the most important parameters determining the aspect ratio of VACNT is growth time [14, 15].

However, the influence of this parameter does not appear to have been sufficiently studied, so our aim was to study the influence of activation and growth time of VACNT obtained by PECVD on their geometry and structural perfection.

2. Experiments and Methods

We had grown VACNT by vertex mechanism in the PECVD module of a cluster nanotechnology complex NANOFAB (NT-MDT, Russia). RCA-cleaned Si (100) wafers were used as substrates. To eliminate the interaction between catalyst centers material and the substrate, a buffer sublayer of the metal film was created. Ni/Cr films have been used as a combination of metals for the catalyst/sublayer, because they provide high homogeneity of the parameters of carbon nanotubes [6-8].

20 nm thick Cr film was used as a buffer sublayer which we deposited from a chromium target (99,95% purity, Kurt J. Lesker Co.) in an atmosphere of Ar with the substrate heated to 100°C. A catalyst layer film of 10 nm thick Ni was deposited from a nickel target (99,995% purity, Kurt J. Lesker Co.) in an atmosphere of Ar with the substrate heated up to 220°C. We deposited Cr and Ni films using a magnetron sputtering set AUTO 500 (BOC Edwards, UK) at a chamber pressure of 83.1 Pa.

We activated and grew VACNTs in the flows of NH3 (210 sccm), at a chamber pressure of 4.5 Torr and a temperature of 750 °C. We used C2H2 (70 sccm) as the carbon-containing gas. We carried out the activation of the experimental samples with DC plasma initiation (45 W) and without it. We changed the activation time in the range from 1 to 5 min. We varied the growth time $t$ for our samples from 5 to 30 minutes.

We investigate the phase composition of the structure of the nickel catalytic layer by X-ray absorption spectroscopy (XANES, EXAFS) at a specialized source of synchrotron radiation (SIC "Kurchatov Institute", Moscow, Russia). The obtained X-ray absorption spectra were compared with reference samples.

We studied the VACNT samples using a scanning electron microscope (SEM) Nova NanoLab 600 (FEI, Netherlands). The diameter and height of the VACNT array obtained were evaluated by means of statistical processing of SEM images. The structural analysis of the VACNT arrays was conducted by a Raman spectrometer Renishaw InVia Reflex (Renishaw plc, UK) in the backscattering geometry at 514 nm excitation wavelength.

3. Results and Discussion

The analysis of the X-ray absorption spectra of the catalyst film prior to the activation process showed that the nickel was predominantly in an oxidized state with a volume of pure Ni ~ 30%. Processing the substrate in an ammonia atmosphere for 1 ÷ 5 minutes, allowed us to restore the oxidized nickel with a metal content of 90-95%. We observed that the activation time and the ammonia plasma initiation did not affect the phase composition of the catalyst.

However, the analysis of the catalyst film by AFM and SEM methods showed a significant influence of the activation time on the geometric dimensions of the formed catalytic centers.

It was found that with increasing activation time, the diameter (Fig. 1a) and height (Fig. 1b) of the catalytic centers diminished, which was associated with the increase of the temperature exposure time (750 °C) during activation.

Thus, during the annealing phase, the difference between the temperature expansion coefficients of the film and the substrate promotes the appearance of a mechanical stress on their contact. As a result, the fragmentation of the metal film with the formation of catalytic centers takes a place. Presumably, as temperature exposure time increases, the simultaneous processes of sublimation and surface diffusion take place, which leads to diameter and height decrease, as well as an increase of CC homogeneity. The presence of plasma in the activation process does not influence the CC dimensions (Fig. 1).
In order to avoid the formation of nanofibers on a large size CC, the further growth of the experimental samples of the VACNT was conducted with 5 min activation time. Having analyzed the SEM images of our samples (Fig. 2), we were able to determine the dependence of VACNT diameter and height on growth time.

With an increase in growth time $t$ from 5 to 15 min CNT diameter increased from 35 to 58 nm (Fig. 3a), which may be associated with the formation of new walls of multilayer VACNTs. However, when we increased growth time $t$ from 15 to 30 min, the CNT diameter decreased to 54 nm (Fig. 3a), which may be due to the undercutting of nanotubes caused by ammonia plasma (Fig. 4).
We observed an increase in VACNT height from 90 to 310 nm occurring within the whole range of growth times (Fig. 3b). However, we noticed an interesting fact that at $t = 30$ min carbon nanotubes began to deviate from the normal position and started getting disoriented (Fig. 2b). This may also be associated with the undercut of the nanotubes at their base, which causes their bending.

In Figure 5 we compare the Raman spectra of the investigated samples measured at 514 nm excitation wavelength. We clearly observe the presence of D- and G-bands. The high intensity of D-band implies the presence of defects in the samples. [16, 17].

![Figure 4. SEM image of VACNTs grown at $t = 15$ min.](image1)

![Figure 5. Raman spectra of the investigated samples measured at 514 nm.](image2)

Having analyzed the intensity ratio $I_D/I_G$ of the D and G bands for different samples, we were able to estimate the impact of growth time on the defectiveness of VACNT. $I_D/I_G$ ratios were 0.95, 0.86 and 0.91 for $t = 5$, 10 and 15 minutes, respectively. We found that the CNTs grown for 5 minutes contained the greatest number of defects ($I_D/I_G = 0.95$). This fact can be accounted for by the influence of catalytic center material which occupies most of the volume of the whole nanotube. The presence of catalytic centers at the tops of nanotubes might cause the asymmetric distortion of the nanotubes' layers and, therefore, led to an increase in D-mode intensity. Having increased growth time to 10 minutes, we observed an increase in the aspect ratio and the volume of the nanotube, which reduced the $I_D/I_G$ ratio to 0.86. Further increase in growth time led to a subsequent increase in the value of $I_D/I_G$, which occurred due to the breakdown of carbon bonds as a result of the etching of nanotube walls in an ammonia plasma.

SEM images of VACNTs grown at $t \geq 15$ min (Fig. 5) confirmed the effect of plasma undercutting of CNT base.

Thus we found that the growth time has a significant impact on the geometry and defectiveness of VACNT, but it is by no means the only key parameter for the nanotube growth. Based on the results obtained, we can assume that in order to grow less defective VACNTs characterized by high aspect ratios, we need to reduce the ammonia plasma power and increase the pressure in the chamber to speed up the carbon gas transfer to catalytic centers.

We should note, however, that the structural imperfection of VACNTs caused by undercutting can be used to create emission structures based on graphenated multi-wall carbon nanotubes [18]. Besides, previous studies have shown [19] that multilayer VACNTs grown under similar conditions have a resistivity of $8.32 \pm 3.18 \times 10^{-4}$ Ohm·m, which indicates the metallic nature of their conductivity.

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