INVESTIGATION ON THE EFFECT OF NUCLEATION TIME ON CNT GROWTH PROCESS USING RF-PECVD

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Abstract: *Carbon Nano Tubes (CNTs) were deposited on Silicon substrate by RF plasma enhanced chemical vapour deposition (RF-PECVD). The deposition was carried out at 550 V bias and 600°C with C_2H_2 precursor gas diluted with H_2 in the ratio of 1:4. Transition metal catalysts are required for CNT growth by PECVD. It is believed that the catalyst on the substrate must be in the form of particles instead of smooth, continuous films. The eventual particle size and the resultant nanotube diameter correlates to film thickness. Thinner films in general lead to smaller particles and tube diameters. While a small grain size is not guaranteed in as-prepared films, steps are taken to break the film into desired particles to form island like structures. This work investigates the effect of Nucleation and the time interval of Nucleation on the CNT growth process.*

Keywords: *CNT, Nucleation, RF-PECVD*

1. INTRODUCTION

A carbon nanotube (CNT) is a rolled layer of exfoliated graphite. Ideally, a nanotube consists of one or more cylindrical tubes of exfoliated graphitic sheets[1,2]. Each tube is made of sp^2 (trivalent) carbon atoms that form a hexagonal network with a capping at the end of the tube comprising the metal catalyst on which it has been grown. CNTs are available in two forms, Single Walled Nano Tubes (SWNTs) and Multi Walled Nano tubes (MWNTs). High temperatures in excess of 1200°C are required to grow SWNT while other conditions shall synthesise only MWNTs[1]. The diameter of CNTs varies from a few nanometers in the case of SWNTs to several tens of nanometers in the case of MWNTs[3]. The growth carbon nanotubes by Plasma Enhanced Chemical Vapour Deposition (PECVD) involves a carbon source; hydrocarbon gas such as ethene, which dissociates in the presence of plasma, aided by a transition-metal catalyst (Fe, Ni, Co, Mo) in a PECVD reactor at low pressure and high temperature aided by RF plasma[4]. This catalyst thickness must be less than 20nm. Thinner films yield smaller catalyst particles leading to small tube diameters. Thin films help in the growth of CNTs as they can be broken into smaller particles. Smaller particles become nucleation site for the growth of CNTs. The catalyst nanoparticles which facilitates the self-assembly of CNTs are deposited on the silicon substrate surface using sputter coating. They seed the nanotube growth, determining both the location and diameter of the deposited nanotubes.

Theseexperiments aim to investigate the effect of nucleation done for various time intervals on the CNT growth and the quality of the CNTs obtained.

2. EXPERIMENTAL DETAILS

CNTsare being developed using a Roth & Rau HBS 500 PECVD system fitted with two plasma generation sources Microwave and Radio Frequency. This experiment utilizes 13.56 MHz RF- PECVD. The chamber volume is 500mm^3. Acetylene is the primary precursor gas used for synthesising the CNT.

CNT films were deposited on to Silicon substrates. The substrates were pre- cleaned with soap water, distilled water and with isopropyl alcohol and acetone in an ultrasonic bath. After cleaning they were kept in desiccator until being introduced into the chamber in order to avoid contamination before processing.

CNTs growth requires a thin layer of a few nanometers of a metal catalyst to be deposited on the substrate before growth. In this study, nickel was used as a catalyst. Nickel was deposited on the substrateusing DC plasma sputtering method.Hydrogen plasma at 120 sccm is introduced prior to admitting the precursor gas and initiating growth where the plasma ion bombardment helps to create catalyst particles which act as nucleation sites.Carbon nanotubes are to be deposited using RF- PECVD setup on the Si substrate placedon a resistively heated graphite stage, which also acts as a cathode for the plasma discharge. C_2H_2 is to be diluted with hydrogenwhich produces reactive species in the plasma to remove any excess carbon by forming H_2 or any other H_2 based compounds.

The gases were let into the chamber through a showerhead that acts as an anode for the plasma discharge where the nucleated specimen is kept for 20 minutes in the ratio of 1:4 i.e. C_2H_2/H_2. The CNT growth process is a high temperature reaction and requires the reaction chamber to be maintained at 600-700 °C.

