NANOTUBE FORMATION ON CATALYTIC SURFACE IN PLASMA DISCHARGE

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The expression for number of layers of multilayered nanotube, which have been generated during the time of its growth in the plasma discharge, is derived.
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INTRODUCTION

Controllable formation of nanotubes, superlong nanotubes, nanotubes with the necessary properties are the very important and now intensively investigated problems (see, for example, [1, 2]). In this paper the formation of carbon nanotubes in the plasma discharge is considered, when on catalytic surface or surface with defects the nanotubes under effect of the flow of carbon plasma, bombarding the surface, are formed. The universal expression for number of layers of multilayered nanotubes, which have been generated during the time of its growth in the plasma discharge, is derived.

THE DESCRIPTION OF NANOTUBE GROWTH

Let us consider the nanotube formation, built in the lattice ordered in an electric field of the nanotubes, perpendicular to the catalytic surface. Atoms of carbon, colliding with a lateral surface of a tube and getting in area of a shadow concerning bombarding plasma stream, are quickly cooled, cease to join to nanotubes and "are blown" from a wood of the nanotubes as a result of bombardment by the following atoms of their stream. That is in the region of a shadow, closer to the basis of the nanotube, layers do not grow on of the nanotubes. In other words, layers of nanotube grow on some distance from its head. We name this interval area outside of a shadow and equal to the length of free run ℓ_{fr} of carbon atom concerning collisions with nanotube walls. As probabilities of connection of atoms to the top and lateral side are practically identical, speeds of lengthening of a lateral side and length of nanotube are identical. Then during lengthening of nanotube on ℓ_{fr} its lateral side also to be extended on ℓ_{fr}. Then the amount of nanotube layers is equal $N_{max}=\ell_{fr}/2\pi R$ at spiral nanotube which cross-section, perpendicular to tube axes, represents an untwisted spiral. Here R is the average radius of nanotube. For first layer R it is approximately equal to fullerene radius. Thus $\ell_{fr}\approx V_z(\ell_{nan}/V_{thc})$. Here ℓ_{nan} is the average distance between nanotubes, V_z is the longitudinal lengthways of the nanotube velocity of carbon ions and atoms, V_{thc} is the thermal velocity of carbon atoms. If $V_z\approx V_{thc}$, then $\ell_{fr}\approx\ell_{nan}$. Thus $\ell_{nan}\approx(n_{fs})^{-1/2}$. Here n_{fs} is the superficial density of the nanotubes. $N_{max}\approx1$, if $\ell_{nan}\approx2\pi R$.

The surface density of the nanotubes σ is derived from that during lengthening with speed V_{nz} of the nanotubes on ℓ_{fr} the density of the particle flow $n_c V_z$ fall on the surface, which with probability ω_z engenders nanotubes. Thus,

$$\sigma=\frac{\ell_{fr}}{V_{nz}}\left(n_c V_z \omega_z\right)=\left(\frac{n_c V_z^2 \omega_z}{V_{nz} V_{thc}}\right)^{2/3} \qquad (1)$$

One mechanism of the growth of the nanotube side is its bombardment by carbon atoms and ions of a plasma flow. The second mechanism of the nanotube growth is the following one. Fallen on the nanotube and sorbed on its surface carbon atom diffuse on its surface up to a growing side, that is growth of a side is reduced to its lengthening with some speed V_{nz}.

Now we show, that can arise as spiral, and azimuthally symmetric nanotubes. Also we find quantity of layers of the azimuthally symmetric nanotube.

For last carbon atom getting between two next carbon atoms and to form closed cluster, which is the basis of the azimuthally symmetric nanotube, it should overcome a power barrier $\varepsilon_з$ on some tens percents higher than to overcome a barrier ε_{np} for carbon atom to join border open-ended spiral cluster. Probabilities to join to open-ended circular w_{np} or to close $w_з$ it are proportional to $w_{np}\sim\exp(-\varepsilon_{np}/T)$, $w_з\sim\exp(-\varepsilon_з/T)$. Hence, the probability to close $w_з$ of open-ended circular cluster is less than probability to join w_{np} to open-ended circular cluster $w_з<w_{np}$. Thus, the probability of origin of spiral cluster is more than probability of origin of closed circular cluster.

