Energy of low-temperature synthesis of graphen-like carbon nanocomposites on porous silicon (Review)

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Abstract. The process of low temperature synthesis of graphene-like nanocomposites films on the porous silicon nanocrystallites (nc-PS) is considered. It was shown that the low temperature synthesis of graphene-like nanocomposites on nc-PS is due to the excess surface energy of porous-Si nanocrystallites and, in this case, nanoscale effects that occur on local parts of the atomically rough nc-PS surface play a specific role. In the report features of the specific role of the atomically rough nc-PS forces and the influence these forces on the energy of low-temperature synthesis of graphene-like nanocomposites on the surface of porous silicon nanocrystallites are considered.

1. Introduction
To improve the quality of graphene and graphene devices and energy reduce of production it, necessary to develop a technology for the low-temperature synthesis of graphene and graphene-like structures. The development of the technology for the low-temperature synthesis of graphene and graphene-like structures is of a great scientific and a practical interest for the development of the fundamental bases for the growth of nanocrystals, including 2D materials, and also for the creation of the various graphene devices of the ultra-low energy consumption and other applications of the graphene materials [1]. The development of low-temperature synthesis of graphene is needed to a greater extent for integration with flexible electronics based on organic polymers, which will expand the field of commercial use of graphene and graphene devices in various industries [1, 2]. In this work we study the possibility of the low temperature synthesis of the graphene on the real surface of nanocrystallites of the porous silicon (nc-PS) using quantum-size effects of the nanoscale self-organization of ordered structures [3, 4]. The mechanism of self-ordered atomic growth of graphene is associated with such nanoscale effects as the influence of the size of nanocrystals on the temperatures melting \( T_m \) and the temperatures crystallization of the nanomaterial [5, 6], the orientation and topological dependences of phase transitions [7], atomic grain boundaries [8], atomic faults, steps and roughness of the crystal growth surface [9] and other quantum-mechanical properties of nanocrystals on an atomically rough surface of crystal [3, 4].

The growth mechanisms study on the atomic surface of nanocrystals will allow us to develop methods for the low-temperature synthesis of graphene with a large area. This paper analyzes the existing methods of the low-temperature synthesis of graphene, considers the self-organization processes of nanosized pores or porous silicon nanocrystallites, which are nucleation
centers for the growth of graphene, at during carbonization of porous silicon, which will allow to overcome the boundaries of faults on graphene islands and to form the large size graphene at low temperatures synthesis by CVD-, ALD- methods or the electrochemical deposition method.

2. Analysis of existing methods of the low-temperature synthesis of graphene

High-temperature technologies of the graphene epitaxial growth on the crystals of the silicon and silicon carbide at $T = 1400$–$1600$ °C [10] and the synthesis of graphene by the sublimation of Si atoms from the SiC substrate at $T_m (\text{SiC}) = 1500$–$2000$ °C for silicon devices in the case of direct growth of graphene on silicon is energy-intensive. The epitaxial growth of graphene on the catalytic surfaces of transition metals Ni, Cu, Ir, Ru, Pd, Pt also are successfully used at lower temperatures of $\sim 1000$ °C [11]. In most cases, polycrystalline Ni and Cu foils are used as catalysts or sacrificial layers to produce high quality graphene layers large sizes at $T = 700$–$1000$ °C [12]. Ni and Cu act as catalysts that lower the energy barrier of the hydrocarbon decomposition reaction and stimulate the growth of graphene. These the high temperature processes use of the methane precursors and are complex due to the use of numerous of chemical reactions and the transfer of graphene on the other substrate that affects on the quality of the transferred graphene and graphene devices and at high energy costs [13].

To reduce the growth temperature of graphene (up to 300 - 600 °C) are used the solid precursors (polystyrene (PS), polyacrylonitrile (PAN), polymethylmethacrylate (PMMA) or the liquid precursors (methanol, ethanol, propanol, alcohol, benzene) with low decomposition temperatures [14]. The graphene growth temperatures are significantly reduced due to the use of these precursors, since the activation energy is reduced, which is important for the dehydrogenation of CH-bonds and the nucleation of graphene C–C bonds [15].