The CNTs thus grown are more obelisk in shape having very large diameters of around 40-50 nm (Fig. 1). It can also be noted that there is significant amorphous carbon deposited both on nanotube sidewalls and the substrate.

This amorphous carbon deposition is undesirable and hampers the quality of the CNT layer. The high rate of amorphous carbon deposition throws light on the fact that the nucleation of the seed layer has not occurred desirably. This compels the study of nucleation and optimization of the nucleation process time for the growth of good CNTs.

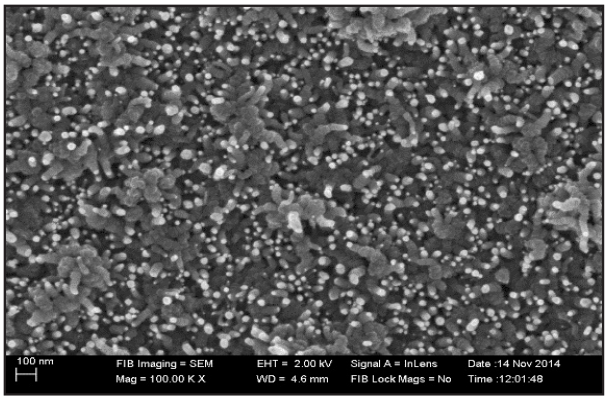


Fig 1. SEM Images of CNTs Grown Initially at Various Magnification of 100kX

Considering the results of the previous experiment, it was proved that the nucleation process has to be optimized in order to obtain good CNT growth. Thus the Ni coated Si wafers were subjected to nucleation using the same parameters as the previous experiments for different time intervals. In the earlier experiment the nucleation was carried out for 40 minutes. In the current experiments the nucleation was done with 3nm and 5nm Ni coated Silicon wafers for 15 minutes, 30minutes, 45minutes and 60 minutes each.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

3.1 Analysis and Optimization of Nucleation Process

The SEM images of the nucleation that has happened on 3nm Ni coated Silicon wafer for 15 minutes, 30 minutes, 45 minutes and 60 minutes are illustrated in Figures 2, 3, 4 and 5.

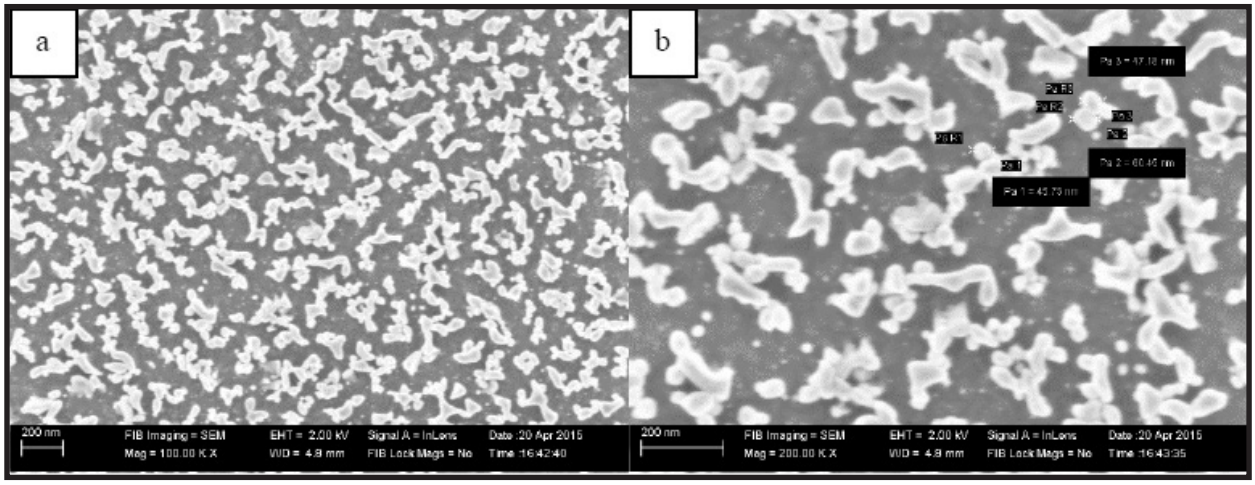
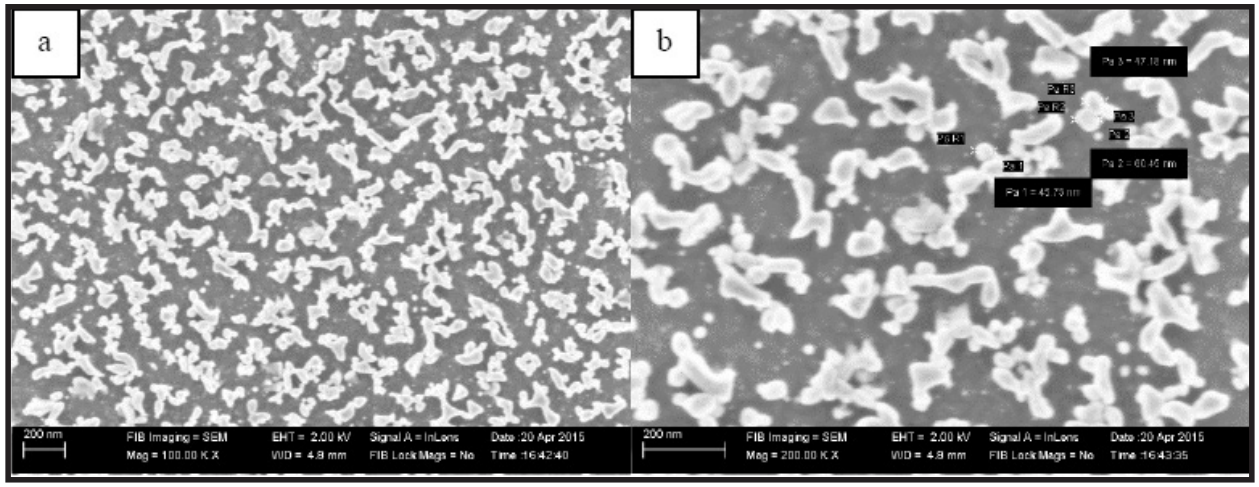


