Technology of functional elements of electronics based on nanotubes and graphene

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Abstract. The state of the field of technologies for the synthesis of carbon nanotubes today allows the production of large volumes of nanotubes with desired properties, however, issues related to their application, as a rule, face difficulties that often require the process to be specialized. This work can help to form approaches to solving possible difficulties in the methods of using carbon nanotubes. The presented technological concept makes it possible to obtain both carbon nanotubes and graphene in a single-type installation from different carbon-containing sources. Using the oxidation of a carbon source, reduce the temperature of synthesis from it to the temperatures of synthesis from carbon monoxide, as well as get rid of excess amorphous phases formed during pyrolysis. Finally, it is precisely the positioning of the catalyst in the right places, without the possibility of its surface diffusion and evaporation, which will make it possible to obtain functional elements based on carbon nanotubes or graphene in these regions.

1. Introduction

Today, the success of silicon technology can hardly be overestimated. This technology has accumulated a wide range of ready-made solutions for the implementation of certain devices and circuitry problems. The existing products on the market satisfy the main trends of miniaturization, however, the trends to expand the functionality of silicon electronic components are reaching their limits today. There are two general approaches to expanding the functionality of electronic components. The first is the creation of a fundamentally new material base for electronic devices, such as molecular electronics. Despite all the promising and globality of this approach, its implementation is an essentially resource-intensive activity and in this regard, in the near future, significant technological breakthroughs in this direction should not be expected. The second approach is to replace functional parts in electronic and electromechanical components with materials with more suitable properties for realizing their functions, so-called functional materials. One of the promising functional materials for the creation of such hybrid devices are carbon materials such as nanotubes and graphenes.

Currently, the technology of carbon nanotubes as applied to electronics is implemented in two ways. The first one consists in large-scale synthesis of nanotube material with their subsequent deposition on a substrate [1], and the methods of deposition vary from homogeneous coatings used for photolithography [2] to electrophoresis-controlled deposition from a solution [3]. The second method is
direct synthesis on nanotubes on a substrate, where their position is determined by a preformed catalyst pattern [4]. Obviously, the first method has a number of significant disadvantages associated with the controllability of the number of nanotubes on the plate element, and as noted by the authors themselves, the large differences in properties from nanotube to nanotube. The second method is the most promising and better compatible with electronic technology; however, in this case, it is desirable that the synthesis of nanotubes takes place at low temperatures [5]. The use of graphenes in electronics is always associated with work on a substrate; today there are ready-made substrates with graphene on the market for experimental work [6, 7], but basically the technology of their production is associated with the synthesis of graphene on a metal [8]. In electronics, it is very important to use graphene as an active element of electronic components, and therefore the author considers the most promising those rare works where the synthesis of graphene is carried out on dielectrics, on sapphire [9] and on silicon carbide [10].

In this work, the author describes approaches to the use of carbon nanotube technology in electronics, in the key of compatibility with technologies for the synthesis of graphene on a dielectric.

2. Technological concept for the synthesis of functional carbon nanomaterials

The most attractive method for obtaining carbon nanomaterials are catalytic pyrolysis processes in view of their introduction into electronic technology [1]. Evaporation methods (arc, ablation) do not allow the growth of nanotubes and graphenes in a given place, however, the material obtained by such methods can be applied to a substrate and used for its intended purpose, in which case the position of the functional material is not controlled.

In the developed technology [11], the process of producing carbon nanotubes is based on the oxidation of ethanol with the formation of carbon monoxide.

$$2O_2+C_2H_5OH=2CO+3H_2O$$

Carbon monoxide, in turn, disproportionate to carbon and carbon dioxide.

$$2CO=CO_2+C$$

If the reaction occurs directly on the catalyst, then a graphene layer is formed on its surface, which, depending on the synthesis conditions, is either stored on the catalyst or aggregates into carbon nanotubes [12].

At higher temperatures, the rate of ethanol pyrolysis is higher and its additional oxidation is not required; ethanol decomposes according to known schemes [13] with the formation of carbon on the catalyst.

