# PECVD Growth of Carbon Nanotubes

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Abstract

Plasma enhanced chemical vapor deposition (PECVD), using inductively coupled plasma, has been used to grow carbon nanotubes (CNTs) and graphitic carbon fibers (GCF) on substrates sputtered with aluminum and iron catalyst. The capacitive plasma's power has been shown to cause a transition from nanotubes to nanofibers, depending on the strength of the plasma. The temperature, placement, and other factors have been shown to affect the height and density of the tube and fiber growth.

## Introduction

Carbon nanotubes (CNTs) have recently been receiving much attention due to their extraordinary properties, both mechanical and electrical. They have potential to be of great use in nanoelectronics, biosensors, field emission devices, high strength composites and other applications. Various methods have been used to grow CNTs including laser vaporization [1], arc-evaporation of graphite electrodes [2], and chemical vapor deposition (CVD) [3]. Of these only CVD has the ability to grow CNTs on patterned substrates, however, for some applications (flat displays for one) highly aligned CNTs are desirable. One way to possibly achieve this is to use plasma enhanced CVD (PECVD). The plasma reduces the temperature needed for growth and also adds other parameters, such as the bias across the substrate, which influence the growth. It is thought that this field will lead to the growth of vertically aligned CNTs. In this paper, we report the findings of an investigation into the parameters influencing CNT growth in an inductively coupled plasma reactor.

## Experimental

Samples are grown using an inductively coupled plasma reactor. The samples are silicon substrates (N-doped, <100>) sputtered with a metal catalyst (Al and Fe) and sometimes an underlayer of Ir or Mo. The catalyst metals and the underlayers are 99.9+% pure and sputtered using a VRC Group Inc. Ion Beam Sputterer, model IBS/TM200S. The chamber is continuously flushed with argon (99.999% pure) as the sample is inserted into the chamber. Once the sample is in place, the chamber is evacuated down to 0.1 torr (± 0.1 torr). The chamber is then heated up to 800°C (except in the instance where temperature is variable), allowing 5 minutes, once 800°C is reached, for the temperature to equilibrate. Then a gas mixture of 1-20% methane in hydrogen (both 99.999% pure, Scott Specialty Gases), with a total flow rate of 100 sccm, is turned on and the reactor pressure is adjusted to 1-20 torr. The capacitive and inductive plasmas are then turned on, each adjusted to the desired power output (0-250W) and the sample is allowed to grow, typically for 10 minutes (total range observed: 5-40 minutes). Once the allotted time has elapsed, the plasma, the heater and the gas flows are turned off and the reactor is evacuated. The chamber is allowed to cool down to below 300°C under vacuum to prevent damage to the CNTs from air. The chamber is once again flushed with argon as the sample is removed.

Results and Discussion

To start with, we used a catalyst formulation that has shown effective in thermal CVD (Ref to be published) and also worked well in PECVD growth: 10 nm Al underneath 10 nm Fe.

First we investigated the temperature dependence on the growth. Two samples with the above mentioned catalyst were grown under the same conditions (10 torr, 20% methane, 10 minutes, 100W inductive power and 70W capacitive power) except one at 800°C and one at 700°C. As seen in Figure 1, the 800°C sample grew taller fibers than the 700°C. In all subsequent runs, 800° was used as the reactor temperature.

Next we varied the gas pressure in the chamber from 1 to 20 torr (figure 2), again using 20% methane, 10 minutes, 100W inductive power, 70W capacitive power and 800°C. At high pressure (20 torr) a large amount of carbon contamination was deposited (figure 2d), obscuring any tubes that may have also grown. As expected the opposite happened at low pressure. Little amorphous carbon was deposited and there was a low density of fibers grown. A pressure of 3 torr yielded fibers that had uniform height and density and appeared to have little carbon contamination; so from this point on, a pressure of 3 torr was used.