Fig 2. SEM Images of 3nm Ni Coated Specimen After 60 Minutes of Nucleation at Magnifications of (a) 100k× and (b)200k×



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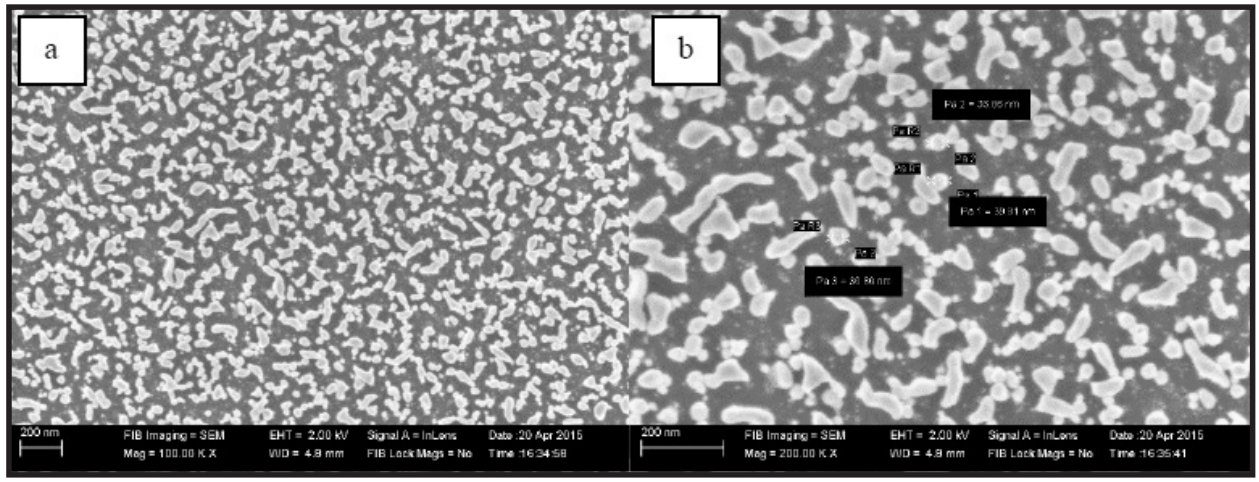

Fig 3. SEM Images of 3nm Ni Coated Specimen After 45 Minutes of Nucleation at Magnifications of (a) 100k× and (b)200k×

