Analysis and optimization of photonics devices manufacturing technologies based on Carbon Nanotubes

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Abstract. The analysis and optimization of optical devices manufacturing technologies based on carbon nanotubes intended for work in the visible range were carried out. These processes studied in the work have practical application for the deposition of carbon nanotubes and their subsequent use as materials for prototypes of the waveguide and sensor of the visible range. To obtain a layer of carbon nanotubes, a chemical vapor deposition chamber was used. A dense horizontal network of CNTs was grown on silicon wafer by utilizing sandwich type catalyst structure. The growth was carried out with two variable parameters: flow rate and flow duration. Various aspects of the CNTs synthesis, mechanism of CNTs growth and power dependent laser sensing are considered in this article. The remarkable properties of as developed photo detector are its fast response and recovery time with 8% sensitivity.

1. Introduction
Carbon nanotubes (CNTs) are a relatively recent discovery. Science has been dealing with CNTs since 1991 [1]. During this time, interest in CNTs has greatly increased throughout the world due to its unique structural and electrical properties. The high mechanical strength of CNTs in combination with their electrical conductivity makes it possible to use them as a probe in scanning probe microscopes, which increases the resolution of devices of this kind by several orders of magnitude and puts them on a par with such a unique device as a field ion microscope. Also, CNTs have high emission characteristics. At room temperature, the current of auto electron emission at a voltage of about 500 V reaches values of the order of 0.1 Volts on cm$^{-2}$. This opens up the possibility of creating a new generation of displays on their basis. The use of CNTs in the field of chemistry is very interesting, because they have high specific surface and chemical stability, as well as the possibility of attaching various radicals to the surface of CNTs, which later can become either catalytic centers or nuclei for various chemical transformations [2]. Due to all these properties, CNTs have a large number of other promising applications in the field of medicines, electronics, optics and many other fields of science and technology [3-4]. Thus, CNT is supposed one of the best materials for producing nanotechnological devices [5-10].

Recently, SWNTs has become a topical theme in modern science due to their tunable direct bandgap, which allows radiative electron-hole generation and recombination and makes CNTs suitable material for photonic devices. SWCNT has high sensitivity to the environment and external fields. The unique properties of CNTs such as a tunable bandgap and high mobility make them a promising material as active centers and materials for charge transfer in photon applications. For active
applications, the exceptional photoluminescent properties of CNTs, such as the excellent stability of light emission at temperature and excitation power, make these materials on a nanometer scale as the main candidates for future active photonics devices with excellent characteristics.

All these advantages encourage researchers to look for new possibilities of using CNTs. Potential optical devices based on them are waveguides and sensors of the visible range. But for their high-quality manufacturing, in order for them to function, certain properties of CNTs are needed. To do this, we need to analyze the growth process of CNT and its characteristics in order to have certain properties. For many years, various approaches have been used to grow CNTs, including arc discharge, chemical vapor deposition (CVD), laser ablation, and others methods. Initially, the arc discharge was considered as an ideal method to grow a bulk CNTs. In these methods, the condensation of hot gas and carbon particles was performed by evaporation of solid carbon. But these methods have several drawbacks, such as: (1) only CNT bundles are produced in powder form, (2) systematic growth of CNTs is impossible on substrates with a selective structure, (3) the need for equipment and energy consumption is very high. These restrictions make these methods less favorable for the growth process of CNTs compared to CVD. Also, the unique properties and structure of CNTs are influenced by the substrate material, the metallization layer material and its thickness, the catalyst layer and its thickness, as well as the flow rate and duration of the carbon precursor gas (C2H2) during chemical vapor deposition.

Copper and aluminum are used as a metal layer in the study. These samples are used to precipitate CNTs with an iron catalyst, as well as without it. As adjustable parameters for gas supply are the speed and amount of gas flow, as well as the time of its supply.

The purpose of this work is to obtain the necessary properties and parameters of CNTs for use in the manufacture of optical devices. The novelty of as developed sensor is that it has less response time (5 seconds) as well as recovery time (10 seconds). It also shows very good sensitivity (more than 8.5 %). In our best knowledge, these are best results for optical sensing so far reported.

2. Experiment
In this work, we used silicon substrates previously cleaned with HF acid. Copper and aluminum layers were deposited with a thickness of 100 nm using magnetron sputtering. When coating by the magnetron sputtering method [4], the film grows due to the sublimation of target atoms, which are deposited on the substrate surface and on the fittings of the vacuum unit. To create the working pressure necessary for the stable operation of the magnetron, a working gas is needed, for which argon was used.

