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# Elaboration of carbon nanowalls using radio frequency plasma enhanced chemical vapor deposition

D.G. Batryshev[a,b], Ye. Yerlanuly[a,b,]*, T.S. Ramazanov[c], M.K. Dosbolayev[b], M.T. Gabdullin[b]

[a]*Laboratory of engineering profile, al-FarabiKazNU, Kazakhstan,050040 Almaty, 71 al-Farabi ave.*
[b]*National nanotechnological laboratory of opened type, al-FarabiKazNU, Kazakhstan,050040 Almaty, 71 al-Farabi ave.*
[c]*Institute of experimental and theoretical physics, al-FarabiKazNU, Kazakhstan,050040 Almaty, 71 al-Farabi ave.*

**Abstract**

In this work, a method of obtaining of carbon nanowalls by plasma enhanced chemical vapor deposition (PECVD) in radio-frequency (RF) discharge is considered. Carbon nanowalls were grown on the surfaces of different substrates. Obtained samples were studied by scanning electron microscopy and Raman spectroscopy. It was found that with increasing of discharge power, the nanowalls are agglomerated into nanoclusters with the formation of defects in the structure. SEM analyses show, that the growth process of CNWs on the surface of a silicon substrate with a thin catalyst nickel nanolayer goes better, than on the surface of copper wafer. Whereas estimated ratio of intensities of D and G modes from Raman spectra of obtained samples corresponds to the same quality of synthesized CNWs.

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*Keywords:* carbon nanowalls, plasma, chemical vapor deposition

## 1. Introduction

Since the discovery of various carbon nanomaterials [1-5], the prospect of their use as energy storage systems has been increasing every day [6-8]. One of the promising carbon materials is carbon nanowalls [5, 9-11]. Carbon

* Corresponding author. Tel.: +7 707 323 43 41;
*E-mail address: yerlanuly@physics.kz*

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nanowalls (CNWs) are one of the allotropic modifications of carbon with vertically oriented graphene sheets [5,9]. Since the discovery of CNW in 2002 and due to their large specific surface area and low density, they have high mechanical strength, high light absorption in the visible range, high electrical conductivity and etc. [9,10,12,13], which opened a new perspective future energy storage applications, as extremely dark thin coating, for bolometers [10] solar cells [14] or CNW electrode for supercapacitors [15,16] etc. Generally, the CNWs are grown from carbon-containing gas such as methane or acetylene on silicon substrate [17], diamond-like film [18] using hot wire chemical vapor deposition (HWCVD) method or by plasma enhanced chemical vapor deposition (PECVD) with different ways of plasma activation [5,14,20-22]. In this work a method of obtaining of carbon nanowalls on different substrates by RF-PECVD method is considered.

## 2. Experimental part

The synthesis of CNWs was carried out on experimental setup (Fig. 1), which consists of vacuum chamber with system of two parallel radio-frequency (RF) electrodes, heater under lower RF electrode, system of pumping and injection of gas. The CNWs were grown on silicon (Si) substrate with nickel nanolayer on its surface and on copper wafer by PECVD method to study their structural properties by scanning electron microscopy and Raman spectroscopy. Further investigation of their electrical properties will be discussed in the next work.

