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Fabrication of Vacuum Chamber and Synthesis of Nanotubes. A Theorical Investigation of Exciton-Photon Interaction in the Nanotubes

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The single-walled nanotubes, is made of a grafyn sheet which is bent to form a hollow cylinder and the combination of single-walled nanotubes with different diameters forms multi-wall nanotubes. There are different methods for the synthesis of carbon nanotubes including, Electric Arc Discharge, Laser Vaporization and Chemical vapor Deposition. Carbon nanotubes produced in arc discharge or laser vaporization of graphite have less structural defects camparing to other methods due to the high process temperatures. The third method comparing to the previous methods, is a simple technique for synthesis carbon nanotubes at low temperature and ambient pressure and leads to mass production. If the laser is used to heat the substrate surface, this method is called LCVD which has some advantages comparing to CVD method. In this paper in addition to nanotube synthesis with this method, a study on the interaction exciton with the CNT surface electromagnetic field is conducted.

Keywords: Carbon nanotube, exciton-photon interaction, grafyn, Laser Chemical Vapor Deposition, Synthesis of CNT.

1. INTRODUCTION

In 1991 the first multi-wall carbon nanotubes were discovered by Iijima, two years later, in 1993, he performed some obsevations on single-walled nanotubes [1,2]. The single-walled nanotubes, is made of a grafyn -a single layer of graphite- sheet which is bent to form a hollow cylinder. The combination of coaxial single-walled nanotubes with different diameters with a distance of 3.4 Å between different layers, forms multi-wall nanotubes. Because of the vandrvals bonds This coaxial nanotubes are put together [3,4].

Given the small diameter single-walled nanotubes- less than two nanometers- If the cylinder length is considered larger than its diameter, regardless of its two semi-sphere ends, it can be considered as a one-dimensional nanostructures with axial symmetry [5].

Carbon nanotubes are usually produced using these three major techniques:

1- Electric Arc Discharge or EAD

2 - Laser Vaporization or Laser Ablation

3 - Chemical Vapor Deposition or CVD

Nanotube growth mechanism is still a research topic, there can even be more than one nanotube growth mechanism. One of these mechanisms is in a way that the substrate is coated with metal catalysts, entering a heated furnace with a mixture of hydrocarbon and inert gases flowing within. Under the high temperature of the furnace, the free carbon atoms are released into the catalyst particles and form semi-stable carbide-a mixture of carbon and metallic elements- particles. Finally The tube-shaped carbon structure grows using spherical catalyst particles and the other grafyn, concentric with main wall, are formed with lower speed [6,7].

Carbon nanotubes produced from carbon vapor in arc discharge or laser vaporization of graphite have less structural defects camparing to other methods due to the high process temperatures. Since 1959 the third method, the so-called chemical vapor deposition, was being used to produce carbon fibers and is comparing to the previous methods, this technique is a simple and economic one for synthesis carbon nanotubes at low temperature (1200-600 °C) and ambient pressure. The advantage of this method is that different carbon sources (solid, liquid, gas) and different substrates can be used in it and grow carbon nanotubes in different forms (powder or film). In addition, the length of the nanotubes obtained from this method is better than the nanotube length with the previous methods. But the problem with this method is its less control over the final product and also impurities and structural defects of the nanotubes produced are more than the last two [8-10]. Depending on the used energy source, CVD is done with different methods. For example, when the laser is used to heat the substrate surface, this method is called LCVD [2]. The advantages of this method in synthesis of nanotubes is:

1- In LCVD's process, laser beam is focused on the substrate and nanotubes are synthesized locally and steadily grow in different parts of the surface

2- Laser can warm the substrate quickly and reach it to a favorable temperature for nanotube growth.

3- With controlling the width of the laser beams, process can be done locally or in a wider area.

4- Since the laser concentrates in specified point on the substrate, unlike the cvd's method, prevents from heating the entire substrate surface and chamber walls [11-14].

