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SYNTHESIS OF CARBON NANOTUBES BY PLASMA ENHANCED CHEMICAL DEPOSITION METHOD IN RADIO-FREQUENCY CAPACITIVE DISCHARGE

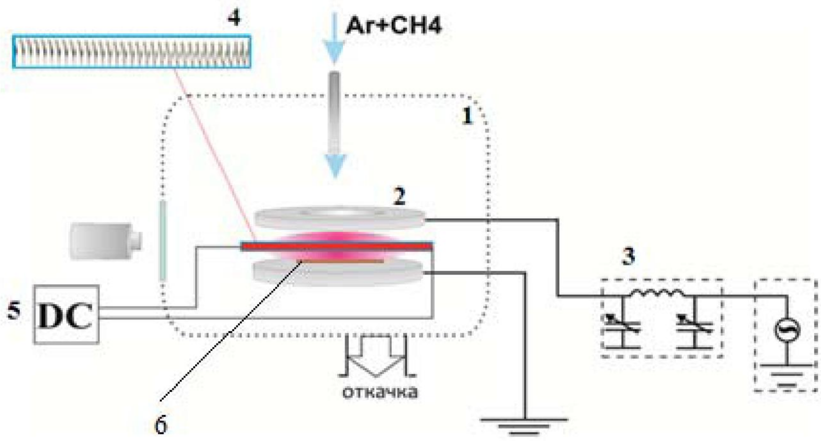
Abstract. In this work a synthesis of carbon nanotubes by plasma enhanced chemical deposition method in radio-frequency capacitive discharge is considered. As a result of the experiment, two samples were obtained – a silicon substrate with a small bright deposition on its surface and soot inside the heating element. These samples have been studied by using Ntegra Spectra Raman spectroscopy and scanning electron microscopy Quanta 3D 200i (SEM, FEI company, USA). The results of analysis indicate that carbon nanoparticles were deposited on the surface of the silicon substrate, whereas SEM and Raman spectroscopy analysis of soot indicates the presence of carbon fibers and nanotubes. The formation of CNTs and other carbonaceous nanostructures inside the quartz tube is explained by the fact that the heater material is nichrome (Ni + Cr) and the heating leads to evaporation of a small fraction of nickel, which served as a catalyst for CNT growth.
Keywords: carbon nanotubes, plasma chemical deposition, plasma.

Introduction

Synthesis of carbon nanotubes (CNTs) by chemical vapor deposition with plasma enhanced (PECVD) is used to produce vertically aligned CNTs on substrates at relatively low temperatures [1,2]. In accordance with the type of gas discharge, there are various PECVD reactors of glow discharge [3,4], radio-frequency discharge (RF) 13.56 MHz [5-8], microwave discharge 2.56 GHz [9]. For synthesis of CNTs are also used other methods, such as electric arc spraying (EAS) of graphite [10], laser ablation [11], method of chemical vapor deposition (CVD) [12]. The advantage of PECVD method compare with other methods is an ability to control and obtain vertically aligned CNTs due to the electrical field of plasma. CNTs have a wide range of applications: in electronics (flexible displays, sensors, high-speed and efficient diodes and transistors) [13,14], in medicine (treatment of cancer, biocompatible functional drugs and markers) [15-17], in energy (creation of solar panels, fuel cells, effective cathode electrocatalyst) [18-20] and etc. Due to these facts, nowadays scientists pay great interest to the research and synthesis of CNTs. Thus, in this work a synthesis of carbon nanotubes by plasma enhanced chemical vapor deposition method at radio-frequency capacitive discharge is considered.

Experiment

In this work the synthesis of CNTs by PECVD method was carried out in the experimental setup, the structure of which is shown in Figure 1. Experimental setup consists of working chamber (1), two parallel electrodes (2), where upper one is RF electrode and lower electrode is grounded, RF generator (3), heating element (4) – quartz tube with nichrome spiral, heater power source (5), pumping system and injection system of reaction gas into the working chamber.