The low temperature (~ 500 °C) graphene growth by low pressure chemical vapor deposition LPCVD- method at low pressure (15 Torr - 150 mTorr) can be carried out as the using catalysts [16,17] and so without them [18, 19] on the flexible organic substrates [20]. This graphene is the non-uniform and instability, to make difficult to integrate into electronic devices and other applications [21].

The Plasma-Enhanced CVD PECVD- method with inductively coupled ICP plasma a power of (50–200) W is used for the low-temperature (~ 300 °C) synthesis of graphene [22]. This PECVD method provides the growth of multilayer graphene (FLG) over a Cu foil and additional growth of graphite carbon films over the graphene layer at 300 °C using a mixture of C$_2$H$_2$ and Ar gases. This low-temperature growth of the few layer graphene FLG film by the PECVD method allows the direct transfer of the FLG film by removing the surface oxide layer on the metal catalyst using plasma treatment with H$_2$ flow.

3. Low-temperature synthesis of graphene on surface-modified porous silicon. The energy of low-dimensional crystals due to an increase in surface energy and elastically strained forces of deformation of the nanocrystal / single-crystal matrix interface

It is well known [5, 6] that the melting temperature $T_m$ of a crystal depends on its size and decreases with decreasing crystal size. $T_m$ of powder individual crystals is lower than $T_m$ of volume bulk materials [6]. Low-dimensional particles have large surface-to-volume ratios and surface thermal effects dominate in them. A decrease in the particle diameter D leads to an increase in the surface energy $E_{\text{surface}} \sim 1 / D$, figure 1 [6].
Figure 1. Experimental and theoretical values of the melting-point temperature of gold particles [6]

The melting process is the vibrational instability of the surface atoms of the crystal lattice, which depends on the amplitude of their thermal vibrations and starts from the surface [6]. The $T_m$ of nanocrystals embedded in the matrix is higher than the $T_m$ of the matrix of the corresponding bulk crystal [8, 9].

Figure 2. Variation of melting point with the particle size for In nanoparticles embedded in an Al matrix in two kinds of In/Al nanogranular samples [9].

$T_m$ depends on the nature and structure of the interface between the nanocrystals and the matrix [9], because the interface undergoes significant structural distortions of the nanocrystal, causing various kinds of mismatch defects [8]. If the interface has a structure coherent with the matrix orientation, the $T_m$ of the nanocrystal is higher than the $T_m$ of the bulk matrix. In the case where the interfacial interface is random, uncoherent, the $T_m$ of the nanocrystals is below the $T_m$ bulk matrix [9]. In nanosize materials the influence of the nanocrystal/matrix interface boundary is extremely huge and
change the atomic structure of the interface boundary, Figure 3 [23]. In this work shown to the interface nanocrystal/single-crystal HOPG leads to a distortion of the atomic structure of the interface and modifies the nature of the atomic bonds sp2 on sp3 and boundary and increase in the intensity of the KRS signal, Figure 1, Figure 3 [23].

**Figure 3.** Raman spectra from the flat surface of a graphite single crystal (1) and on the same single crystal from a site with atomic terraces (2) [23]

The low-temperature synthesis of graphene and graphene-like nanostructures on the surface of porous silicon nanocrystallites proceeds similarly to the epitaxial growth of silicon carbide SiC on Si [10] and epitaxial films of graphene single crystals on the Ni (111) surface [24]. In all these cases, a special role is played by quantum size effects on the atomic steps of the atomically rough surface of the silicon crystal, on the nano-bounded surfaces of the nanocrystallites, on the interface between the nanocrystal / single crystal matrix, which cause an excess energy of the nanocrystallite surface sufficient for the synthesis of graphene and graphene-like nanocomposites.

All this shows that the boundary conditions of the nanocrystallite/matrix lead to quantum size effects, which are dominated by the energetics of the nanocrystals themselves, as well as the boundaries of the nanocrystal/matrix interface.

Thus the use of the energy of nanocrystallite/matrix interface systems is a key factor in the development of a low-temperature graphene synthesis method [25].
As a result of the interaction of carbon gases, in our case C\textsubscript{2}H\textsubscript{2}, with high-energy free bonds of nc-PS silicon nanopores, the synthesis of carbide Si – C and carbon graphene C – C bonds occurs on the PS surface [25].