To implement such a technological scheme, an installation for producing carbon nanomaterials was developed, which implies the possibility of producing carbon nanomaterials both on catalysts of arbitrary shape and on round plates with a diameter of up to 80 mm, with a pre-formed catalyst pattern [14].

The growth of nanotubes in a given location can be determined by the position of the catalyst intended for this. To date, many methods of lithography in general and photolithography in particular are successfully used to implement this idea [4]. Using these methods, a catalyst pattern is formed, on which nanotubes grow as a result of the reaction.

The growth of nanotubes in a given direction may be due to the direction of action of the growth forces. The actions of the growth forces of nanotubes can be directed by a group of methods. The first is the action of an electrostatic field [15,16], which directs the growth of nanotubes due to the polarization of carbon atoms in this field. The second possible action of a magnetic field, which directs the growth of nanotubes due to the magnetization of the nanotube nucleus in this field. The third is a decrease in the degrees of freedom of nanotube growth [17]. The first two methods are implemented by a simple application of an external force to the substrate, where the nanotubes grow. The last method is implemented using a mask layer. A layer of an inert substance is applied to a catalyst drawing prepared by lithography. In this layer, using lithographic methods, grooves are etched in the directions where the
nanotubes should grow. Thus, during a chemical reaction, nanotubes have no choice but to grow strictly along the previously etched grooves. After a chemical reaction, the mask is selectively removed if necessary.

The physical meaning of the technological approach of these methods consists in changing the internal energy of the catalyst surface area to a value at which the growth of the nanotube is initiated. In the third case, under the conditions of the technological process, the catalyst has sufficient internal energy to initiate the growth of nanotubes, but the growth of a nanotube is possible only along a single degree of freedom. In the other two, by external action, in the catalyst, under the conditions of the technological process, regions with internal energy sufficient to activate the growth of carbon nanotubes are formed.

3. Synthesis of carbon nanotubes
During the synthesis of carbon nanotubes, ethanol feeding the chamber is decomposes with the formation of carbon monoxide. The formed carbon monoxide is adsorbed on the surface of the catalyst particles, on which the molecules are disproportionated to carbon and carbon dioxide dissolving in the catalyst. The process takes place until an equilibrium state of the system "carbon solution in the catalyst" - "quasi-liquid adsorbate of carbon monoxide" appears. A catalyst particle in which carbon dissolves floats in a drop of its own adsorbate of carbon monoxide. Upon cooling, the carbon dissolved in the particle begins to "leave" it and the carbon is desorbed from the drop. A drop moving along the surface leaves behind desorbed carbon in the form of a carbon nanotube. During the desorption process, the catalyst particle can either remain inside the nanotube or be exposed as a result of the consumption of the adsorbate. Moreover, in the latter case, the catalyst particle is oxidized in the residual atmosphere and dispersed (figure 1c). During the growth of a nanotube, a catalyst particle can behave in different ways, and it is this behavior that will determine the structure of nanotubes [12].

![TEM images of carbon nanotubes](image_url)

**Figure 1.** TEM images of carbon nanotubes. a) -nanotube grown on a non-spherical catalyst particle, b) -TEM image of a nanotube with an intercalate inside, c) -TEM image of a nanotube at the end of which the particle was destroyed, which led to the growth of smaller nanotubes, d) -TEM image of a nanotube presented on figure 1b, in the nickel reflex.
In addition to translational motion, a particle can also perform rotational motion, which, provided that the particle is nonspherical, will affect the structure of the nanotube (figure 1a). During the movement, fragments can be separated from the catalyst particle, which, remaining inside the nanotube, do not oxidize in the atmosphere, even if the end of the nanotube is not closed (figure 1c). It should be noted that in most nanotubes the diameter of the end particle and the diameter of the nanotube itself are approximately the same, this allows us to assert that in this technological process the diameter of a nanotube is determined by the diameter of the particle that initiated its growth.

The nanotube material obtained by our method has magnetic activity. This fact is due to the presence of a single-crystal ferromagnetic intercalate inside the nanotubes (figure 1b, d).