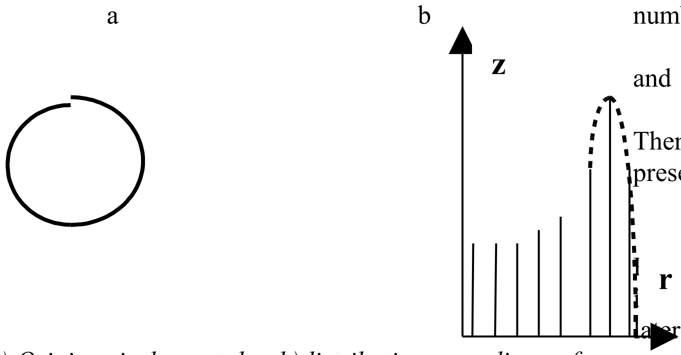
However, the spiral nanotube (Figure a) is less favourable from the power point of view, because there are many nonsaturated connections. Hence, if during the nanotube growth the bombardment is intensive the part of the spiral nanotubes decreases due to "heating".

Probability to arise new layer - cluster around azimuthally symmetric nanotube is small. It is proportional to nanotube radius. The factor of diffusion of carbon atoms on the nanotube surface is also proportional to nanotube radius. Thus, at formation of multilayered azimuthally symmetric nanotube the distribution on radius r lengths of layers along z-axis has qualitatively kind submitted in Figure b.

The number of carbon atoms getting in time unit on the external surface of the nanotube we estimate as follows:

$$dN_{cmax}/dt=n_p v_p 2\pi R_{max} H$$

Here H is the height of the nanotube, n_p, V_p are the density and velocity of carbon ions in the flow (plasma) accordingly, $2\pi R_{max}$ is the length of "circle" of an external layer of the nanotube.



a) Origin spiral nanotube; b)distribution on radius r of lengths of nanotube layers

The nanotube growth rate upwards due to carbon atom connection, which are placed on the nanotube surface, to a face edge is determined by the following expression:

$$V_{\|}^{(1)}=dH^{(1)}/dt=(aw_0\, dN_{\|}/dt)/N_a \qquad (2)$$

Here a is the size of internuclear distance in nanotube structure, w_0 is the atom, diffused from the nanotube surface, probability of connection to the edge, $dN_{\|}/dt$ is the number of carbon atoms getting in time unit on a face edge, N_a is the number of carbon atoms on a face edge. Taking into account that

$$dN_{\|}/dt=w_{\|}dN_{cmax}/dt \qquad (3)$$

and

$$N_a=L/a \qquad (4)$$

we derive the following expression:

$$dH^{(1)}/dt=(a^2w_0w_{\|}dN_{cmax}/dt)/L \qquad (5)$$

Here $w_{\|}$ is the probability of that the carbon atom, which is placed on the nanotube surface, diffuse on the face edge, L is the length of the lateral face edge. With the account (1) the expression (5) has the following kind:

$$dH^{(1)}/dt=(a^2w_0w_{\|}n_pv_p2\pi R_{max}H)/L \qquad (6)$$

Now we take into account direct hits of carbon ions from the discharge plasma flow on a face edge of the nanotube:

$$V_{\|}^{(2)}=dH^{(2)}/dt=(aw_{00}\, dN_c/dt)/N_a \qquad (7)$$

Here w_{00} is the probability of connection of a carbon ion to a face edge at direct hit from the plasma flow, dN_c/dt is the number of carbon ions getting from the plasma flow on the end face in time unit. It can be estimated as follows:

$$dN_c/dt=n_pv_pL\Delta R \qquad (8)$$

Here R is the nanotube "thickness". Then, with the account (4) and (8) the equation (7) can be presented as:

$$dH^{(2)}/dt=a^2\, w_{00}n_pv_p\Delta R \qquad (9)$$

Then the full growth rate of the face edge is equal

$$V_{\|}=dH/dt=dH^{(1)}/dt+dH^{(2)}/dt=$$
$$=a^2n_pv_p(w_{00}\Delta R+w_0w_{\|}2\pi R_{max}H/L) \qquad (10)$$