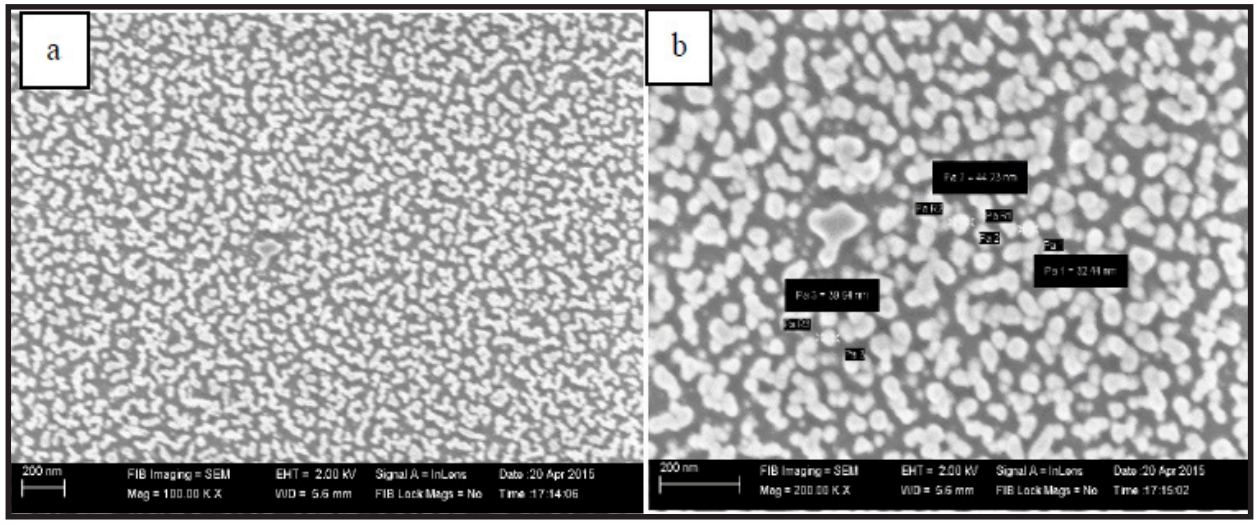

Fig 4. SEM Images of 3nm Ni Coated Specimen After 30 Minutes of Nucleation at Magnifications of (a) 100k× and (b)200k×

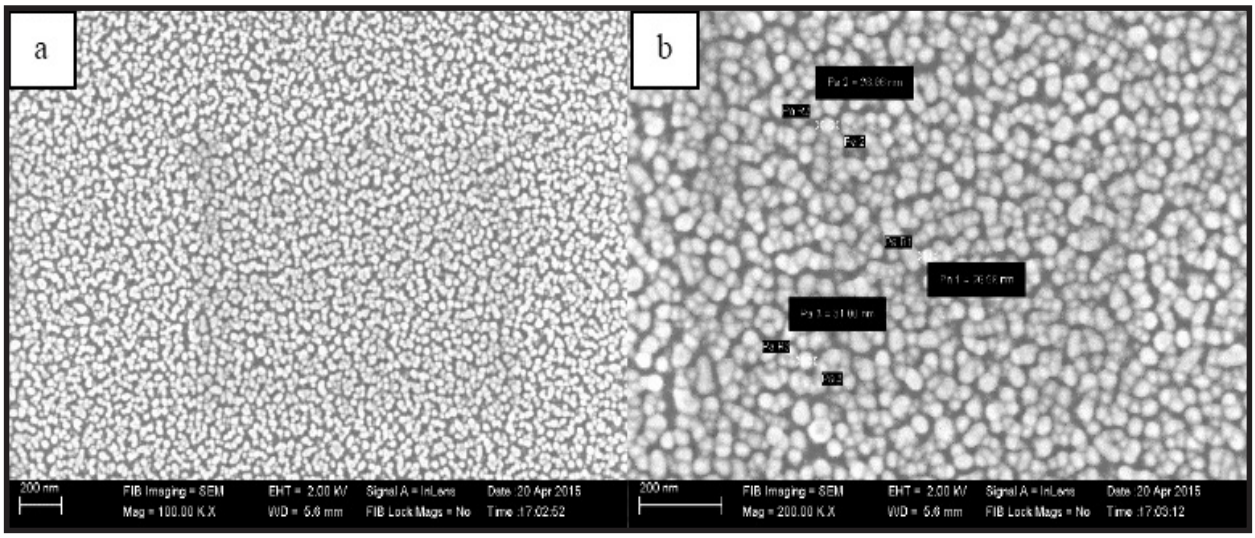

Fig 5. SEM Images of 3nm Ni Coated Specimen After 15 Minutes of Nucleation at Magnifications of (a) 100k× and (b)200k×