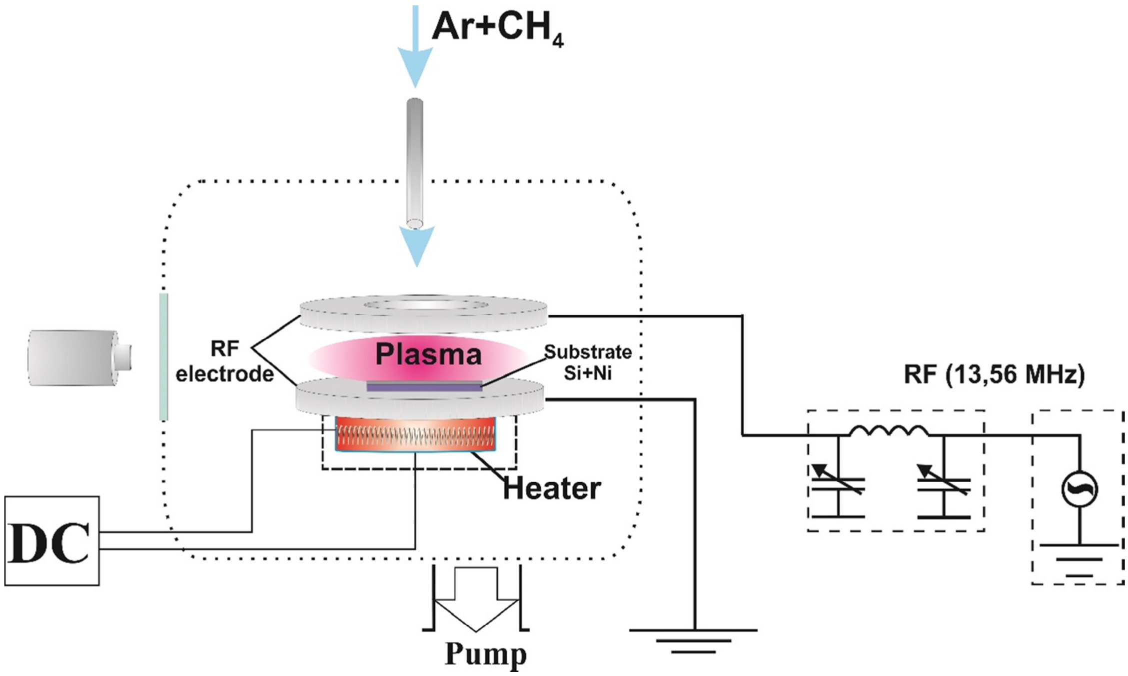


Fig. 1. Experimental setup for CNWs synthesis.

Nickel (Ni) catalytic nanolayer was deposited on silicon substrate by electron beam deposition method. Obtained Ni/Si substrate was located on the surface of lower RF electrode, as shown in Fig. 1. Before PECVD synthesis of CNWs, a vacuum ($10^{-5}$ Torr) is created inside of working chamber, then argon gas is injected into to the chamber up to the 1 Torr and the Ni/Si substrate is heated at $500^0$C, after RF plasma is activated at 10-15 W. At this stage, a preliminary annealing of the samples is carried out to form nanoclusters of nickel for growth of CNWs. After the formation of nanoclusters, a carbon-containing gas is injected into the chamber with argon gas at proportion ($Ar/CH_4$:10/0.9 sccm). The working mixture pressure was 1.5 Torr at the start and was increased up to 2 Torr.

## 3. Results and discussion

At the result of experiments, CNWs grow on the surface of Ni/Si substrate. SEM and Raman analyses of obtained samples are shown in Fig. 2-5.

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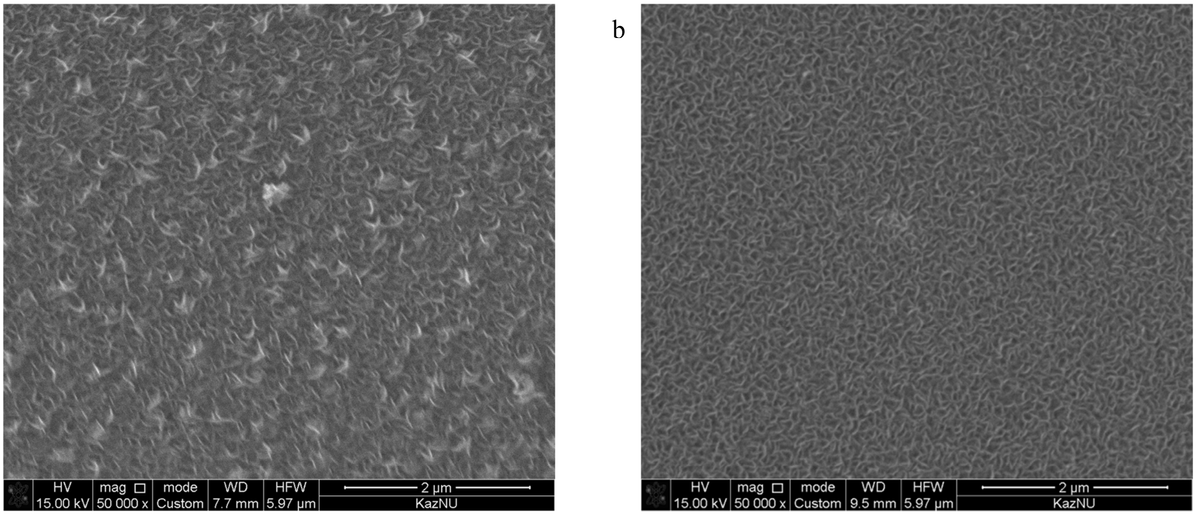



