On the Role of Plasma Electrons in CVD Synthesis of Carbon Nanostructures with the Addition of a Plasma Component of a Carbon-Containing Gas

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The paper presents the results of experimental studies of the process of vacuum CVD synthesis of carbon nanostructures on substrates of Si, SiO\textsubscript{2}/Si, Ti, with controlled addition of the plasma component of the working gases C\textsubscript{2}H\textsubscript{2} and CH\textsubscript{4} to the synthesis zone. In the physicochemical processes of the synthesis of the obtained nanostructures, the main role is played by the electronic component of the plasma, which reaches the substrate and recombination of ions with plasma electrons occurs on the substrate surface. The plasma component in the synthesis zone significantly changes the structure of nanocarbon phases, their ratio, and distribution over the substrate, which determines the properties of the resulting coatings. The effect of the plasma component of the working gases becomes significant when the proportion of plasma in the total amount of gas is about 1%. Wherein, regardless of the physical nature of the substrate, specific carbon nanostructures with a significant amount of polymeric carbon components are formed on it.

Key words: carbon nanotubes, vacuum CVD synthesis, plasma technologies, polymer synthesis.
The plasma component of the working gas (ions, excited molecules, electrons, active radicals) strongly affects the synthesis of carbon nanostructures on a substrate [1]. Even a small addition of plasma to the synthesis zone leads to the excitation of the substrate atoms and to the intensification of surface processes. In the presence of a plasma component in the working gas under different technological conditions, a wide range of carbon structures is formed on the substrate: amorphous carbon, carbon nanotubes with a specific morphology, carbon-containing surface coatings with an ordered structure [2, 3]. Elucidation of the role of each of the plasma components in the formation of a specific structure is the subject of a separate study. In addition, as shown in [4], the products of synthesis from carbon-containing gases also strongly depend on the ratio of the concentrations of hydrogen components in the working mixture and various modifications of carbon $sp^2$, $sp^3$. The appearance of hydrogen when using, for example, gases $C_2H_2$ or $CH_4$ in the technological process is strongly dependent on the processes of dissociation of these gases in the plasma of discharge, which are used for ionization.

This paper presents the results of experimental studies of the synthesis of carbon nanostructures with the addition of about 1% of the plasma component to the working gas, as well as the role of individual plasma components in this process. A Penning cell with an incandescent cathode is used as a plasma source, which ensures stable operation of the discharge in a very wide range of discharge voltages, discharge current, and working gas pressure.

2. EXPERIMENTAL CONDITIONS

A detailed description of the setup and methods of obtaining results is given in [5, 6]. In these works, $C_2H_2$ and $CH_4$ were used as the working
gas. Substrates made of Si, Si/SiO2, or titanium foil (0.3 mm thick) were located in the centre of the vacuum chamber, where there was a little table with samples, which could be heated up to 1000°C. The plasma was supplied to the synthesis zone from a separate isolated plasma source, which was made in the form of a Penning cell with an incandescent cathode. Such a source, together with constructive improvements [5] allows you to smoothly control the ratio between the neutral and plasma components of the working gas in the synthesis zone. As catalysts for the dissociation of the working gas in the form of nanoparticles 5–40 nm size, we used Ni, Fe, which were formed during vacuum annealing of a thin (~ 5 nm) film at a temperature of ~ 900°C. Thin films of metal catalysts were deposited on cold substrates using a source in the form of a separate high-current vacuum arc discharge located in a vacuum chamber, and in which the metal catalyst was evaporated from cathode spots on a metal cathode. With this method of deposition of thin films, a micro-droplet phase of the catalyst material was, of course, also present on the surface of the substrates. The processes of synthesis of carbon materials on the surface of such microdroplets with a very high purity of the metal catalyst and a specific surface structure are of independent interest, and some original results of such studies are presented in [6].

Carbon nanostructures obtained under different modes of formation with the addition of a controlled plasma component of the working gas to the synthesis zone are presented below.

3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

When in the composition of the working gas that entered the substrate, the plasma component did not exceed 0.05%, on the catalytic centres of the substrates were synthesized carbon nanotubes (CNTs), which we studied earlier [2]. A typical view of such tubes is shown in Fig. 1.

However, with an increase in the fraction of the plasma component to ~ 1% and higher, the nature of the synthesized carbon material on the substrate changed dramatically. A typical view of such a coating is shown in Fig. 2.

This type of synthesized coating does not depend on the presence or absence of a catalyst on the substrate surface. So, for example, the coating applied to the SiO2/Si surface (see Fig. 3), on which a thin nickel film was first applied, and then the catalytic centres were annealed from the film and a standard synthesis process was carried out, has the same appearance as in Fig. 2.

In the lower part of Figure 3, a microdrop of material is visible, which, during vacuum-arc deposition of a thin catalyst film, spread in a liquid state over the surface of the substrate when falling onto the surface at a small angle. The carbon structures on the microdroplet, as can be seen, do not differ from the rest of the regions. The shape of the
observed structures is somewhat similar to vertically oriented curved sections of graphene planes (petals), which were observed in [7].