1 – working chamber, 2 – electrodes, 3 – RF generator, 4 – heating element,
5 – heater power source, 6 – silicon substrate with a catalytic nanolayer

Figure 1 – Structure of experimental setup for synthesis of CNTs by PECVD method

On the basis of proposed scheme the experimental setup of combined radio-frequency discharge with a thermal heater was installed for the primary initiation of pyrolysis process. Figure 2 shows photos of working mode of RF plasma combustion with nichrome heater at different electrical parameters.

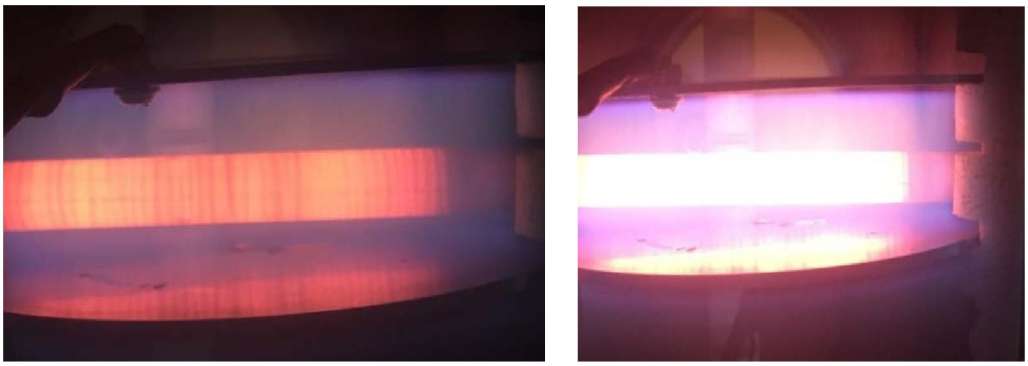
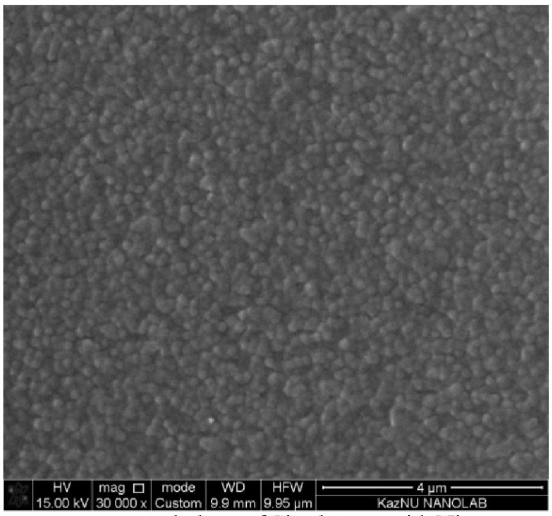
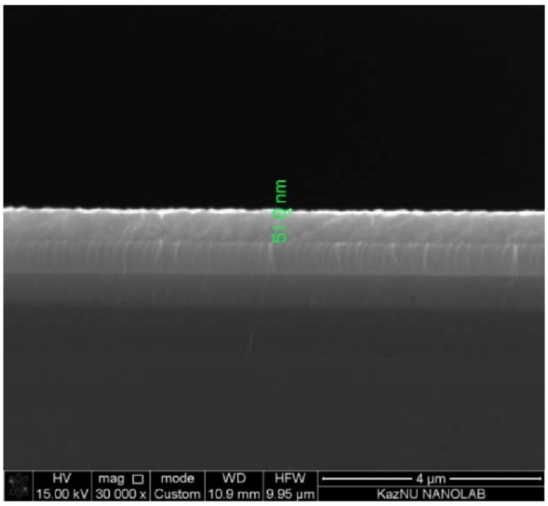


Figure 2 – PECVD process in working mode



a – morphology of Si substrate with Ni



b – thickness Ni film

Figure 3 – SEM analysis of silicon substrate with a catalytic nanolayer of nickel