Fig. 2. SEM images of CNWs synthesized on Ni/Si substrates at RF powers of 15 W (a) and 10 W (b).

As seen from the SEM images, after the synthesis process, vertical carbon sheets formed on the surface of the silicon substrate, which are CNWs. With increasing the value of RF power an agglomeration of nanowalls can be observed – nanoclusters of walls (Fig. 3).

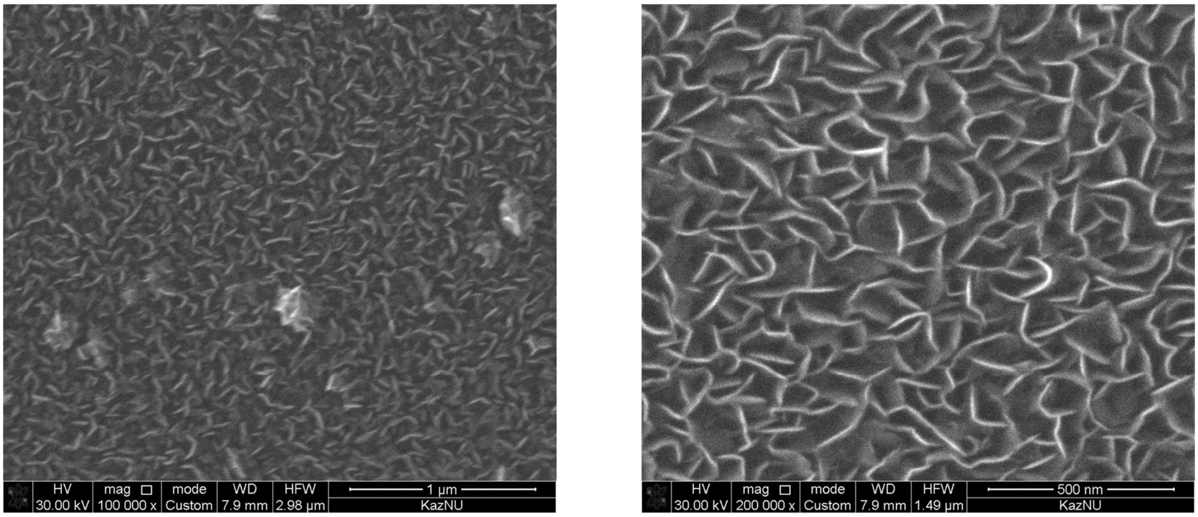



Fig. 3. SEM images of CNWs synthesized on Ni/Si substrate at RF power of 15 W.

Raman spectrum of obtained samples corresponds to the typical CNW spectrum [9,18,23], with *G* mode, which usually observed for graphite-based materials, distinguished *D* and *D'* modes, which associated with defects in structure, *2D* (*G'*) mode that corresponds to second order of the *D* mode and *G+D* mode the nature of which is still not clear. Intensity ratio of *D* and *G* modes, which is related to the crystal imperfection of a graphene sheet, varies from 1.7 to 1.9. Estimated in-plane correlation length $L_a$ varies from 2.5 to 2.3 nm, which is related to size scale over which CNW can be considered defect-free. As it's mentioned above, the increasing the value of RF power leads to agglomeration of nanowalls, maybe this is the one of the reason why the I(D)/I(G) ratio increases and value of La decreases.