Sputtering metal targets in a pure argon medium led to the formation of a metal film 100 nm thick. Before starting the process, the vacuum chamber was pumped out to a working pressure of about $2.5 \times 10^{-1}$ Pa. After that, a solution of iron nitrate was prepared. 5 mg of Fe(NO3)3 was added to 100 ml of DI water, this mixture was placed in an ultrasonic bath for 2 hours. After that, each of the samples was divided into two parts. One aluminum and one copper sample were placed in the solution for 40 minutes. The temperature of the system was maintained at 50 degrees. As a result, 2 aluminum and copper samples were obtained, one with iron deposited as a catalyst, the other without. After that, all samples were placed in a CVD chamber for heating to 400 degrees. As a result, oxide films formed on the surface. Further, using magnetron sputtering, aluminum and copper were deposited on the surfaces of the samples with thickness of 10 nm. Next, CNTs were deposited on the samples by CVD method. The substrates were placed in a tubular chamber CVD system. The diagram of CVD system is shown on Figure 1.

![Figure 1. Schema of the experimental chamber for the growth of CNTs by CVD method: 1 – Ar supply valve; 2 – C2H2 supply valve; 3 – manifold; 4 – heaters; 5 – chamber; 6 – samples.](image-url)
Table 1. Table shows the catalyst film preparation process for all samples.

| S.No. | Substrate | Supporting layer-1 (in nm) | Catalyst | Supporting layer-2 (in nm) | Annealing | Atmosphere of annealing |
|-------|-----------|---------------------------|----------|---------------------------|-----------|------------------------|
| 1.    | Si        | Al(150)                   | Fe(NO₃)₃ | Al(10)                    | Yes       | Ar                     |
| 2.    | Si        | Cu(200)                   | Fe(NO₃)₃ | Cu(10)                    | Yes       | Ar                     |
| 3.    | Si        | Al(150)                   | Fe(NO₃)₃ | Al(10)                    | No        | -                      |
| 4.    | Si        | Cu(200)                   | Fe(NO₃)₃ | Cu(10)                    | No        | -                      |
| 5.    | Si        | Cu(200)                   | Fe(NO₃)₃ | Cu(10)                    | No        | O₂ + Extra layer of catalyst |
| 6.    | Si        | Al(150)                   | Fe(NO₃)₃ | Al(10)                    | No        | O₂ + Extra layer of catalyst |

Figure 2. Figure shows the SEM images for sample no. 1, sample no. 2, sample no.3 and sample no. 4.

Figure 3. Figure shows Raman spectra for sample no. 1, sample no. 2, sample no. 3 and sample no. 4 with their I_D/I_G ratios.
The process of growing CNTs includes heating the samples in argon atmosphere to a temperature of 800 degrees in a tube furnace, and then the gas supply of hydrocarbon gas $C_2H_2$ through the tube reactor is turned on for 10 minutes. As grown CNTs samples are unloaded from CVD chamber while the temperature of the system decreases to room temperature. The important parameters of CNTs growth by the CVD method are hydrocarbon (in our case it is $C_2H_2$), the catalyst (iron) and the temperature of growth (800 degrees). Active catalytic particles were formed on the supporting layer, in our case it is alumina and copper oxide. The general mechanism of CNT growth in the CVD process involves the dissociation of hydrocarbon molecules catalyzed by the transition metal, their dissolution and the saturation of carbon atoms with metal nanoparticles. All samples with different materials and processes indicated in table number 1. Obtain structure for carbon nanotube growing presented on figure 4.

![Figure 4. Multilayer structure which used for carbon nanotube growing.](image)

### 3. Results and discussion

In present work, six experiments were conducted using different materials as a supporting layer with different structure of catalyst and supporting layer. Overall catalyst preparation process is mentioned in table no.1. The obtained samples with deposited CNTs were analyzed on a scanning electron microscope and Raman spectroscopy.