It is known, that growth mechanism for CNTs can be explained by widely-accepted vapor-liquid-solid (VLS) model, where catalyst plays a main role for CNTs growth. Therefore, in order to synthesis of CTNs on silicon (Si) substrate a catalytic nickel (Ni) was deposited on the surface of silicon substrate (6) by electron-beam deposition. After deposition, obtained sample was investigated by scanning electron microscopy (SEM). SEM analysis shows that surface of silicon substrate has a uniform nickel nanolayer with thickness ~ 50 nm. SEM images of Si substrate with Ni are shown in Figure 3.

Thus, the obtained silicon substrate with catalytic nanolayer is loaded into working chamber on the surface of lower electrode and then an air is pumped out from chamber, after vacuuming, a flow of working argon gas (Ar) is supplied up to the pressure of about 4 Tor and then heating element is switched on. As soon the heating element is reached the temperature of 750^{o}C, a RF voltage is supplied to the upper electrode with power of 5-15 Wts by RF generator; as a result the argon RF plasma is ignited and held for 15 minutes. At this stage, nanoclusters (islands) of nickel are formed on the surface of the silicon substrate due to the plasma and heat treatments. These nanoclusters are the basis for the growth of CNTs on the VLS model. Indeed, Figure 4 shows a SEM image of resulting nickel nanoclusters on the surface of silicon substrate. The Figures 3 and 4 show, that before plasma and heat treatment, the surface of silicon substrate had a continuous nickel nanolayer, but after plasma and heat treatment process a separate islands of nickel nanoclusters with an average diameter of 20-70 nm were formed. According to the VLS model, the diameter of these nanoclusters determines the diameter of the synthesized CNT.

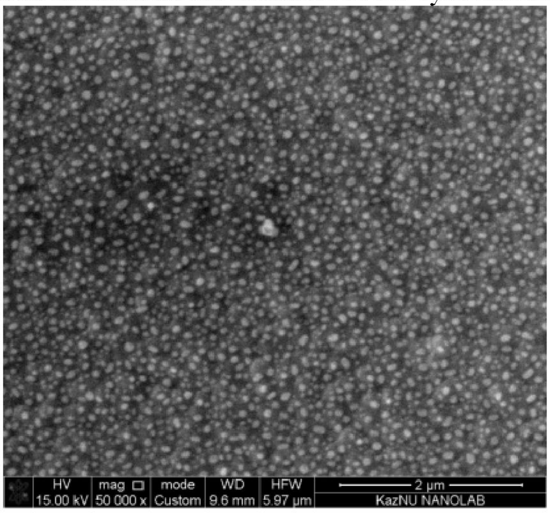


Figure 4 – SEM image of nickel nanoclusters on the surface of silicon substrate

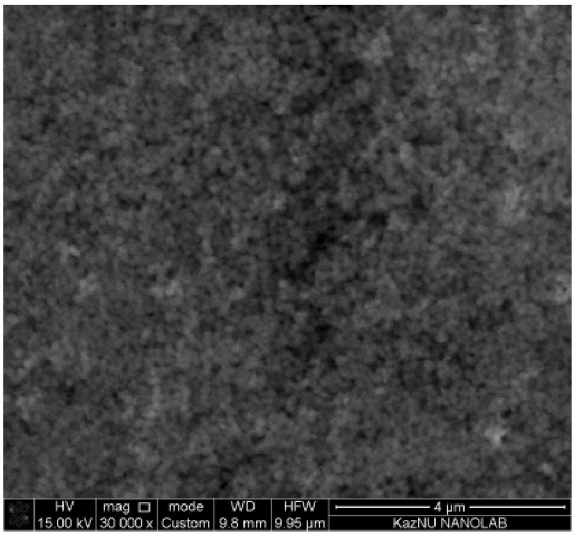
For the formation of nickel islands on the surface of silicon substrate 15 minutes is enough, then for CNTs synthesis the working chamber was filled with an additional reaction carbonaceous gas – methane (CH4) up to the pressure of 5 Tor, the synthesis process takes 15-30 minutes.