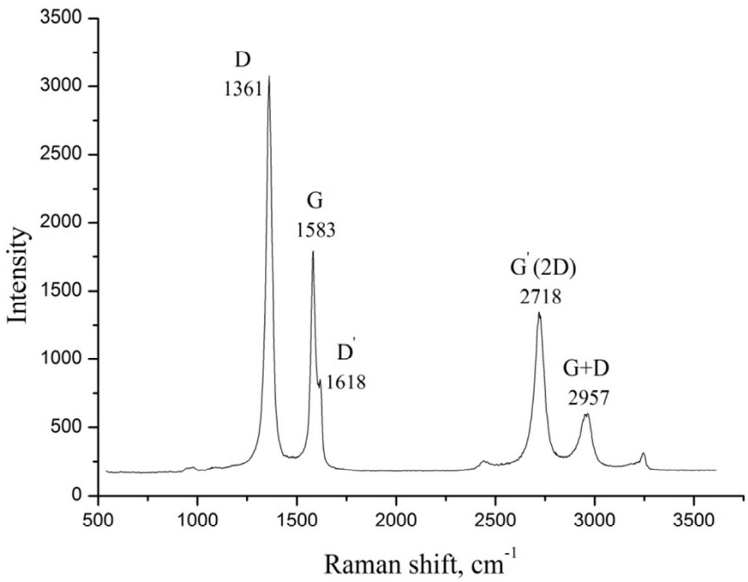



Fig. 4. Raman spectrum of CNW synthesized on Ni/Si substrate at RF power 10 W.

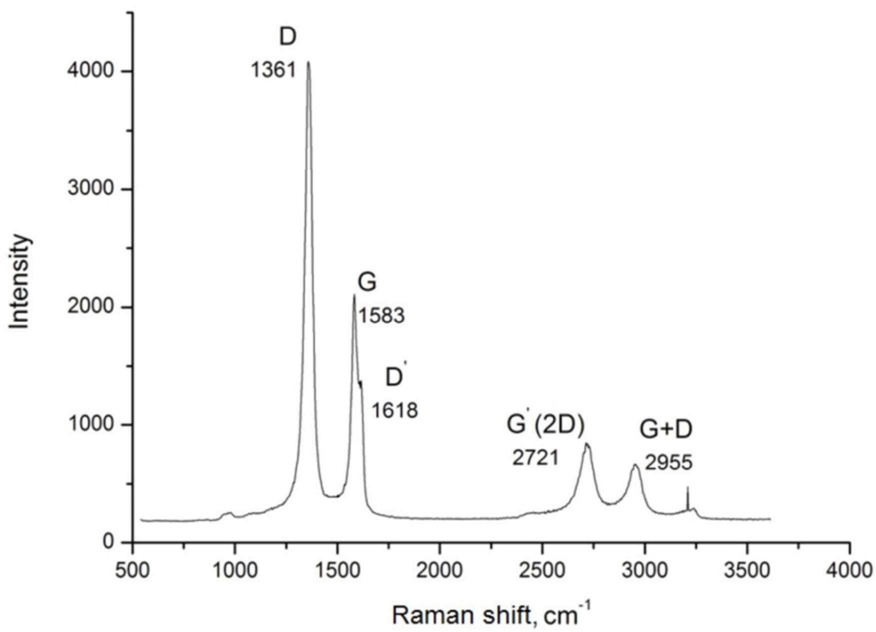
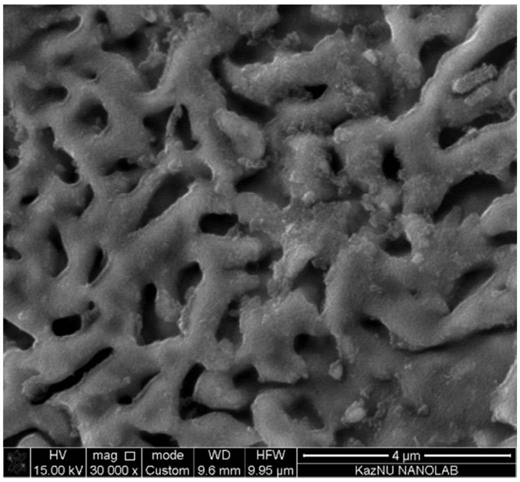