The capacitive power was varied from 0 up to 120W, as seen in figure 3. It was found that at low power (0-20W) maginally-aligned CNTs were grown (3a). From 30-40W there is a transition phase where these CNTs were mixed with graphitic carbon fibers (GCFs). Past 50W, the aligned GCFs are the predominate feature seen. However, once the power exceeded 70W, the density began to decrease. Growth at powers greater than 140W were not investigated due to the large amounts of reflected power that were experienced in our system at those powers. Our work shows that a power of 70W provides straight GCFs without sacrificing the overall density; this power was used in further trials.

The inductive power was also altered to see its effect. As the inductive power changed from 0 to 250W, very little change was seen in the grown fibers (Figure 4). In subsequent runs, the inductive power was kept at 100W as previously had been used.

In order to increase the conductivity of the substrate, an underlayer of Ir or Mo was added. It was found that if the Al was replaced with an equal layer of Ir, either there was very short growth ( <50nm) or a layer of carbon contamination was deposited. If Mo was used, there was growth of about 250nm but the fibers were extremely sparse. When the Ir and Mo were deposited beneath the layer of Al, the results were very similar. Both had a mix of the GCFs along with CNTs, very similar to the growth using a capacitive power of 40W with the Al/Fe catalyst. Following the trend found in the capacitive power, increasing the power completes the transition from the nanotubes to the graphitic fibers. At 100W it was seen for both the Ir/Al/Fe and Mo/Al/Fe catalysts that the growth is comparable to the growth at 70W with only Al/Fe as the catalyst.

We then varied the thickness of the Fe layer (using only Al and Fe) from 1-40 nm (figure 6). As expected, the diameter of the fibers increased as the Fe layer increased, from about 20nm for the 50nm layer to over 75nm for the 40nm thick layer. Below 5nm, no CNTs or GCFs formed, showing the lower limit of catalyst thickness.

The percentage of methane in the gas mixture was then varied from 1 to 20% (figure 7). When there was less than 5% methane, no tubes or fibers grew, even after 40 minutes. As the percentage increased from 5%, to 10% finally to 20%, little change was noted. The diameters of the fibers remained the same. The 5% sample yielded fibers 150-200 nm taller than the 10% and 20%, which were the same height; however, in another trial at 5%, the growth was not of uniform height, so no clear conclusions can be drawn until further investigated. Since there was no obvious better choice than 20% methane, it was continued to be used.

As mentioned previously, the samples were allowed to grow for 10 minutes. We discovered that if the samples are allowed to continue to grow, the growth continues; it does not become poisoned at any point up to 40 minutes (figure 8). The samples continue to grow, but not at a linear rate. Growth of 300 nm was achieved after 5 minutes, 450 nm after 10 minutes, 500 nm after 15 minutes, 750 nm after 20 minutes and 1200 nm after 40 minutes. It can be extrapolated that growth will continue for longer periods of time.

By growing a sample that spanned over half of the electrode, a growth profile was found; the type of growth was not affected, only the height. At the center of the electrode 350 nm tall fibers were grown. On the edge of the blackened spot, fibers 250 nm tall were grown. The shortest fibers were grown in the area closest to the very edge of the electrode and were 100 nm tall. Also of interest is the color of the sample, as seen in figure 9. The colors seen correspond to the fiber heights.

Samples of both the fibers that were typically grown and the CNTs (grown at low capacitive power) were imaged using a high-resolution transmission electron microscope (TEM). The TEM results indicate that the larger stuctures seen are not CNTs but are GCFs instead. The smaller tubes seen at lower capacitive powers are CNTs though defective ones. Unfortunately no TEM images are available in this paper.

## Conclusions

There are many factors that affect PECVD growth of carbon nanotubes and all of their effects are not well known. We investigated the effects caused by changes in temperature, pressure, capacitive power, inductive power, various additional underlayers, catalyst thickness, gas mixtures, time, and placement. Of these only the capacitive power and the additional underlayers affected the type of growth (CNTs versus GCFs). Also, only the capacitive power affected the alignment of the tubes and fibers. The others affected the height grown, density of growth, and sometimes, as in the case of thin layers of iron, the presence or absence of growth. This type of PECVD can be used to grow

GCFs of various diameters (depending on catalyst layer thickness) that are well aligned and of uniform density.