Let us estimate the growth rate of the nanotube surface sideways:

$$V_\theta=dL/dt=(aw_0dN_\theta/dt)/N_{a\theta} \qquad (11)$$

Here dN_θ/dt is the number of atoms, diffused from the nanotube surface on the lateral edge in time unit, $N_{a\theta}$ is the number of carbon atoms on the lateral edge. In our case

$$dN_\theta/dt=w_\theta dN_{cmax}/dt=w_\theta n_pv_p2\pi R_{max}H \qquad (12)$$

and

$$N_{a\theta}=H/a \qquad (13)$$

Then with the account (12) and (13) the equation (11) we present in the following kind:

$$dL/dt=a^2w_0w_\theta n_pv_p2\pi R_{max} \qquad (14)$$

[illegible] w_θ is the probability of that the carbon atom, which [illegible]ced on the nanotube surface, is diffused on the lateral edge.

As a result we have derived the following system of the equations describing the nanotube growth upwards and sideways:

$$dH/dt=a^2n_pv_p(w_{00}\Delta R+w_0w_{\|}2\pi R_{max}H/L) \qquad (15)$$
$$dL/dt=a^2n_pv_pw_0w_\theta 2\pi R_{max} \qquad (16)$$

It is necessary to take into account, that in system of the equations (15) - (16 three values, namely $w_{\|}$, R_{max} and w_θ are the functions of variables H and L.

The length of an external lateral surface of the nanotube can be found from the assumption that it can be presented as Arhimed's spiral. Then

$$L=\delta R\varphi^2/4\pi \qquad (17)$$

Thus, we derive

$$2\pi R_{max}=L(\varphi)–L(\varphi-2\pi)=\delta R(\varphi^2–(\varphi-2\pi)^2)/4\pi=$$
$$=\delta R(\varphi-2\pi)/2 \qquad (18)$$

Here δR is the distance between layers of the nanotube, φ is the angular coordinate. From (17) we obtain dependence $\varphi=\varphi(L)$:

$$\varphi=2(\pi L/\delta R)^{1/2} \qquad (19)$$

From here, using (17) and (19), we find

$$2\pi R_{max}=\delta R((\pi L/\delta R)^{1/2}-\pi) \qquad (20)$$

Taking into account, that $L>>\delta R$, we have from (20) the following expression:

$$2\pi R_{max}=\delta R(\pi L/\delta R)^{1/2}=(\pi L\delta R)^{1/2} \qquad (21)$$

Then the system of the equations (15) - (16) becomes:

$$dH/dt=a^2n_pv_p(w_{00}\Delta R+w_0w_{\|}(\pi\delta R/L)^{1/2}H) \qquad (22)$$
$$dL/dt=a^2n_pv_pw_0w_\theta(\pi\delta RL)^{1/2} \qquad (23)$$

QUANTITY OF LAYERS IN GROWING IN THE DISCHARGE MULTILAYERED NANOTUBE

Under a shadow we believe that part of the nanotube surface on which bombarding carbon ions and atoms get only after collision with another nanotube. We believe that on the nanotube surface, located outside of the shadow there appears fast (induced) surface diffusion. We believe that the atom, which is placed on the nanotube surface, diffuses with equal probability in any direction. Therefore on the end face of the nanotube which length is equal $2\pi\bar{R}N$, the following part of atoms comes

$$\omega_{up} = \frac{2\pi \bar{R} N}{2\left(z_{sh} + 2\pi \bar{R} N\right)} .$$

On the lateral side of the growing nanotube, which length is equal z_{sh}, the following part comes

$$\omega_{\text{¿}} = \frac{z_{sh}}{z_{sh} + 2\pi \bar{R} N}$$

Here $\dot{N}$ is the number of carbon atoms, settling on the lateral surface of the nanotube outside of a shadow in time unit:

$$\dot{N} = 2\pi \mathrm{R}_{\max} z_{sh} n_o V_{th} \omega_s$$

$\bar{R}$ is the average radius of the multilayered nanotube, N is the quantity of layers in multilayered nanotube, $R_{\max}$ is the radius of the multilayered nanotube. $R_{\max}$ is possible to express through N and distance between layers in multilayered nanotube

$$R_{\max} = N r_{\ell} .$$

The quasi-stationary density of sorbed carbon atoms n_{cs} is determined by balance of sorption with probability ω_s and a leaving with probability ω_{ds}

$$\omega_s n_o V_{thc} = \omega_{ds} n_{cs} .$$

Here n_o is the plasma density. It is necessary to note, that ω_{ds} depends on induced effective temperature of sorbed atoms.

Speed of lengthening of growing nanotube is equal

$$V_{II} = \frac{\dot{N} a \omega_o \omega_{up}}{2\pi \bar{R} N / a}$$

Here ω_o is the probability of carbon atom connection to a growing side or the end face of the nanotube.

The growth rate of the lateral side of the nanotube is equal

$$V_{\text{¿}} = \frac{\dot{N} a \omega_o \omega_{\text{¿}}}{z_{sh} / a}$$

V_{II} and $V_{\text{¿}}$ are connected between themselves by the following ratio

$$\frac{V_{II}}{V_{\text{¿}}} = \frac{z_{sh}}{2\pi \bar{R} N}$$

From here we find quantity of layers in multilayered of the nanotube

$$N = \sqrt{\frac{z_{sh}}{2\pi \mathrm{r}_{\ell}} \frac{V_{\text{¿}}}{V_{II}}}$$

The nanotube length, located outside of a shadow, is equal

$$z_{sh} = R_n \frac{V_{IIe}}{V_{th}}$$

Here V_{IIe} is the component of the carbon atom velocity, directed perpendicularly to the catalytic surface; $R_n = n_{sn}^{-1/2}$ is the distance between nanotubes; n_{sn} is the surface density of the nanotubes.

$$N = \sqrt{\frac{R_n}{2\pi \mathrm{r}_{\ell}} \frac{2\pi \bar{R} N}{z_{sh}} \frac{V_{IIe}}{V_{th}} \frac{\omega_{\text{¿}}}{\omega_{up}}} =$$

$$\text{¿} \sqrt{\frac{R_n}{\pi r_{\ell}} \frac{V_{IIe}}{V_{th}}} = \sqrt{\frac{1}{\pi r_{\ell} \sqrt{n_{sn}}} \frac{V_{IIe}}{V_{th}}}$$

Since $\pi \bar{R} N \approx z_{sh}$, the area of cross-section of multilayered nanotube is equal $S_{up} = \pi R_{\max}^2 = 4\pi \bar{R}^2$. The area of its lateral surface, on which the carbon atoms are sorbed and fastly diffuse due to surface diffusion, is equal $S_c = 2\pi \bar{R} N \pi R_{\min}$. Taking into account that $\bar{R} = N r_{\ell} / 2$, we derive $S_c = \frac{4\pi^2 \bar{R}^2 R_{\min}}{r_{\ell}}$. Thus, we obtain that S_{up} is not much less S_c, i.e. $\frac{S_c}{S_{up}} = \frac{\pi R_{\min}}{r_{\ell}} > 3$.

In the case of azimuthally symmetric nanotube

$$N = \omega_{\ln} \sqrt{\frac{z_{sh}}{2\pi \mathrm{r}_{\ell}} \frac{V_{\text{¿}}}{V_{II}}}$$

$\omega_{\ln}$ is the probability of origin of a new layer.

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ФОРМИРОВАНИЕ НАНОТРУБОК НА КАТАЛИТИЧЕСКОЙ ПОВЕРХНОСТИ В ПЛАЗМЕННОМ РАЗРЯДЕ

В.И. Маслов, В.Н. Третьяков, Н.А. Азаренков, А.М. Егоров, И.Н. Онищенко

Получено выражение для количества слоев многослойной нанотрубки, которое успевает сформироваться за время ее роста в плазменном разряде.

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Отримано вираз для кількості прошарків багатошарової нанотрубки, що встигає сформуватися за час її росту в плазмовому розряді.