Ferromagnetic intercalate is a nickel catalyst dispersed inside a carbon nanotube, which is obtained from a precursor through a cascade of reactions.

\[
\text{NiCl}_2 + 6\text{NH}_4\text{OH} \rightarrow [\text{Ni(NH}_3)_6]\text{Cl}_2 + 6\text{H}_2\text{O} \quad (3)
\]

\[
[\text{Ni(NH}_3)_6]\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{Cl}↑ + \text{NH}_3↑ + \text{NiO}↓ \quad \text{(heating)} 
\]

\[
\text{NiO} + \text{CO} \rightarrow \text{Ni} + \text{CO}_2
\]

Nickel catalyst makes it possible to obtain carbon nanotubes from ethanol in the temperature range 500-900 °C.

The production of single-walled carbon nanotubes requires the solution of a technical contradiction arising from the synthesis of nanotubes on a catalyst deposited on a substrate. Annealing of nanoparticles deposited on a substrate causes their surface diffusion, and, consequently, runaway and enlargement of catalyst particles. Thus, it turns out that no matter how small particles are formed on the substrate, as a result of annealing, they will necessarily enlarge due to their surface diffusion. The diameter of the clusters on the substrate is determined by the annealing temperature and the heating rate of the sample. There are two ways to suppress the enlargement of catalyst particles. First, arrange the catalyst particles so that the distance between them is greater than their free path. The second is to limit surface diffusion, the surface over which particles can move.

In the first case, a large distance between nickel clusters was achieved due to a decrease in the concentration of the precursor in the initial solution. The process of synthesis of carbon nanotubes was carried out at 600 C using catalyst precursors of different concentrations: \(3\times10^{-2}\) mol/l (reference), \(3\times10^{-3}\) mol/l, \(3\times10^{-4}\) mol/l, \(3\times10^{-5}\) mol/l. When studying the results by atomic force microscopy of a sample with a concentration of \(3\times10^{-5}\) mol/l, carbon nanotubes with a diameter of about 2 nm were found (figure 2). This is close to the diameter of single-walled carbon nanotubes.

![Figure 2](image-url). Carbon nanotubes obtained on a diluted catalyst. Topography 8x8 microns.
In the second case, the limitation of the surface over which particles can move was carried out by drinking the zeolite with a solution of an ammonia complex of a nickel salt. If the zeolite is saturated with a solution of nickel salt, then carbon nanotubes will form in the pores of the zeolite, the diameter of which will be determined by the pore diameter. It is convenient to use this method to obtain single-walled carbon nanotubes.

Zeolite brand CaEN, Y or ZSM-11 is calcined in vacuum at a temperature of 200-600 °C for 3 hours, then placed in a solution of hexaammonium-nickel dichloride in ethanol. After a daily exposure in solution, the catalyst is washed in 2-propanol, after which it becomes ready for use. Carbon nanotubes (figure 3) are produced in a narrow temperature range from 650 to 700 °C.

Figure 3. Carbon nanotubes obtained in zeolite. (a) SEM image, (b) TEM image

Since carbon nanotubes are obtained from desoluted carbon to the catalyst surface, ethanol, in the presented technology, is only a model carbon source, which means that in principle any carbon source can be used. Moreover, at low temperatures (up to pyrolysis temperatures) from its combustion in the atmosphere to obtain carbon monoxide from which carbon nanotubes will grow.

An example of such use is a household propane-butane mixture burned in the atmosphere according to the reaction:

\[ 2\text{C}_3\text{H}_8 + 7\text{O}_2 \rightarrow 6\text{CO} + 8\text{H}_2\text{O} \]
\[ 2\text{C}_4\text{H}_{10} + 9\text{O}_2 \rightarrow 8\text{CO} + 10\text{H}_2\text{O} \]

In this case, carbon nanotubes will also be obtained (figure 4b), however, in the case of high-carbon compounds, it is very important to observe the stoichiometric ratio, because a lack of oxygen will lead to carbonization (figure 4a) of the nanotube material.