2. MODEL

As mentioned above with regard to the high ratio of length to diameter nanotubes and regardless of the end caps, it can be considered quasi-one-dimensional. In a theoretical model nanotubes can be considered in the form of a one-dimonsional anisotropic semiconductive cylinder and regardless of azimuthal conductivity and Considering axial conductivity, we study the interaction of exciton with surface electromagnetic field single-walled carbon nanotube and calculate interaction Hamiltonian with respect to creation and annihilation operators of an exciton. This model, due to cylindrical symmetry, uses the orthonormal basis $\{\vec{e}_r, \vec{e}_\varphi, \vec{e}_z\}$, in the cylindrical coordinate system and the $\vec{e}_z$ vector is considered in the direction of the axis of the nanotube. The total Hamiltonian of the coupled exciton-photon system on the nanotube surface is of the form [15]:

$$\hat{H} = \hat{H}_F + \hat{H}_{ex} + \hat{H}_{\text{int}} \qquad (1)$$

where the three terms represent the free EM field, the free (noninteracting) exciton, and their interaction, respectively. the second-quantized field Hamiltonian is:

$$\hat{H}_F = \sum_{n \in CN} \int_0^\infty d\omega \hbar\omega \hat{f}^\dagger(\vec{n},\omega)\hat{f}(\vec{n},\omega) \qquad (2)$$

where the scalar bosonic field operators $\hat{f}, \hat{f}^\dagger$, annihilate and create, respectively, the surface EM excitation of frequency ω at an arbitrary point $\vec{n} = \vec{R} = \{R_{CN}, \varphi_n, z_n\}$ associated with a carbon atom (representing a lattice site) on the surface of the CN of radius R_{CN}. The summation is made over all the carbon atoms. The f operator is related to current density operator with [16]:

$$\hat{\vec{f}}(\vec{n},\omega) = \frac{\hat{\vec{J}}(\vec{n},\omega)}{\sqrt{\alpha(\vec{n},\omega)}} \quad , \quad \alpha(\vec{n},\omega) = \frac{\hbar\omega \,\mathrm{Re}(\sigma_{zz}(\vec{n},\omega))}{\pi} \qquad (3)$$

In this equation, σ_{zz} is the axial conductivity per unit length on the nanotube surface. The interaction Hamiltonian has the following form (Gaussian system of units):

$$\hat{H}_{\text{int}} = \hat{H}^{(1)}_{\text{int}} + \hat{H}^{(2)}_{\text{int}} = -\sum_{n,i} \frac{q_i}{m_i c} \hat{\vec{A}}(\vec{n} + \hat{\vec{r}}^{(i)}_n) . \left[\hat{\vec{p}}^{(i)}_n - \frac{q_i}{2c} \hat{\vec{A}}(\vec{n} + \hat{\vec{r}}^{(i)}_n) \right] + \sum_{n,i} q_i \hat{\varphi}(\vec{n} + \hat{\vec{r}}^{(i)}_n) \qquad (4)$$

where c is the speed of light, $m_i, q_i, \hat{\vec{r}}^{(i)}_n, \hat{\vec{p}}^{(i)}_n$ are, respectively, the masses, charges, coordinate operators, and momenta operators of the particles (electrons and nucleus) residing at the lattice site

$\vec{n} = \vec{R} = \{R_{CN}, \varphi_n, z_n\}$ associated with a carbon atom on the surface of the CN of radius R_{CN}. By extending $\hat{\varphi}\,\hat{\vec{A}}$ around lattic site , we have**:**

$$\hat{\varphi}(\vec{n} + \hat{\vec{r}}_n^{(i)}) = \hat{\varphi}(\vec{n}) + \hat{\vec{r}}_n^{(i)}.\vec{\nabla}\hat{\varphi}(\vec{n}) + \ldots \qquad (5)$$

$$\hat{\vec{A}}(\vec{n} + \hat{\vec{r}}_n^{(i)}) = \hat{\vec{A}}(\vec{n}) + \hat{\vec{r}}_n^{(i)}.\vec{\nabla}\hat{\vec{A}}(\vec{n}) + \ldots \qquad (6)$$

We use the Coulomb gauge in our calculations and assume there is no external free charge or current. Regarding the first non-zero sentence in extension of the above and replacing it in equation (4) yields:

$$\hat{H}_{\text{int}}^{(1)} \approx -\sum_{n,i} \frac{q_i}{m_i c} \hat{\vec{A}}(\vec{n}).\hat{\vec{p}}_n^{(i)} + \sum_{n,i} \frac{{q_i}^2}{2m_i c^2} \hat{\vec{A}}^2(\vec{n}) \qquad (7)$$

$$\hat{H}_{\text{int}}^{(2)} \approx \sum_{n,i} q_i \vec{\nabla}_n \hat{\varphi}(\vec{n}).\hat{\vec{r}}_n^{(i)} \qquad (8)$$