Acknowledgement

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References:

[1] T. Guo et al, **Chemical Physics Letters** 243 (1995) 49-54.
[2] C.H. Kiang et al, **Carbon** 33 (1995) 903.
[3] A.M. Cassell, S. Verma, L. Delzeit, M. Meyyappan, **Langmuir** 17 (2001) 260.

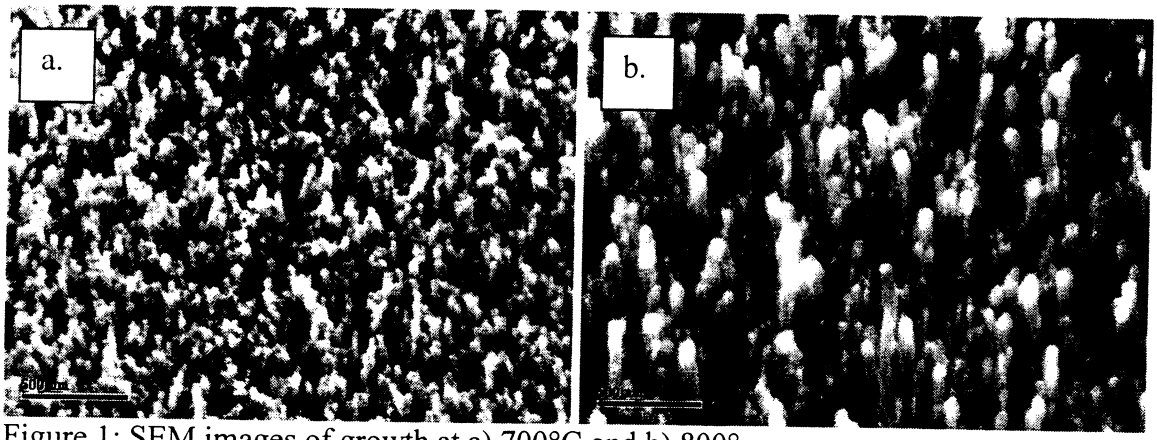

Figure 1: SEM images of growth at a) 700°C and b) 800°.