The carbonization of the PS surface by C atoms has been studied in many works [26 - 30]. On all these examples of PS carbonization are shown, the temperature carbonization of PS are lower than the temperature of 1400 °C for the epitaxial growth of SiC on c-Si [10]. In all these cases, the presence of quantum silicon or nc-Si filaments is a prerequisite for low-temperature SiC formation [28, 30] and the low temperature carbonization of the c-Si depends from of surface energy of nc-Si porous silicon [29], which decrease with decreasing size crystallites [5, 6]. The synthesis of graphene coating on the PS surface using the CVD method from C\textsubscript{2}H\textsubscript{2} acetylene vapors at atmospheric pressure were carried out at T = 750 - 800 °C [28, 29] and 350 -500 °C [25].

The high energy of low-dimensional materials on an atomically rough surface of crystal [3, 4], nanocrystals, nanoparticles, nanowires[5, 6], the orientation and topological dependences of phase transitions [7] of thin films, nanophasic materials, the nanocrystal/matrix interface [23] can be used to decompose carbon precursors without the use of metal catalysts in a high-temperature method or a high-energy PECVD method.

Thus, the use of the energy of nanoscale crystals and the interface boundaries of a nanocrystal/crystal matrix is of particular scientific and practical interest for the development of technology for the low-temperature synthesis of graphene using the CVD- and ALD- methods.

In this work, energy is considered and the results of low-temperature (300 - 500 °C) synthesis of graphene and graphene-like carbon nanocomposites by carbonization of the pore surface PS are presented. The growth mechanisms study on the atomic surface of nanocrystals will allow us to develop methods for the low-temperature synthesis of graphene with a large area.

4. Experimental technique

Samples of porous silicon were prepared by electrochemical etching of a single crystalline c-Si substrate (Si (100), p-type, 100Ω cm, Sigma Aldrich) in a electrolyte HF (40%) : (CH\textsubscript{3})\textsubscript{2}CHOH (90%) : CH\textsubscript{3} (CH\textsubscript{2})N(CH\textsubscript{3})\textsubscript{3}Cl = 200 : 50 : 1 at \textit{j}_{\text{etch}} = 2.5mA/cm\textsuperscript{2} for 30 min. Optical images of the PS samples cross-section shown on the Figure 4. The pores deeps 285 mkm, diameters 10 mkm, and diameters of the nc-PS 10 – 20 nm [25].

![Figure 4. Optical images of the cross section of PS samples, pores depth — 265 μm, pore diameters — 10 μm](image)

Graphene was synthesized on the PS surface by the CVD method with acetylene C\textsubscript{2}H\textsubscript{2} precursors at T=1050, 500, and 350 °C of 20 min time deposition and atmospheric pressure on a modified set-up the original installation of the flowing type [25]. Parts of the samples after carbonization were etched in a solution of 10% HF: 40% HNO\textsubscript{3}: 23% CH\textsubscript{3}COOH: 27% H\textsubscript{2}O for 4 h to remove the upper porous layer passivated by carbon.
The Raman spectra of PS samples with optical images of pores in the places of light focusing with a wavelength of $\lambda = 532$ nm (Figs. 4) were recorded using Senterra Micro-Raman System and LabRAM HR spectrometers with laser power of 3 mW, SEM-images by the electron microscope Carl Zeiss Auriga Crossbeam 540 with an X-ray energy-dispersion analyzer. The crystallinity of the nanomaterial was characterized with XRD Bruker D8 Discover.

5. Experimental Results and Discussion
Raman spectra of the initial $c$-Si, PS, and PS $<C>$ samples (Figure 5), carbonized at temperatures $T = 1050$ °C, $500$ °C, and $350$ °C (Figure 6) are show the characteristic D-, G-, 2D- peaks of graphene on different parts of the deep pores, Figure 7.