Thus, two samples were obtained from the experiment – a silicon substrate with deposited carbon nanoparticles (Figure 6) and soot into the heating element (Figure 5).

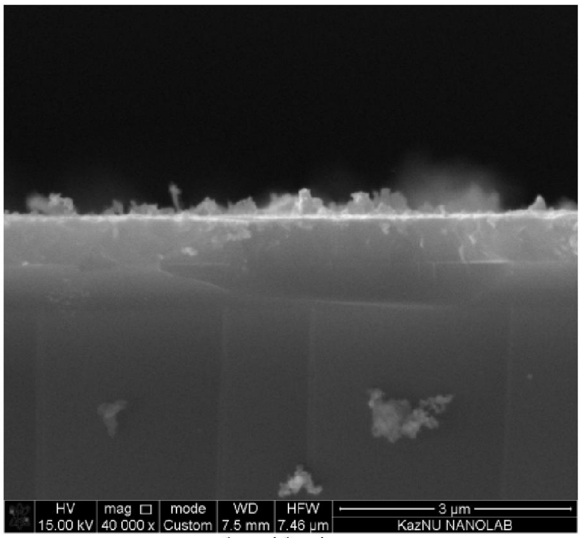
a

б

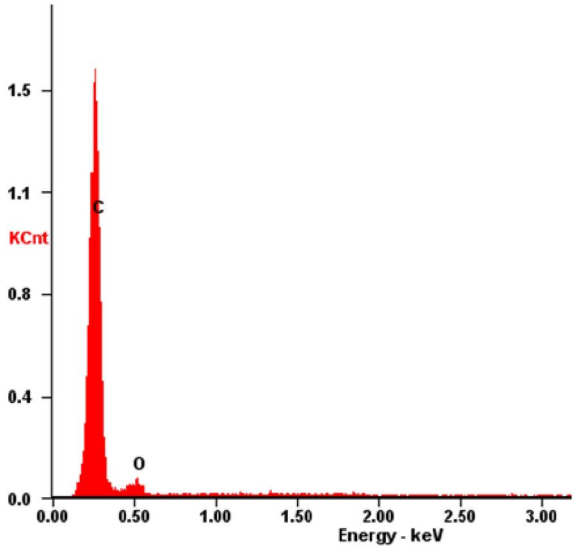
Figure 5 – Quartz tube before (a) and after (b) synthesis of CNTs by PECVD method



a – top view



b – side view



c – chemical composition

Figure 6 – SEM images and chemical composition of carbon nanoparticles deposited on the surface of silicon substrate