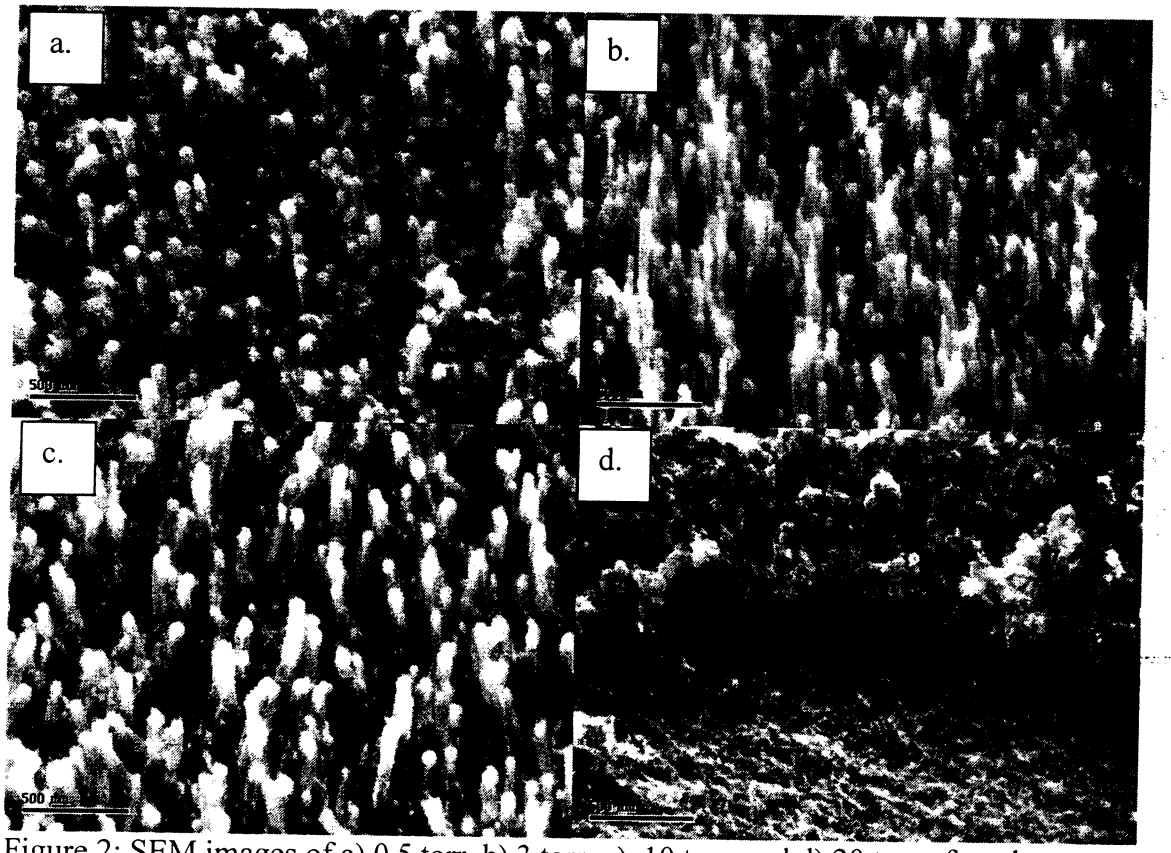

Figure 2: SEM images of a) 0.5 torr, b) 3 torr, c). 10 torr, and d) 20 torr of total pressure, while keeping all other parameters the same.