Figure 5. Raman spectra of samples of the initial c-Si, PS and carbonized at a temperature of $1050$ °C PS $<C>$ [25]
Figure 6. Raman spectra of the surface layer of porous silicon passivated by carbon atoms PS<\text{C}> at different temperatures [25]

Figure 7. Raman spectra of the PS <\text{C}> sample, 1050 °C. 1- top, 2- middle, 3- bottom [25]

The analysis of intensities changes at the peaks on frequencies 304.5, 433.5, 521, 619.5, 631.29, 677.98, 826.8 and 970 cm\(^{-1}\), which characteristic for c-Si, PS and PS <\text{C}> shows, that the peak intensities of these peaks are higher for PS and PS <\text{C}> than for c-Si, and grows with increasing temperature, Figure 5. The highest intensity is observed for PS <\text{C}>. It is known [31, 32] that an
increase the intensity peak is associated with an increase the phonon scattering intensity, which grows with an increase of the density of phonones scattering centers. Thus in the process of PS carbonization, the density of scattering centers increases due to a decrease in the size of nc Si nanocrystallites in PS. The decrease the sizes of nc-Si in PS occurs due to the removal of volatile gaseous silicon monoxides SiO formed during the carbonization of PS at 1050 °C according to the reaction [10]

\[
\text{nc-Si (solid) + CO (gas) = SiC (solid) + SiO ↑ (gas)}.
\]

The Raman spectra of the PS <C> sample shows, in addition to the characteristic peaks for c-Si and PS, a peak at the frequency range 150.5 cm\(^{-1}\), which is absent in the Raman spectra of the samples c-Si and PS. This peak of 150 cm\(^{-1}\), is characteristic of silicon carbide SiC, caused by phonon scattering from transverse acoustic phonons (TA) [31].

The X-ray diffraction spectra of the samples carbonized at 1050 °C for porous silicon PS <C> also shows the peaks characteristic of SiC, Figure 8 [25].

![X-ray diffraction spectra of samples PS <C> carbonized at 1050 °C - a, and after removal of the carbonized layer – b [25]](image)

**Figure 8.** X-ray diffraction spectra of samples PS <C> carbonized at 1050 °C - a, and after removal of the carbonized layer – b [25]

The XRD-spectrum of the PS <C> sample carbonized at 1050 °C (Figure 8a) contains diffraction peaks of cubic SiC (110), SiC (220) and hexagonal SiC (101), SiC (104), SiC (008), SiC (0012) silicon carbide. The X-ray diffraction spectra of the PS <C> sample, after removal of the carbonized layer (Figure 8b), contain peaks only of hexagonal SiC (104), SiC (208). This indicates that, in the process of pore carbonization, silicon carbide structures of various configurations (cubical, hexagonal) are formed on the surface of the pores, while the formation of a hexagonal SiC (208) structure, which is due to the c-Si crystal structure, is observed on the surface of the silicon matrix (100).
In our case, SiC is formed on nc-PS at 1050 °C that is more low temperature than 1200 – 1300 °C of the epitaxial growth of the SiC [10]. It’s explained by reducing of the melting point of nanoparticles [5]. These energetic effects of nc-Si PC size manifested itself in the reaction of hydrogen evolution from water, when the energy efficiency of the nc-Si PC was higher than that of the standard platinum electrode [33].

To study the graphenization of PS in detail, the PS<C> samples were etched in hydrofluoric acid to remove the surface layer of porous silicon passivated with carbon atoms. The Raman spectra of the porous silicon sample carbonized at T=1050 °C after etching in hydrofluoric acid is shown in Figure 9.

![Figure 9. Raman spectra of the porous silicon sample carbonized at T=1050 °C after etching in hydrofluoric acid. The red line shows the spectrum of the porous surface, the black line presents the spectrum of the pore-free surface [25]](image)