As observed from Figure 1 and 2, 60 minutes and 45 minutes of nucleation has eroded considerable Ni coated on the substrate leading to the formation of obelisk islands with sizes ranging from 40 nm-60nm which seems inadequate for CNT growth.

The images of the specimen with nucleation time of 30 minutes and 15 minutes (Figure 3 and 4) forms globular islands with size of 30-40 nm. This kind of seed formation is suitable for synthesis of CNT. As observed from Figure 4, a nucleation time of 15 minutes seems to form perfectly globular closely spaced islands. These formations are most desirable for the synthesis of CNTs with lower content amorphous carbon.

3.2 CNT Growth Analysis

These samples are subsequently subjected to CNT growth under the earlierparameters for 20 minutes in order to visualise and observe which of them yields best quality CNTs**.** The SEM images of the CNT growth that has happened on the nucleated specimens are illustrated in Figures 6, 7, 8 and 9.

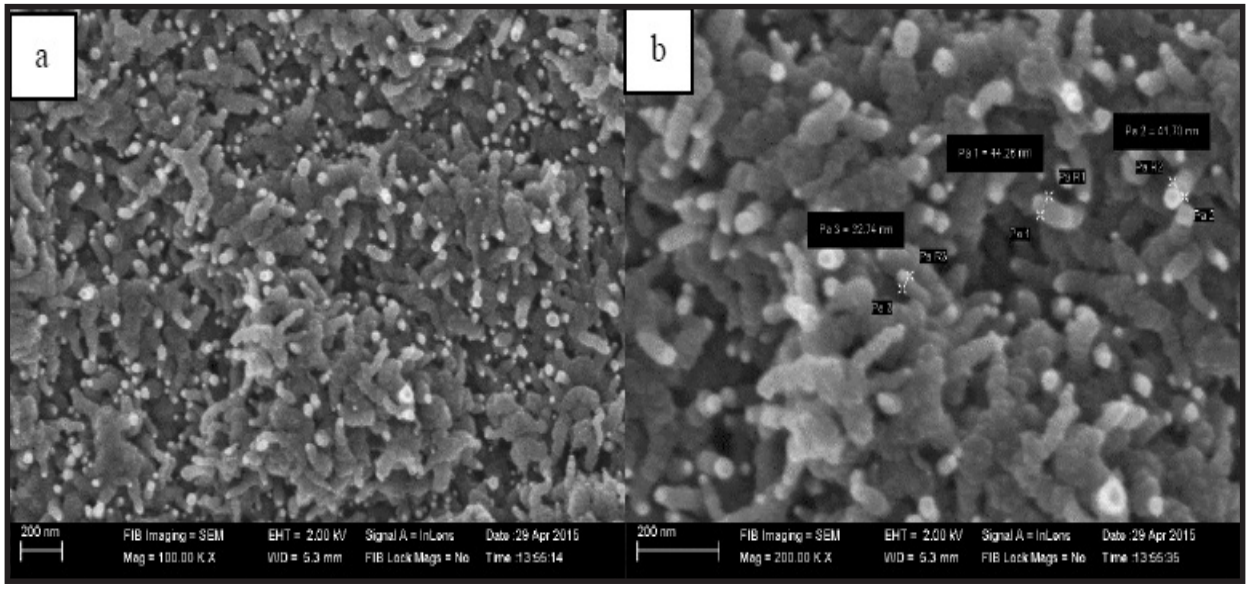

Fig 6. SEM Images CNT Grown on 3nm Ni Coated Specimen After 60 Minutes of Nucleation at a Magnification of (a) 100k×(b)200k×