Fig. 5. Raman spectrum of CNW synthesized on Ni/Si substrate at RF power 15 W.

The synthesis of CNWs on copper (Cu) wafer was carried out at same parameters as with a silicon substrate. Obtained composite material based on copper-CNW can be used as electrode for the creation of supercapacitors [15-16]. SEM image and Raman spectrum of CNWs/Cu sample after PECVD synthesis is shown in Fig. 6. As seen, after

PECVD synthesis a thin film can be observed on the surface of copper wafer, where Raman spectrum corresponds to the typical spectrum of CNW and estimated value of $L_a$ and I(D)/I(G) ratio are 2.6 nm and 1.68, respectively.



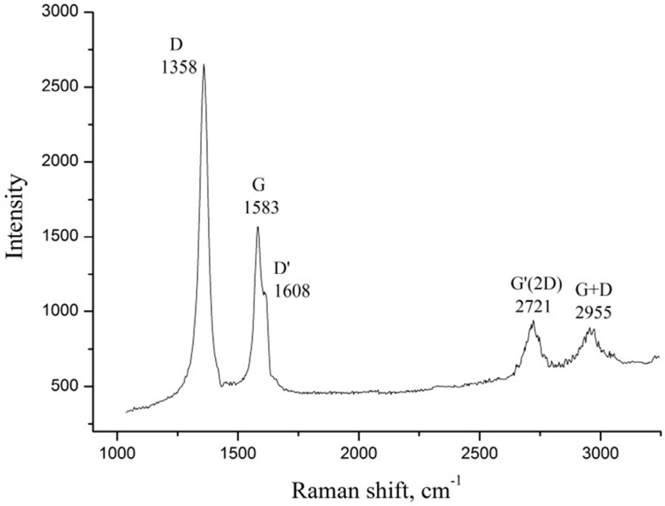




Fig. 6. SEM image and Raman spectrum of CNWs/Cu sample after PECVD synthesis.

Table 1 shows the intensity ratio of *D* and *G* modes and estimated in-plane correlation length $L_a$ for the samples CNWs/Ni-Si synthesized at 10 and 15 W and CNWs/Cu, whose Raman spectra are shown in Fig. 4-6.

Table 1. Raman data for obtained samples CNWs/Ni-Si and CNWs/Cu

| Samples | I(D) | I(G) | I(2D) | I(D)/I(G) | La |
|---|---|---|---|---|---|
| CNWs/Ni-Si at 10 W | 3079 | 1791 | 1345 | 1.7 | 2.3 |
| CNWs/Ni-Si at 15 W | 4085 | 2108 | 849 | 1.9 | 2.5 |
| CNWs/Cu | 2652 | 1570 | 942 | 1.68 | 2.6 |

## Conclusion

In this work, the growth of CNWs on the surface different substrates by plasma enhanced chemical vapor deposition in radio-frequency discharge was presented. It was found that by increasing discharge power, the nanowalls are agglomerated into nanoclusters with the formation of defects in the structure. SEM analyses show that the growth process of CNWs on the surface of a silicon substrate with a thin catalyst nickel nanolayer gives better result than on the surface of copper wafer. Whereas estimated ratio of intensities of *D* and *G* modes from Raman spectra of obtained samples corresponds to the same quality of synthesized CNWs.

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