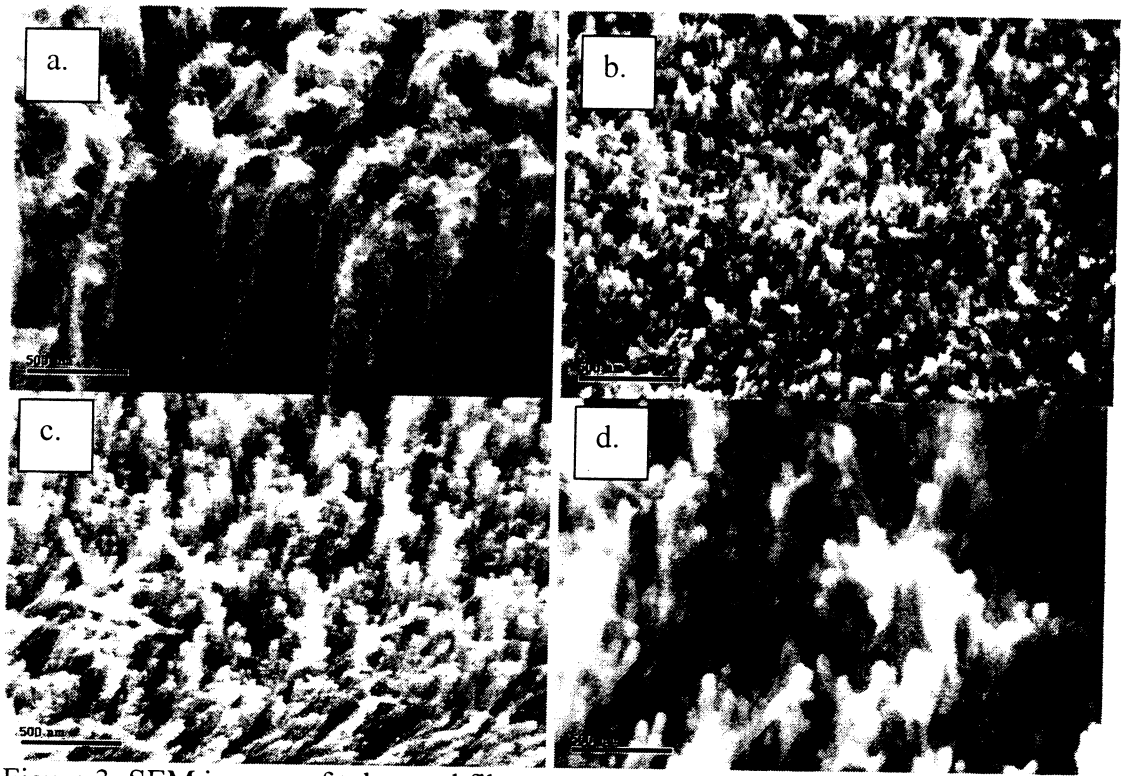

Figure 3: SEM images of tubes and fibers grown at a) 20W, b) 40W, c) 70W and d) 120W capacitive power, all under the same conditions.

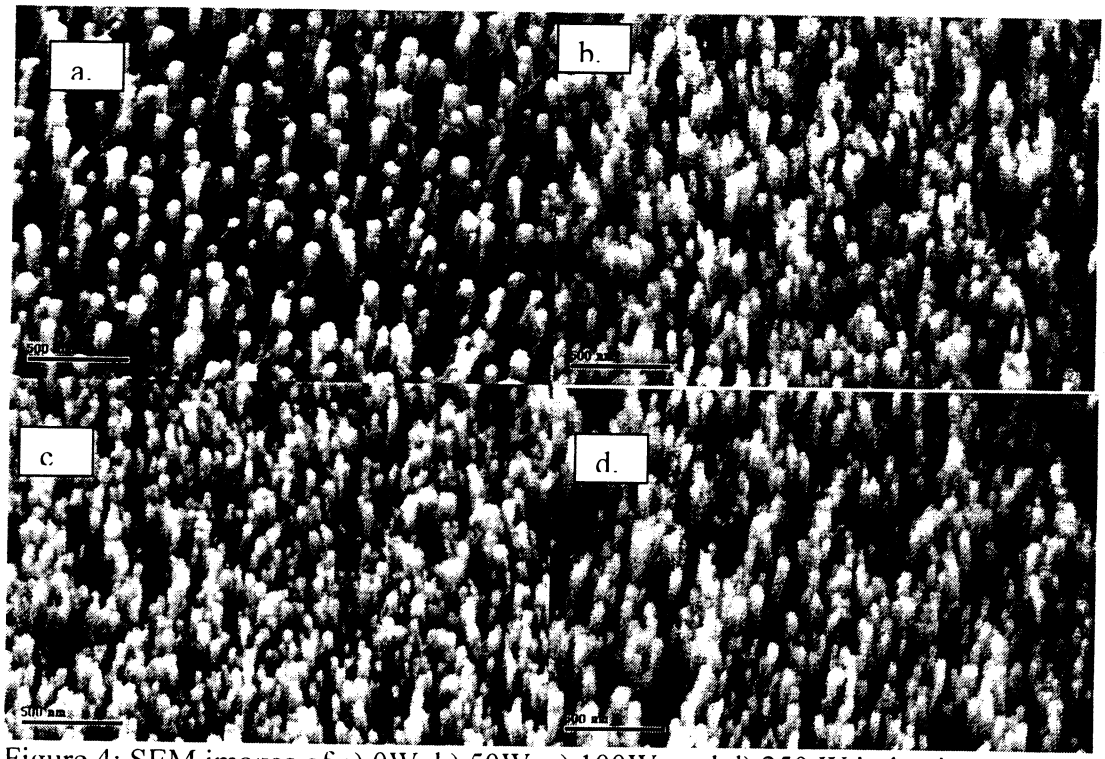

Figure 4: SEM images of a) 0W, b) 50W, c) 100W, and d) 250 W inductive power.