It follows from the well-known Ferrari–Robertson diagram [4] that, depending on the quantitative ratio between the carbon elements with sp², sp³ bonds and the amount of hydrogen, synthesis from a carbon-containing gas can lead to different results, in particular, they can be present in the synthesized material simultaneously as pure carbon structures, and polymeric (–CH–) component. The diagram of the authors would be extremely useful if it were possible to artificially set the percentage of each of the three indicated components in the synthesis zone. The necessary thermodynamic conditions for the existence of each of the components for the implementation of the areas highlighted in the diagram, in which the predominant type of the synthesized material is indicated, does not follow from the diagram. Nevertheless, it is very valuable in that it gives options for the existence of possible phases of carbon structures, which, in principle, can be synthesized in the presence of the three noted basic components of synthesis reactions. In a real technological synthesis, various physicochemical processes coexist at the same time, which generate a certain amount of each of the components, which are marked on the diagram.

The structure of the synthesized phases, which is shown in Figs. 2, 3, always looked more contrasting and clearer when CH₄ gas was used. This means that the necessary components for its implementation, i.e., precursors were more easily formed during the dissociation of CH₄ gas. The

![Fig. 1. View of CNTs synthesized on a SiO₂/Si substrate (Ni catalyst) from C₂H₂ gas at a pressure of 1.4 Pa. The synthesis temperature is 700°C. The content of the plasma component is not more than 0.02% .](image-url)
most probable pyrolysis reactions of this gas during ordinary thermal dissociation are [8]: \( \text{CH}_4 \rightarrow \text{CH}_2 + \text{H}_2 \) with the formation of methyl and \( \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \), which results in the formation of carbon and hydrogen. Of course, the reactions \( \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} \) with the formation of methylene or \( \text{CH}_4 \rightarrow \text{C} + 4\text{H} \) are not excluded. Possible in principle further sequential reactions of thermal dissociation of methylene in the form of a series of \( \text{CH}_3 \rightarrow \text{CH}_2 + \text{H} \), \( \text{CH}_2 \rightarrow \text{CH} + \text{H} \), \( \text{CH} \rightarrow \text{C} + \text{H} \) become less and less probable for each subsequent stage of dissociation. This means that even during thermal dissociation, free carbon in a very active atomic state is highly likely to appear in the reaction zone, as well as hydrogen, which, as follows from the Ferrari–Robertson diagram, can strongly influence the nature of synthesis reactions. And this takes place in ordinary thermal dissociation. When there was no plasma from the working gas of methane in the synthesis zone, only amorphous carbon was synthesized on the substrate in the form of soot—no ordered structures were observed. Obviously, the appearance of the plasma component not only significantly intensifies the processes of gas dissociation, but can strongly affect the type of dissociation itself, since in the Penning discharge, the electron distribution function contains a significant fraction of electrons with energies close to the discharge voltage [9]. In our experiments, the voltage was maintained at about 100 V. In gas discharges, it is the collisions of electrons with molecules of the working gas that lead to the production of the excited and ionic components [10], and the main role in these processes is played by high-energy electrons.
What types of methane dissociation are decisive in the presence of fast electrons in our reaction chamber, which are capable of destroying the molecule in a variety of ways, we cannot say. This requires additional research, but it is an experimental fact that the appearance of the plasma component in the synthesis zone radically changes the synthesis process itself and, therefore, affects the formation of carbon structures on the substrate. It is clear that plasma also provides a sufficient amount of a prepared precursor for fusion reactions and promotes physicochemical processes for the implementation of these reactions.

It is important that a regular structure of the type shown in Figs. 2 and 3 was formed only when an intense plasma component appeared in the synthesis zone, which constitutes at least a few fractions of a percent of the total amount of gas. To determine which of the plasma components (ions, electrons, excited neutral gas, excited radicals) influence the physicochemical processes the most during the synthesis of the observed structures, the following experiments were carried out.

On different substrates, there was a 0.4 mm thick nickel grid with cells (see Fig. 4), inside which the neutral gas component (always cold) and all excited neutral components, including various radicals, could freely enter (the temperature of the excited components could be higher than the temperature of the walls of the vacuum chamber). The electronic component, which also entered the cell, was subjected to the

Fig. 3. View of a carbon coating with microdroplets on the SiO₂/Si surface (Ni catalyst is present).
action of the retarding electric field of the ion layer due to the fact that
the grid had a potential that was always lower than the plasma potential,
and the cells were sufficiently deep (not less than 0.4 mm).

The thickness of the ionic layer near the grid can be calculated from
the known expression (see, for example, [11]):

\[ d_{\text{ion}}^2 = 0.4 \frac{V^{3/2}}{9\pi} n_e \sqrt{ekT_e}, \]

where, \( d_{\text{ion}} \) is the thickness of the ionic layer near the nickel grid, \( V \) is the
potential difference between the plasma potential and the grid poten-
tial, \( n_e \) is the plasma density, \( e \) is the electron charge, \( k \) is the Boltzmann
constant, \( T_e \) is the electron temperature of the plasma.