Figure 9(1) shows the Raman spectra of the parts of silicon matrix surface left after the removal of the top carbonized PS<C> layer and the silicon matrix surface without pores, Figure 9 (2). Photos of these parts are presented in the inset in Figure 9, which show that the pore-free surface of c-Si after etching (2) is strongly damaged whereas the carbonized part of PS<C> (1) is of dark color and shows no signs of etching. This indicates that the carbonized surface of porous silicon has a high chemical resistance and is not etched compared to the c-Si surface, which has been etched through. In the Raman spectrum Figure 9(2) of the un-etched part of the c-Si sample, there are no characteristic D-, G-, and 2D peaks of graphene, neither do the spectra of initial silicon c-Si samples and PS samples not subjected to passivation with carbon atoms (Figure 2). The Raman spectrum of the un-etched part of the PS sample surface annealed at 1050 °C under the above conditions does not display any peak at 150.5 cm⁻¹ and analogy of the c-Si Raman spectrum, Figure 5. It should be noted that in our case, graphene-carbon nanocomposite was synthesized at 1050 °C as a result of the passivation of the surface of pores PS. Therefore the data of the Raman spectra of the PS<C> sample annealed at 1050 °C suggest that carbonization at this temperature occurs only on the porous part of PS which contains nc-Si. Thus silicon carbide is formed on the PS surface only in the presence of nc-Si PS [25].

The presence of the D- and G-peaks of high intensity in the Raman spectrum of the structure grown on the PS surface indicates that the structure grown on the PS surface consists of the graphene nanocomposites. At lower synthesis temperatures of 500 and 350 °C the graphene nanocomposites carbon layers contain graphene oxides are formed. At lower synthesis temperatures of 500 and 350 °C the formed graphene carbon layers contain graphene oxide as the main inclusion (D- and G-peaks). The spectra of these samples do not show bands typical for CNT and SiC. The CNT and SiC are not formed at temperatures 350 and 500 °C because of low activation energy for the C–C and Si–C bonds at these temperatures. The characteristic CNTs- and SiC- bands on the Raman spectra are absted
because the formation of CNTs and SiC at 350 °C and 500 °C does not occur due to the low activation energy unengough for decomposition of C-C and Si-C bonds. A low-temperature at 

t \text{ synthesis} = 350 - 500 \text{ °C synthesis of graphene carbon nanocomposites in the form of graphene oxides and CNTs with inclusions of various allotropic forms of carbon are observed.}

On the single crystal c-Si surface does not observe the carbonization at 1050 °C, not SiC synthesis. Graphene carbon nanocomposites are synthesized only on the surface of nc-PS [25].

Thus the energy of the low-temperature synthesis of graphene and graphene-like structures is associated with the surface energy of nc-PS, resulting from pore formation during electrochemical etching.

The carbonized surface of porous silicon PS <C> has a high chemical resistance.

6. Conclusions and conclusions

1. The possibility of low temperature synthesis of graphene and graphene-like nanocomposites in the temperature range T = (350 - 500) °C was shown experimentally by the example of carbonization of energy-saturated porous silicon nanocrystallites with an increased energy of free bonds of the nanocrystal / matrix skeleton.

2. The low temperature (~ 300 - 500) °C synthesis of graphene are possible due to the using of quantum-size effects of nanocrystals, in which the energy states of both the nanocrystal surface and the nanocrystal / matrix interface are dominant, that is a key factor in the development of a low temperature method for the synthesis of graphene. The high energy of low-dimensional materials (nanocrystals, nanoparticles, nanowires, thin films, nanophase materials) can be used to decompose carbon precursors without using metal catalysts. Low temperature synthesis of graphene is possible on the real surface of nc-PS using quantum-size effects of self-organization ordered nanostructures.

3. The mechanism of self-ordered of graphene is associated with such nanosize effects as the influence of nanocrystal size on the melting and crystallization of the nanomaterial, the orientation and topological dependences of phase transitions, atomic grain boundaries, atomic faults, steps and roughnesses of the crystal growth surfaced.

4. The use of the energy of nanoscale crystals and the interface boundaries of a nanocrystal / single crystal matrix is of particular scientific and practical interest for the development of technology for the low temperature synthesis of graphene using the ALD method. To create energy-saturated quantum-dimensional structures, nanoscale crystals and the interface of the nanocrystal / single crystal matrix, the methods of direct formation of ordered nanostructures due to the effect of spontaneous morphological transformation of an elastically stressed layer are promising, the the following technological methods are most promising: - 1) by electrochemical etching; 2) by radiation exposure with low-energy ions of gas clusters of high current density, large processing area and high processing speed.

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