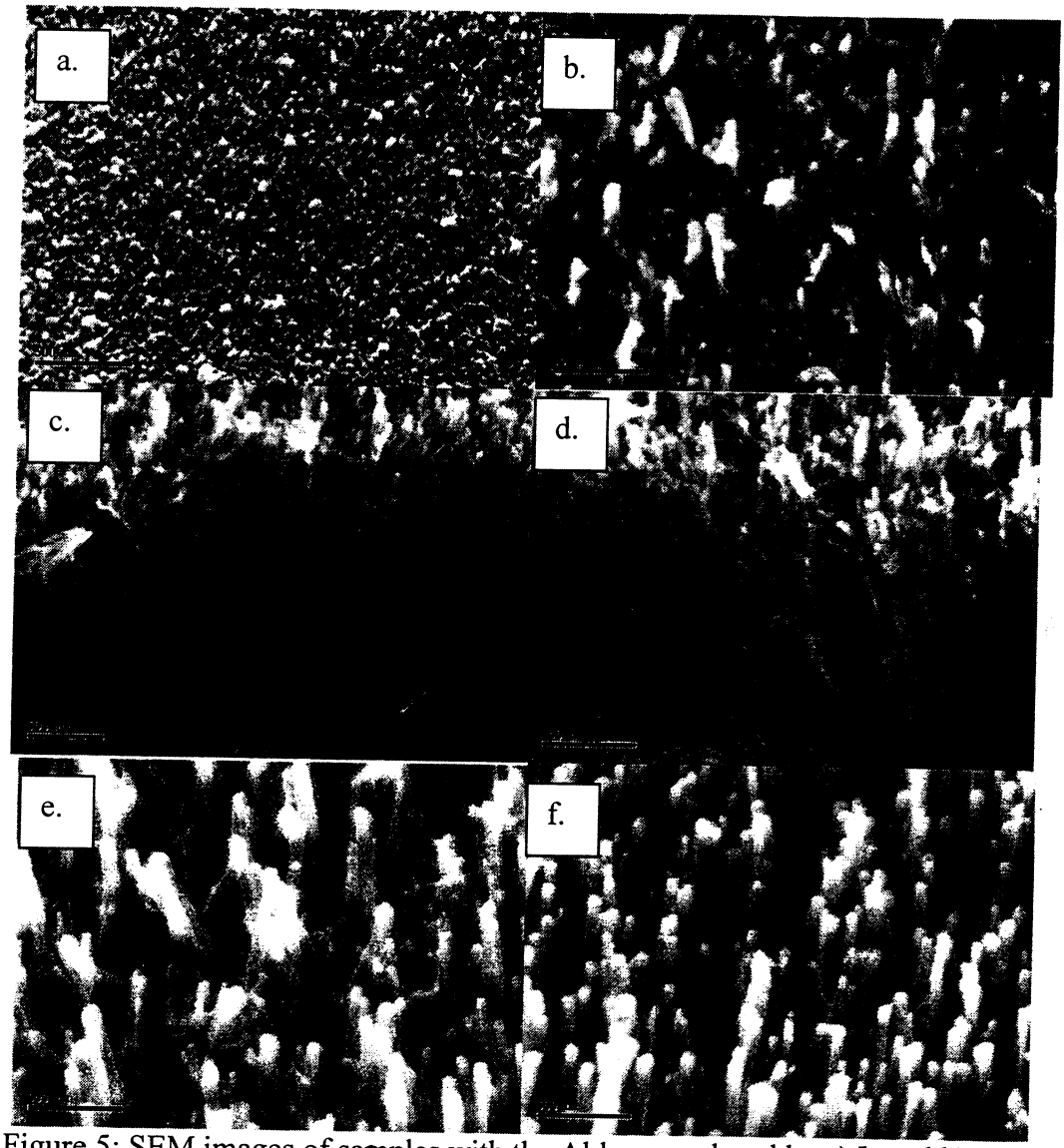

Figure 5: SEM images of samples with the Al layer replaced by a) Ir and b) Mo. Here an additional underlayer of c) Ir and d) Mo were added under the Al and grown at 70W and then also at 100W for e) Ir/Al/Fe and f) Mo/Al/Fe.