The figures no. 2 shows the SEM images of best four samples and respective Raman spectra presented in figure 3. It is clearly observable in figure 2 that sample no 2 have best results among three samples. As grown CNTs have diameter in the range of 20nm to 30nm with good yields. Sample no 1 also have same type of CNTs but it have lots of impurity as compare to sample no. 2. In case of sample no. 3, it has good quality of CNTs but yield is very poor. And in sample no. 4 yield and quality of CNTs, both are poor. For the analysis of structural quality of CNTs, Samples were investigated by Raman spectroscopy. For analysing CNTs structural quality, Raman spectra have three important peaks i.e. RBM ($100 - 300 \text{ cm}^{-1}$), D-Band ($1323 \text{ cm}^{-1}$) and G-Band ($1582 \text{ cm}^{-1}$). Presence of RBM is signature of SWNTs and intensity ratio of D-Band to G-Band gives structural quality of CNTs. The peak located at 500 cm$^{-1}$ represents silicon mode. For best quality of CNTs, ratio must be minimum. Figure 3 shows the $I_D/I_G$ ratio for best 4 samples. We found that sample no. 2 has minimum ratio of $I_D/I_G$. So, sample no. two have best morphological as well as structural properties of CNTs.

Therefore, sample no.2 was used for analysis of laser sensing. For same purpose, we made two silver electrodes on as grown CNTs sample for electrical connections. The sensing experiment was conduct by scheme, which imaged in figure 5. Its included laser, power supply with power control, laser beam reflection system, multimeter and pad for samples with connectors to electrodes (see Figure6). We performed optical sensing by green laser source (wavelength=532nm) in the power range from 0.8W to 2W. Initially, the base resistance of our sample was observed around 3112Ω. When we incident laser beam on sensor then its resistance is decreases sharply. The sensing experiments were conducting with five values of laser beam power i.e. 0.8 W, 1.1 W 1.4 W, 1.7 W and 2 W. The changes in resistance were measured for five cycles for every value of power.
When power of laser is maximum (2W), the maximum resistance drop was observed, which amounted to 261 Ohm. The response and recovery time observed around 20sec and 10sec respectively. It shows sensitivity of sensor around 8.5%.

When the power of laser is reduced to 1.7 watts, the maximum resistance drop from 3112 to 2987 Ohm was registered, which amounted to 125 Ohm. And its sensitivity also decreased from 8.5% to 7%. When we further reduce the power of laser, the drop in resistance of sensor also reduces sharply [see Figure 7], which makes our sensor very sensitive for laser beam power. The changes in drop of resistance with respect to laser power are an important property of resistive sensor for making device prototype.

In second experiment, we changed the power in steps. It was started with 0.76W laser power and after one minute, the power of laser was increased to 1.06W. We further increased the laser power to 1.32W, 1.57W and 1.57W in same manner step by step [see figure 8]. And as expected, the resistance of sensor was reduced in steps as we increases the power of laser beam. It verified that the CNTs are very sensitive for laser power and also an ideal material for developing photonics devices. Figure 9 shows the response of as developed sensor and it can clearly observed in graph that the sensor’s response is increases with increment in laser power. CNTs based sensor shows the maximum response for 2W laser power and minimum response for 0.8W. Figure 10 shows the sensitivity vs. laser power graph. We can see that, at low powers, the increase in sensitivity goes smoothly, while as it approaches the maximum power, the growth becomes sharper. The steepest rise is observed at a power of 1.3 to 1.7 W.

Sensitivity of sensors continuously increases and at the same time their sensitivity spectrum expands. [11]. To check further sensitivity of as developed sensor, we increased the laser power from 0.76W to 1.82W in steps in single experiment (see Figure 11).

In this experiment, first we set the laser power on 0.78W for one minute and then the laser power increased to 1.06W for one minute. Laser power was increases in steps in same pattern until 1.82W. As per expectation, resistance drop of sample also reduces in sharp steps. It verifies that as developed CNTs baser sensor is highly sensitive for power detection of laser light. To make sure that it is due to CNT that the sample reacts to radiation, we also checked sensing property of sample prior to CNTs growth and in that case, we found almost zero sensitivity.
Figure 7. Image shows the resistance drop vs. time plot for different laser power.

Figure 8. Figure shows the combined plot for drop in resistance vs. power for real time.

Figure 9. Figure shows the response of sensor for different laser power.

Figure 10. Figure shows the sensitivity of sensor for different power.

Figure 11. Figure shows drop in resistance vs. time graph, when laser power is increasing in steps.
4. Conclusion

We successfully optimized the CNTs growth conditions for producing CNTs for visible range optical detector. It was found that sandwich type of catalyst structure is very good for growing CNTs with high crystallinity, less diameter and high yield. The analysis and optimization of photonics devices manufacturing technologies based on CNTs applied for work in the visible range (wavelength 532nm) range has been developed. We developed a highly sensitive optical detector for detection of power of laser beam with sensitivity is more than 8% and very short response and recovery time.

5. References

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