THE STUDY OF FORMATION CONDITIONS OF CARBON FILMS WITH DIFFERENT STRUCTURE DIMENSION

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Abstract: The influence of thermal and geometrical properties of a substrate on the structure of carbon films synthesized by the high temperature methods was studied theoretically and experimentally. It is shown that the carbon films deposited on various substrates had the identical morphology of structure at equality of the temperature conductivity-thickness ratio in condition of identical the other technological parameters of growth films.

It is known that the physical and geometrical properties of substrates strongly influence on the growth mechanism of the films. For example, in identical technological conditions the nanotube film and the diamond-like film were grown on a surface of the quartz plates with various thicknesses. There is no criterion for the optimum substrate choice, which would take into account its physical and geometrical parameters.

In our work the influence of the physical and geometrical parameters of the substrates on the structure of carbon films, which were synthesized in a single high temperature technological process, is studied. Thus the temperature and the density of carbon vapor flow to substrates and also surface temperature of substrate were equal for all substrates on the nucleation stage of films.

One of the basic factors determining the nucleation mechanism of films is the efficiency of energy equipartition between the substrate's surface and carbon particles of vapor flow named accommodation coefficient $\alpha = (T_v - T_r)/(T_v - T_s)$, where $T_v$ is a temperature of carbon vapor flow; $T_r$ is temperature of adatoms; $T_s$ is surface temperature of substrate. As the carbon films on various substrates are formed at single process, $T_s$ has dominant influence on the growth mechanism. It is known that the significant parameters for forming a carbon structure such as the coefficients of adsorption and desorption of carbon particles, their diffusions on the substrate's surface exponentially depends on the surface temperature of the substrate.

In our experiments the flat substrates from Si, KBr, NaCl, LiF, polycor and cover glass with thickness from 0.01 mm to 5 mm were used. The carbon films with thickness 120 nm on various substrates were grown at a single technology process by the thermic evaporation of graphite in vacuum in the pulse-periodic regime (time length of impulse – 2 s, frequency – 0.5 Hz and film growth rate $\nu = 5-6$ nm/sec). The films structure was researched by the SEM, STM, and AFM methods.

The calculation of change of the surface temperature was proceeded for our flat substrates. The heat conduction equation (1) was solved for the one-dimensional case (flat substrate)

$$\frac{\partial T_s}{\partial \tau} = a \frac{\partial^2 T_s}{\partial x^2}$$

(1)

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where $\dot{a}_i$ is the temperature conductivity; $\frac{\partial T}{\partial \tau}$ and $\frac{\partial T}{\partial x}$ are change of the surface temperature during time and along thickness of substrate, respectively. The model of thermal stresses allowing to take a surface temperature at any moment of time [1] was used for solution of equation (1). At boundary conditions $\lambda \frac{\partial T}{\partial x} |_{x=0} = -q$ and $\frac{\partial T}{\partial x} |_{x=d} = 0$ the solution of equation (1) according to [2] is

$$T_i = T_0 + \frac{2qa_i}{\dot{a}_i} \sqrt{\frac{\tau}{\pi}} \left[ 1 + 2 \sum_{n=1}^{\infty} \left( \exp(-n^2\alpha^2) - \sqrt{\pi n} \alpha \left[ 1 - \Phi(n\alpha) \right] \right) \right]$$

(2)

According to [2] at the nucleation stage $\alpha = \frac{d}{\dot{a}_i \sqrt{\tau}} > 1.2$ the solution of equation is

$$\dot{\alpha}_s = \dot{\alpha}_0 + \left( \frac{2qa_i}{\dot{a}_i \lambda d} \right) \sqrt{\frac{\tau}{\pi}}$$

(3)

Using an equation (3) the surface overheats curves (T$_s$-T$_0$) were built by step-by-step method for the first impulse at conditions $q = 4$ kW and $t = 2$s (Figure 1). From figure 1 we can see, that all substrates may be divided on three groups having the near value of the substrates overheating. In each group the flat substrates were made from the various materials with different thicknesses but had the approximate equal value of $\kappa = \frac{d}{\dot{a}_i}$, where $d$ - thickness of substrate, $a_n$ - coefficient of its temperature conductivity. Thus the different substrates had the identical temperature conditions for the nucleation of carbon films.