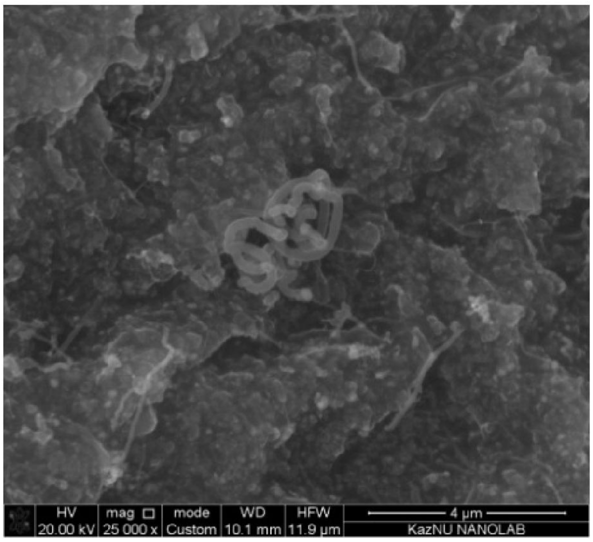
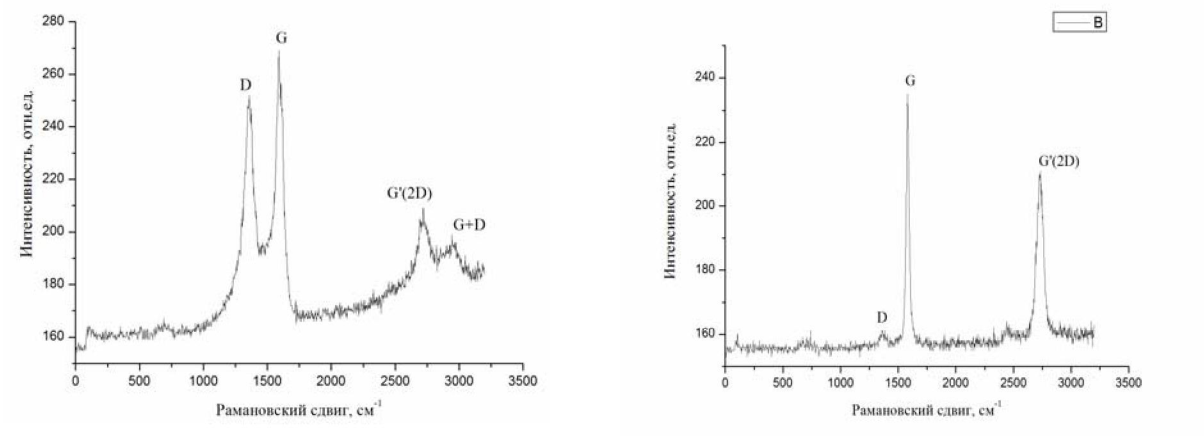


Figure 7 – SEM images of CNTs

The study of obtained samples by scanning electron microscope and Raman spectroscopy (RS) shows that formation of carbon nanoparticles during PECVD process is true ant they are deposited on the surface of the silicon substrate. Figure 6 shows the SEM images of deposited carbon nanoparticles, while the SEM and RS analysis of soot indicate the presence of carbon fibers and nanotubes (Figure 7). Initially, the purpose of this work was to synthesize of CNTs on the surface of silicon substrate, but as obtained results show, there is no CNTs on silicon substrate. Perhaps, the reason is still low temperature of environment near the substrate for the growth of CNTs, but sufficient for the formation of nanoclusters of nickel.

Due to the high temperature of nichrome heater, the Ni nanoparticles were formed because of the thermal emission from heater, which led to CNTs growth and formation of soot in heating element.

Raman spectra of soot are shown in Figure 8. Raman spectrum shown in Figure 8a corresponds to the typical spectrum of multiwalled CNTs (MWCNTs) with main G, D and G' (2D) bands at frequencies of 1591 cm^{-1}, 1360 cm^{-1} and 2719 cm^{-1}, respectively, and also G+D band at frequency 2950 cm^{-1}. G-band of this spectrum corresponds to a tangential vibrations of two adjacent carbon atoms in the CNT lattice, G' (or 2D) band corresponds to overtone of D-band, caused by two-phonon inelastic scattering. The presence of D-band and G'- band in the spectrum enables to indicate the defects in the structure and its perfection. Thus, to assess the structure the following formula of G and D bands intensity ratio can be used: $L_a = 4{,}4 \cdot \frac{I_G}{I_D}$, where L_a- area of homogeneous dispersion in the carbon structures. The value of bands intensity ratio for the spectrum is L_a= 4,7, indicating that the synthesized MWCNTs has not so bad quality. Also, the expressed 2D band in spectrum says about good quality of obtained CNTs. But fusion of D and G bands indicates the presence of amorphous phase in sample. Raman spectrum represented in Figure 8b is a typical to spectrum of Few-layer graphene (FLG). This is evidenced by the weak D band (1359 cm^{-1}) and relatively narrow and intense G bands (1581,8 cm^{-1}) and 2D (2733.6 cm^{-1}).