With introducing the lattice-site Hamiltonian and completeness relation and performing some mathematical calculations, we reach relationships which describe the interaction of exciton with surface electromagnetic field of single-walled carbon nanotube:

$$\hat{H}_{\text{int}}^{(1)} = \sum_{n,f} -\frac{i\omega_f}{c}(\hat{\vec{A}}(\vec{n}).\vec{d}_n^f)(\hat{B}_{n,f}^{\dagger} - \hat{B}_{n,f}) \qquad (9)$$

$$\hat{H}_{\text{int}}^{(2)} = \sum_{n,f} (\vec{\nabla}_n \hat{\varphi}(\vec{n}).\vec{d}_n^f)(\hat{B}_{n,f}^{\dagger} + \hat{B}_{n,f}) \qquad (10)$$

.

Which $\hat{B}_{n,f}^{\dagger} = |f\rangle\langle 0|$, $\hat{B}_{n,f} = |0\rangle\langle f|$ is creation and annihilation operators of an exciton.

3. SYNTHESIS OF CARBON NANOTUBE IN THE VACUUM CHAMBER

In this section the carbon nanotubes is made of laser irradiation by the method of Laser Chemical Vapor Deposition (LCVD) and The second harmonic of the Nd: Yag laser with wavelenght of 532 nm is used as a heat source. For synthesis of nanotube a chamber is required to create a vacuum to grow a nanotube in. The chamber used in this project, with our equipments, is made of the same

chamber in Figure1 and is consists of the following components: Cylindrical glass chamber, Plexiglas or aluminum lid, Barometer, Connector, Quartz window, Lens for concentrating a laser beam on the substrate.

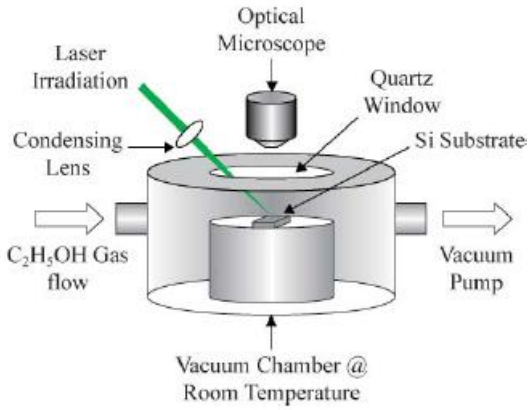

Figure 1. illastration chamber used in the experiment[17]

Also in the substrate at the center of the chamber, some elements for increasing the temperature and a thermocouple for measuring it, is constructed. So the chamber has the ability to control and change the temrature of the substrate and if there is a need for higher temrature for synthesis, we can easily prepare it. Moreover in this chamber, a cuprous pipe is placed to pass the ethanol vapor from near the substrate and enable us to be confident about the presence of hydrocarbon vapor near the substrate surface.

After making chamber, during the process, various parameters to achieve desired results were changed to reach the best possible conditions for conducting the experiment. The summary of the procedures are as following:

- AL_2O_3 and $Fe(No_3)_3.9H_2O$ and standard molybdenum solution catalysts mixed with different molar ratios were used for the synthesis, and those with less alumina nano particle were better suited for our experiment.
- Ultrasonic mixer compared with the ultrasonic cleaner is more suitable for mixing the catalysts.
- Selecting a short time for mixing catalyst,causes the separation of the surface substrate, therefore the time amount should be increased to make it stable.
- Spin coating device, decomposes the catalyst uniformly on the substrate and is more appropriate for this purpose.

After the catalyst preparation and decomposing it on the N-type silicon wafer with thickness of 5mm, substrate is heated in oven with a specific temperature. The substrate then enters into the chamber and after the evacuation by the rottary pump, ethanol vapor enters then second harmonic Nd :Yag laser irradiation of the wavelentgh 532 nm is used to heat the substrate and form the carbon nanotubes in the presence of a catalyst.