Estimates show that, under our conditions, the thickness of the ion
layer \( d_{\text{ion}} \) exceeded half the grid cell size, and the plasma electrons were
retained in the ion layer without reaching the surface of the silicon or
titanium substrates, which were covered by the grid. At the same time,
ions not only freely penetrated to the substrate surface, but also accel-
erated up to \( \sim (2–3)kT_e \), when approaching the ion layer in the so-called
‘Bohm sheath’ of plasma [11] and arrived at the substrate with an en-
ergy not less than \( \sim 3kT_e \) (all neutral components, of course, freely en-
tered the substrate inside the cell in the same way as they entered the
open, grid-free surface of the substrate). The electron temperature of
the plasma in our case was about 0.5–0.7 eV.

As can be seen from the data in Figure 4, carbon structures are also
synthesized directly on the surface of the nickel mesh, which are similar
to the view in Figs. 2, 3. However, the clarity of the image is worse than
in Figs. 2, 3, despite efforts to improve it. The reason is that this result-
ing structure is poorly conductive, i.e., with high electrical resistance.

Fig. 4. View of the nickel mesh after the synthesis process: general view (a),
fine structure of the coating that formed on the grid (b).
Most likely, on the nickel surface there is a large amount of a polymeric, non-conductive (more precisely, poorly conductive) component, and its synthesis on a nickel substrate, which is an active catalyst material, is facilitated. It is unexpected that the synthesis was carried out in the temperature range of 650–750°C, and the melting of the polymer component was never observed on any of the substrates.

But structures that are similar to Figs. 2, 3 have never been synthesized inside a grid cell. In Figure 5, a view of the surface of SiO₂ and Ti substrates inside a grid cell after the synthesis process is presented.

It can be seen from the last given data that only amorphous carbon is observed on the substrate inside the mesh cells. On the rough surface of the titanium substrate (titanium foil here without special polishing, i.e., as supplied), carbon was synthesized in the form of very small nanocrystalline fragments. This implies that it is the electronic component of the plasma that plays a decisive role in the formation of regular structures, which are presented in Figs. 2–4. It remains a mystery how exactly the slow, thermal electrons, which are effectively decelerated in an electric field of the ion layer, can have such a drastic effect on the fusion processes on the substrate. The neutral cold component of the gas, and all excited hot plasma components, and the ion component freely come to the area of the substrate inside the grid cell—only the electronic component does not come to the substrate. It can be hypothesized that the processes of ion recombination on the substrate surface with plasma electrons play a very important role for fusion reactions. Electrons arrive continuously together with ions, first to the surface of a clean substrate, and then to the

![Fig. 5. View of the substrate surfaces inside the grid cells: from SiO₂ (a), from Ti (b). Before the start of synthesis, catalytic nanocentres were formed on the surface of the substrates, then the vacuum chamber was opened, a grid was placed on the substrate surface, and then the standard procedure of vacuum synthesis was performed. Vertical and horizontal stripes on the surface of SiO₂ are the boundaries of the fine-grained structure of the initial state of the material.](image-url)
surface of the structure that has formed and continues to grow. The recombination of ions is carried out on the surface of the growing structure not due to Auger processes of ejection of electrons from the surface of the structure, but ions recombine precisely with free plasma electrons. It is possible that it is the specific recombination spectrum of the radiation of ions neutralized on the surface that so strongly affects the physicochemical processes during the formation of the observed structures, that transfers carbon atoms and other precursors to an active state, which is most conducive to chemical reactions of building structures.

It should be noted separately that any ordered structure (for example, a nanocrystal or nanotube, or two-dimensional structures such as graphene, etc.), which is artificially synthesized during some technological process, is subject to the universal requirement that a new element that is added to this structure (let this new element be an atom, a molecule or a radical) must correspond in its initial quantum state (you can call it activation) to the surface into which it is to be embedded.

In the scientific literature, this process is often called 'self-organization', but this term does not carry a physical content. In fact, the laws of crystal chemistry work here and this is discussed in detail in [12], but it is very important to understand that not any element with the desired chemical formula can be built into some growing structure. A certain quantum state of this element is needed, and this quantum state, in our opinion, is provided in the above case by a special recombination radiation spectrum, which occurs when ions recombine on the surface of the structure we observe with plasma electrons, that is in fact, on the surface of the structures we observe, photochemical reactions take place with the absorption of suitable light quanta.

4. CONCLUSION

The experiments performed to study the effect of plasma components on the CVD synthesis of carbon structures from CH4 and C2H2 gases showed that the controlled addition of a plasma component to the synthesis zone in an amount of ~ 1% of the total amount of the working gas leads to the appearance of specific regular structures on the heated substrate, the form of which does not depend on the nature of the substrate. On the surface of the nickel substrate, the synthesized structures contain a large proportion of the polymer component. The polymeric mass of carbon material that forms between the observed regular structures withstands high temperatures without melting or modification.

It is shown that the electronic component of the plasma entering the synthesis zone plays a decisive role in the formation of synthesized structures. The plasma ions of the working gas recombine on the surface of the substrates with electrons dynamically arriving on these surfaces from the ion layer. The resulting specific recombination radiation of
ions due to their recombination with slow plasma electrons transfers ‘building’ elements into the desired quantum state.

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