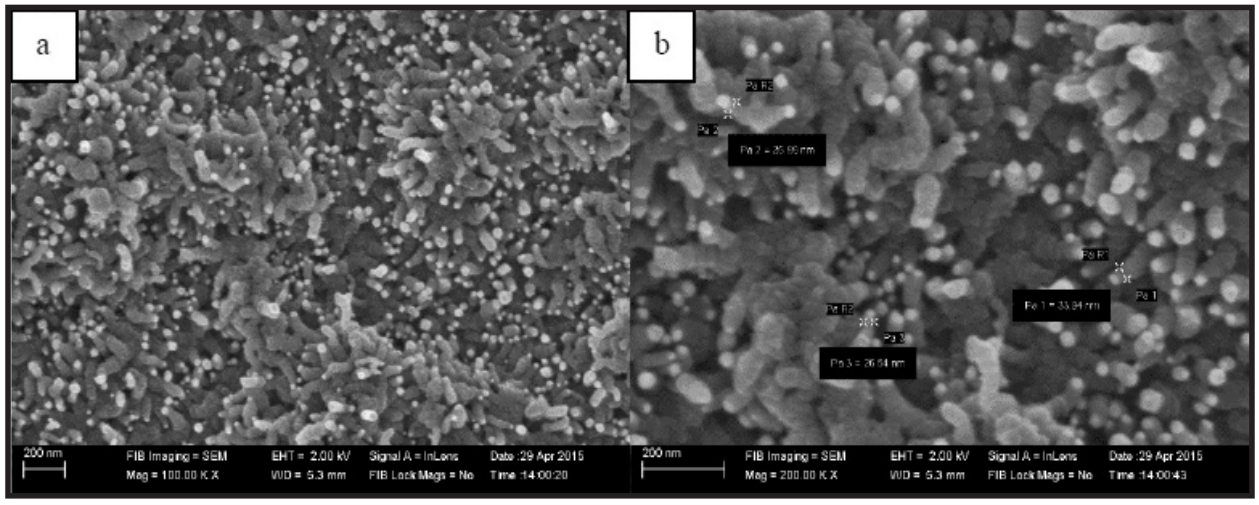

Fig 7. SEM Images CNT Grown on 3nm Ni Coated Specimen After 45 Minutes of Nucleation at a Magnification of (a)100k×(b)200k×

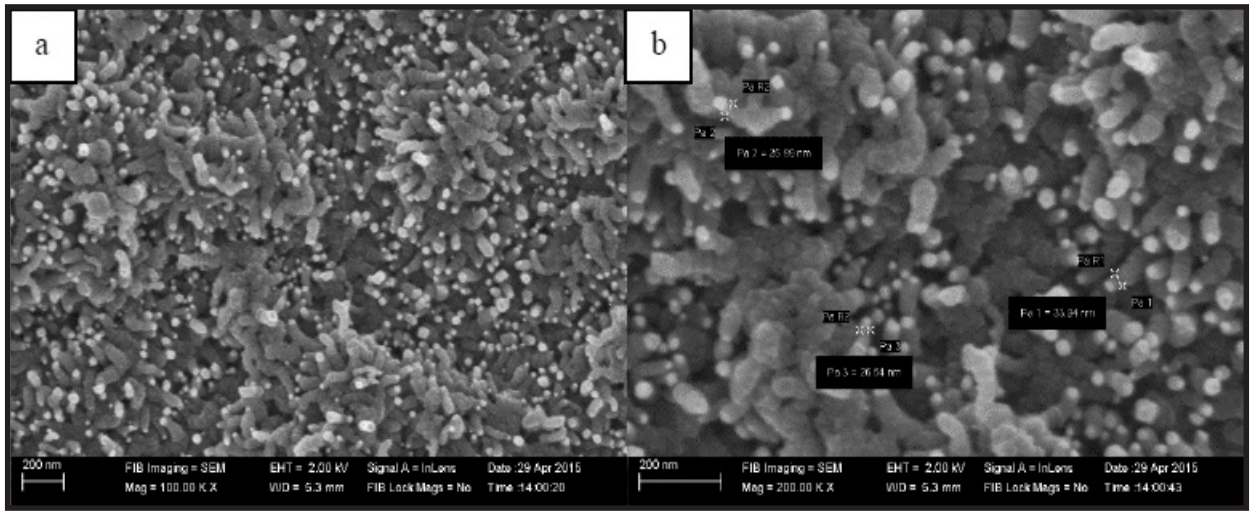

Fig 8. SEM Images CNT Grown on 3nm Ni Coated Specimen After 30 Minutes of Nucleation at a Magnification of (a)100k×(b)200k×