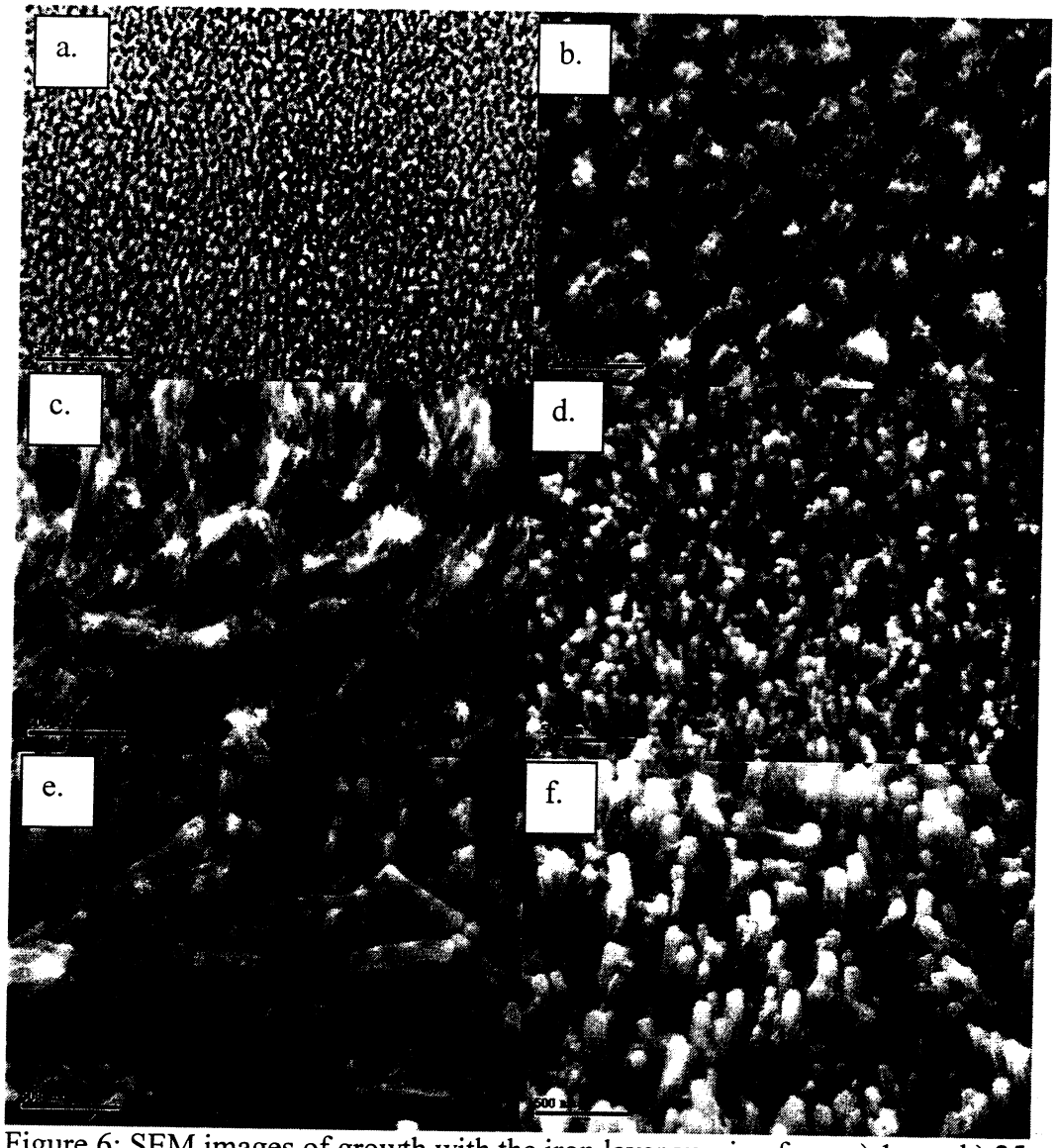

Figure 6: SEM images of growth with the iron layer varying from a) 1 nm, b) 25 nm, c) 50 nm, d) 75 nm, e) 100 nm, to f) 400 nm.