Figure 4. Carbon nanotubes obtained from propane-butane gas mixture (a) without stoichiometric ratio, (b) with stoichiometric ratio.
4. Formation of graphene layers
Using this technology, it is possible to form graphene layers on the surfaces of the catalyst, nickel [18] and copper [19]. For the experiments, we used silicon substrates with the (001) orientation with a thermally grown silicon oxide layer with a thickness of at least 250 nm. Before being loaded into the reactor, the plates were subjected to a standard cleaning method. A copper layer with a thickness of at least 600 nm was deposited on the surface of silicon oxide by magnetron sputtering of a target in an Emitech K575X setup.

To start annealing the prepared Cu/SiO2 structure, the chamber was purged with argon for 10 min. After that, the substrate was heated at a rate of 100 degrees per minute. To reduce copper from copper oxide, hydrogen was added to the chamber in a ratio of 1:9 with argon at a gas flow rate of 0.5 l/min. The working pressure in the chamber was maintained at 10 mbar. The cleaning time of the copper surface was chosen empirically and amounted to 10 minutes. Then, for 10 minutes, graphene was grown by the method of catalytic pyrolysis of carbon-containing gas (propane), the flow rate of which was 0.15 l/min. The process ended with the blowing of the working chamber with argon and cooling at a rate of 15 degrees per minute to a temperature of 600 °C and further natural cooling of the sample to room temperature.

To reveal the properties of the obtained graphene film, copper was etched. For this, a 25% aqueous solution of ammonia was used, which forms a water-soluble complex. The required reaction to remove copper looks like this:

$$\text{Cu}_2\text{O} + 8\text{NH}_3\text{OH} = 2[\text{Cu}(\text{NH}_3)_4](\text{OH})_2 + 5\text{H}_2\text{O}$$

However, the etching resulted in incomplete copper removal. During the annealing of the copper film in hydrogen, silicon was reduced from oxide, and copper oxide was partially formed in the copper film. The Raman scattering study showed that it was precisely copper oxide Cu2O that was formed.

To detect graphene on the surface of the samples after copper etching, studies were carried out by methods of optical and probe microscopy (figure 5).

**Figure 5.** Image of a graphene layer under partially etched copper, obtained in an optical microscope (a), an atomic force microscope (b).

Based on the obtained images of the features of these structures, figure 5, the places for taking the Raman spectra are selected. The locations for taking the spectra are shown in figure 6a. The Raman spectrum on the surface of the etched copper film is shown as curve 5 in figure 6. It can be seen from the figure that there are characteristic vibration peaks D 1332 cm\(^{-1}\) and G 1586 cm\(^{-1}\), corresponding to carbon in the graphite phase emerging from the copper film, a characteristic 2D peak indicates that these are layers of graphene less than 10.
Figure 6. Raman spectra on the Cu/SiO/Si structure after copper etching.

The main advantage of the method shown is the production of a graphene layer on a dielectric, which fundamentally simplifies the technology of forming a graphene channel in transistors. Ideally, it is required to obtain a homogeneous graphene layer on a dielectric substrate, in which case contacts are formed to it and then a gate through the dielectric, thus, leakage currents in such a transistor will be due only to the properties of the gate dielectric, and leakage through the substrate will be excluded.

5. Conclusions
Considering the entire spectrum of carbon nanomaterial technologies, it is necessary to select the technology that is most suitable for the required functionality of the nanomaterial. The functionality of nanomaterials is determined by properties such as electrophysical and mechanical. For carbon nanotubes, these will be elasticity and conductivity. To implement such a functionality, nanotubes need to be grown in specified places so that they can move freely, thus using their electromechanical properties. For graphenes, they are primarily important as channels with high mobility in field effect transistors; therefore, it is very important to realize the growth of graphenes on a dielectric. To implement these concepts, in works, preference is given to chemical methods, as the methods with the widest possibilities.

The presented technological concept makes it possible to obtain both carbon nanotubes and graphenes in a single-type installation from different carbon-containing sources. Using the oxidation of a carbon source, reduce the temperature of synthesis from it to the temperatures of synthesis from carbon monoxide, as well as get rid of excess amorphous phases formed during pyrolysis. Finally, it is precisely the positioning of the catalyst in the right places, without the possibility of its surface diffusion and evaporation, which will make it possible to obtain functional elements based on carbon nanotubes or graphenes in these regions.

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