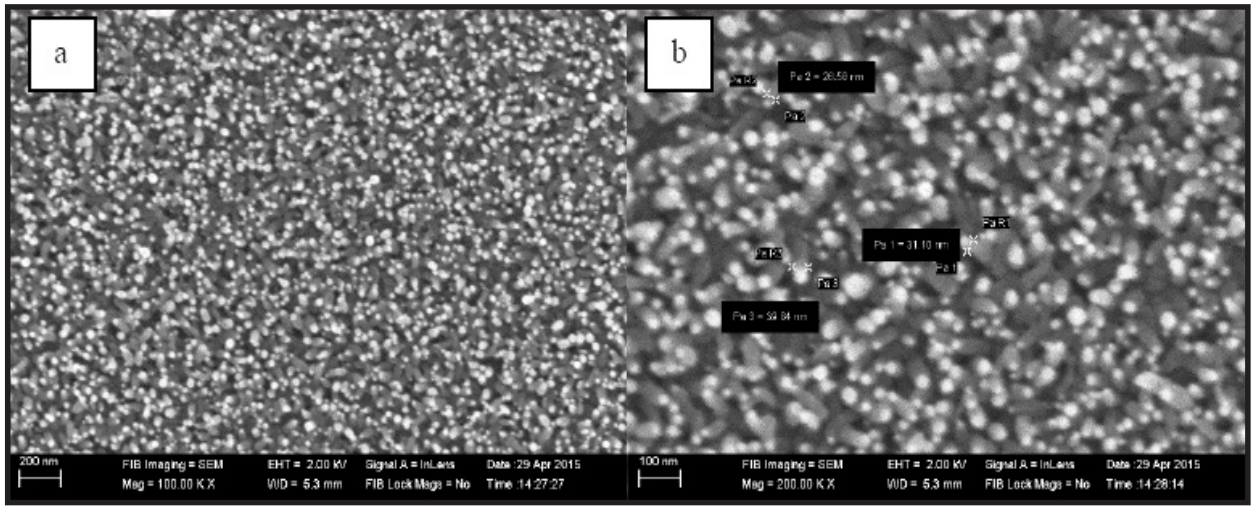

Fig 9. SEM Images CNT Grown on 3nm Ni Coated Specimen after 15 Minutes of Nucleation at a Magnification of (a)100k×(b)200k×

From the SEM Images of the CNT growth it is clear that a nucleation time of 15 minutes yields best CNTs. For 60 minutes and 45 minutes nucleation times the CNTs obtained are stub like and has large quantities of amorphous deposits making it unsuitable for any applications. This was because the seeds formed in both cases prior to growth were irregularly shaped islands. The CNTs obtained from specimens which underwent nucleation for 30 minutes and 15 minutes had considerably less amorphous carbon deposits. The last sample of 15 minutes nucleation gave the best CNTs as inferred from the SEM images. The CNTs obtained had a diameter of 30-40 nm much like the globular size of Ni particles obtained after nucleation.

4. CONCLUSIONS

1. At higher nucleation time of 60 minutes and 45 minutes there is a considerable erosion of Ni coated on the substrate leading to the formation of obelisk islands with sizes ranging from 40 nm-60nm which seems inadequate for CNT growth. The specimens with lesser nucleation time of 30 minutes and 15 minutes forms closely spaced globular islands with size of 30-40 nm. This kind of seed formation is suitable for CNT growth.
2. Subsequent CNT growth reveals thata nucleation time of 15 minutes yields best CNTs. For 60 minutes and 45 minutes nucleation times the CNTs obtained are stub like and has large quantities of amorphous deposits making it unsuitable for any applications. This was because the seeds formed in both cases prior to growth were irregularly shaped islands. The CNTs obtained from specimens underwent nucleation for 30 minutes and 15 minutes had considerably less amorphous carbon deposits.
3. It has been established through this investigation that nucleation prior to CNT growth impacts the quality of the CNT yield significantly. Optimization of the nucleation time and parameters is extremely essential to obtain good CNT yield using PECVD.

5. REFERENCES

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