4. SETTING THE EXPERIMENT SETUP

- For the experiment, duration of laser irradiation on the substrate was changed from 5 minutes to three hours, The best results were achieved during a period of one hour and longer periods of time only lead to the burning and loss of catalyst.
- Entering hydrocarbon vapor into the chamber was tested without a carrier gas and also in the presence of argon gas, with argon gas, better results were reached.
- Laser light without the glass lens and also in its presence, was focused on the substrate, the lens increased the laser concentration on the substrate and also lead to the increase of radiation intensity and synthesis of nanotubes in radiation center.

After the synthesis of nanotubes on the substrate surface, the taken SEM images that represents the growth of carbon nanotubes in the laser radiation center, are as following:

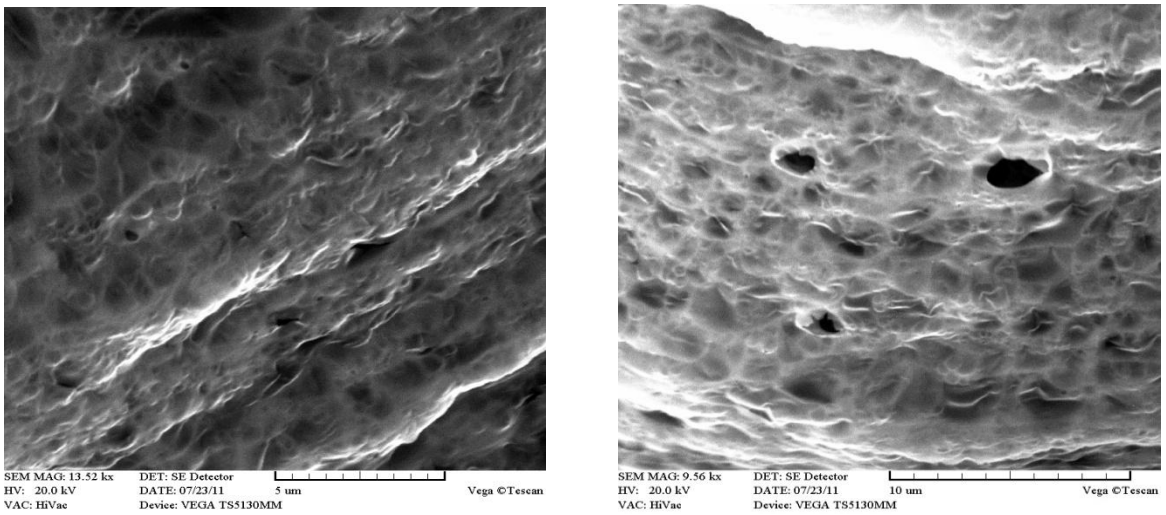

Figure 2. SEM images of nanotubes grown at laser irradiation center

5. CONCLUSION

Equations obtained in Section 2, for the coupling system Hamiltonian, using advanced techniques of quantum electrodynamics, are transformed into the equations that describe the coupled exciton- photon system in carbon nanotubes. Due to the quasi-one-dimensional nanotube, the transversely-polarized surface electromagnetic mode of the field in the interaction Hamiltonian (equation 9) with a longitudinally polarized mode field (equation 10) is negligible**.** Therefore the longitudinal modes create plasmon on the surface of the nanotubes and produced plasmon couple with these exciton. After the creation of plasmon on the surface of the nanotubes, we can modify the Hamiltonian in order to describe the interaction of the plasmon-exciton**.** In Section 3, we changed the test conditions with various methods and ultimately achieved the following results to obtain suitable conditions for growth**:**

1- The catalyst solution with less alumina nanoparticles, had a better stability on the substrate.

2- In the molar ratio of catalyst that we considered, gradual and sudden drying had little difference in the stability of the catalyst on the substrate surface.

3- The Spin coating device, uniformly decomposed the catalyst on the substrate.

4- Laser radiation without lens due to the low light energy in the radiation center, did not help the synthesis process. Therefore, in order to increase the light energy of the laser, lens was placed in the path of the light to increase the received energy per unit area and also the temperature.

5- Laser irradiation on the substrate, in the short amount of time lead to no results and a long amount of time lead to the burning of the catalyst. The best amount time to carry out the synthesis process in our experimental conditions was about an hour**.**

Images taken from test samples shows that in the areas where the surface temperature is suitable for nanotube growth, catalyst, nanoparticles are formed with a suitable size and nanotubes with high density and appropriate length are grown**.**

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