а б

Figure 8 – Raman spectra of obtained CNTs by PECVD method

Conclusion

In this work the synthesis of carbon nanotubes by plasma enhanced chemical vapor deposition method in a radio capacitive discharge was considered. As the result of the experiment two samples were produced – a silicon substrate with a small and white deposition on its surface and soot inside the heating element which have been investigated using SEM and RS analysis. The results of the analysis indicate that the carbon nanoparticles were deposited on the surface of silicon substrate, whereas SEM and RS analysis of soot indicate the presence of carbon fibers and nanotubes. The formation of CNTs and other carbon nanostructures inside the quartz tube is explained by the fact that the heater material is nichrome (Ni+Cr), during heating, a small fraction of nickel, which served as a catalyst for CNT growth, was allocated.

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ЖОҒАРЫ ЖИІЛІКТІ СЫЙЫМДЫЛЫҚ РАЗРЯДЫНДА ГАЗДЫҚ ФАЗАДАН ПЛАЗМОХИМИЯЛЫҚ ӘДІСІМЕН КӨМІРТЕК НАНОТҮТІКШЕЛЕРІН СИНТЕЗДЕУ

Аннотация. Бұл жұмыс жоғары жиілікті сыйымдылықты разрядта газдық фазадан плазмохимиялық әдісімен көміртек нанотүтікшелерін синтездеу тақырыбына арналған. Эксперимент нәтижесінде екі үлгі алынды – беттік қабатында қандай да бір ашық қондырмасы бар кремнийлік төсем және қыздыру элементінің ішіндегі күйе. Аталған үлгілер Рамандық Ntegra SPECTRA спектроскопиясымен жәнеQuanta 3D 200i (SEM, FEI company, USA) электроды сканерлеуші микроскопия көмегімен зерттелді. Анализ нәтижелері кремнийлі төсемнің беттік қабатында көміртекті нанобөлшектердің қондырылғанын, ал күйенің ЭСМ және РС анализі көміртекті талшықтардың және нанотүтікшелердің бар екендігін дәлелдейді. Кварцтық түтікшенің ішінде КНТ және басқа да көміртекті наноқұрылымдардың пайда болуы қыздырғыш нихром (Ni+Cr) материалынан болғанымен түсіндіріледі. Қыздырғыштың температурасын жоғарылатқанда материалдан КНТ өсуініне себеп болатын никель катализаторы бөлінеді.

Түйін сөздер: көміртекті нанотүтікшелер, плазмохимиялық қондыру, плазма.

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СИНТЕЗ УГЛЕРОДНЫХ НАНОТРУБОК ПЛАЗМОХИМИЧЕСКИМ МЕТОДОМ ОСАЖДЕНИЯ ИЗ ГАЗОВОЙ ФАЗЫ В ВЫСОКОЧАСТОТНОМ ЕМКОСТНОМ РАЗРЯДЕ

Аннотаци.Данная работа посвящена синтезу углеродных нанотрубок плазмохимическим методом осаждения из газовой фазы в высокочастотном емкостном разряде. В результате эксперимента были получены два образца – кремниевая подложка с неким светлым осаждением на ее поверхности и сажа внутри нагревательного элемента, которые были исследованы с помощью Рамановской спектроскопией Ntegra SPECTRA и сканирующей электронной микроскопией Quanta 3D 200i (SEM, FEI company, USA). Результаты анализа свидетельствуют, что на поверхности кремниевой подложки были осаждены углеродные наночастицы, тогда как СЭМ и РС анализ сажи свидетельствует о наличии углеродных волокон и нанотрубок. Образование УНТ и других, углеродосодержащих наноструктур внутри кварцевой трубки объясняется с тем, что материалом нагревателя является нихром (Ni+Cr), при нагревании которого из материала выделялась малая доля никеля, который служил катализатором роста УНТ.

Ключевые слова: углеродные нанотрубки, плазмохимическое осаждение, плазма.

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