On figure 2 the images of four different structures of four carbon films from the various substrate groups (see figure 1), which were synthesized in the one technological process are shown. Probably, the structures of films on figures 2a and 2b may be classified as 3D and 2D allotropic carbon forms, which had nucleation on the substrate surface. The carbon films on figures 2c and 2d
may be classified as 1D carbon nanostructure, which had nucleation in volume of carbon vapor flow near the substrate surface.

| $\Delta T_e, K$ (calculat.) | Structure | Hypothetical models of growth |
|-----------------------------|-----------|------------------------------|
| 1 K (LiF)                   | ![SEM image of carbon films on glass. d=0.015mm](image) | ![](image) (Polycrystal 3D growth model of film) |
| 6 K (glass)                 | ![SEM image of carbon films on NaCl. d=1mm](image) | ![](image) |
| 36 K (KBr)                  | ![SEM and STM images of carbon films on polyco.r d=0.2mm](image) | ![](image) (Layers growth of graphene at conditions of the limited diffusion of atoms) |
| 45 K (NaCl)                 | ![AFM image of carbon films on Si. d=0.3mm](image) | ![](image) (Layers growth of graphene (substrate-substrate interaction is strong)) |
| 180 K (Polycor)             | ![SEM image of carbon films on glass. d=0.015mm](image) | ![](image) |
| 230 K (Si)                  | ![SEM image of carbon films on glass. d=0.015mm](image) | ![](image) |

**Figure 2.** Structure and hypothetical models of films growth on various substrates formed in single technology process:
- a) SEM image of carbon films on glass. $d=0.015\text{mm}$
- b) SEM image of carbon films on NaCl. $d=1\text{mm}$
- c) SEM and STM images of carbon films on polyco.r $d=0.2\text{mm}$
- d) AFM image of carbon films on Si. $d=0.3\text{mm}$
The first group of substrates (LiF and cover glass; k~23) had a minor overheat. The image of structure of these films is shown on figure 2a. The films have a polycrystalline structure with size of crystallites near 120 nm. Crystallites have crystallographic faceting with angle, representative for diamond. Initiation of the such germs completely agrees with the Folmer-Veber scheme of the films growth [3], which expects three-dimensional growth (figure 2a). This is possible if the binding energy between carbon adatoms of the vapour flow near substrate surface and a carbon nucleus is more than theirs bonds with the substrate surface.

The second group of substrates (KBr and NaCl; k~110) had overheat ($T_s - T_0$) near 45K. The film on NaCl (Figure 2b) has wavy structure, generated by the parallel planes of, hypothetically, graphite. This structure can grow by the Stranskogo-Krastanova mechanism. The third group of substrates (polycor and Si; k ~ 250 and k~325 respectively) had overheat ($T_s - T_0$) near 180K for polycor and 250 for Si. The images of the carbon films structure on polycor and Si are shown on fig. 2c and 2d. The films have the various structure (aligned 1D carbon structures, nanorings, and amorphous). The carbon film on the polycor has oriented columnar structure with diameter 2-4 nm (figure 2c). The growth of graphite fibrous is impossible at such high temperatures of the substrates surface because it is necessary bordering according to diffusion of the graphite’s adatoms. We suggest the following mechanism of growth of 1D carbon structure. The coefficient of adatoms’ desorption is high because the substrate’s surface has high temperatures. The part of carbon adatoms were evaporated diffusely from substrate to a hot laminar flow. The part of cold carbon adatoms were evaporated from substrate to a hot laminar flow diffusely. There are the conditions for the clusters (fullerenes) forming in the vapor carbon flow near the substrate surface. The cluster’s mass is very big. So, the clusters have not possibility to evaporate from the substrate. The fullerenes like the adatoms diffuse on a substrate surface and form nucleuses. Growth of the nanotubes in the carbon flow direction begins after the complete filling of surface by the fullerenes. The formation of nanorings (figure 2d) may be caused by the high desorption coefficient of carbon adatoms and the high diffusion coefficient of fullerenes on the substrates surface.

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