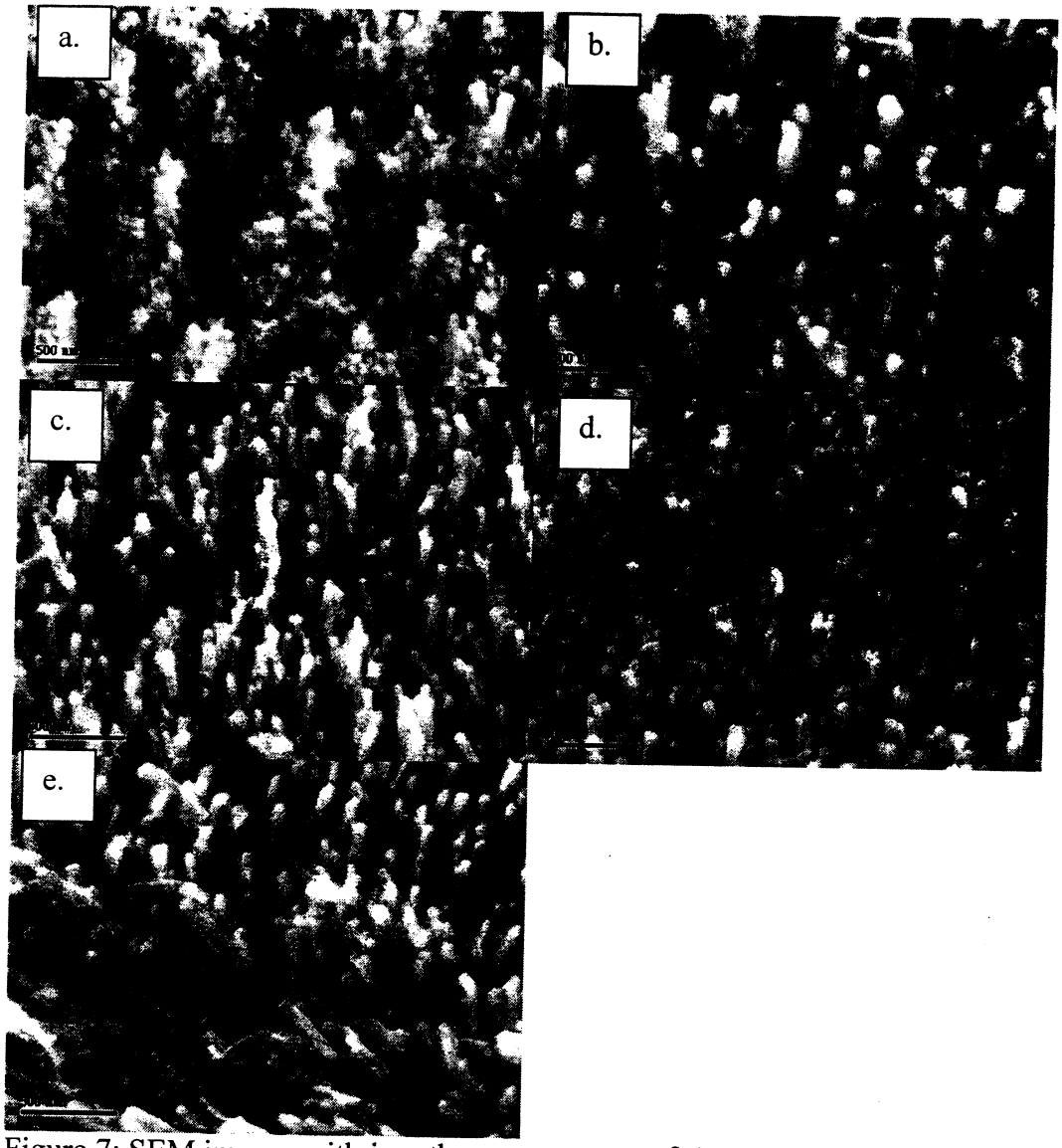

Figure 7: SEM images with a methane percentage of a) 1%, b) 2.5%, c) 5%, d) 10%, and e) 20%.

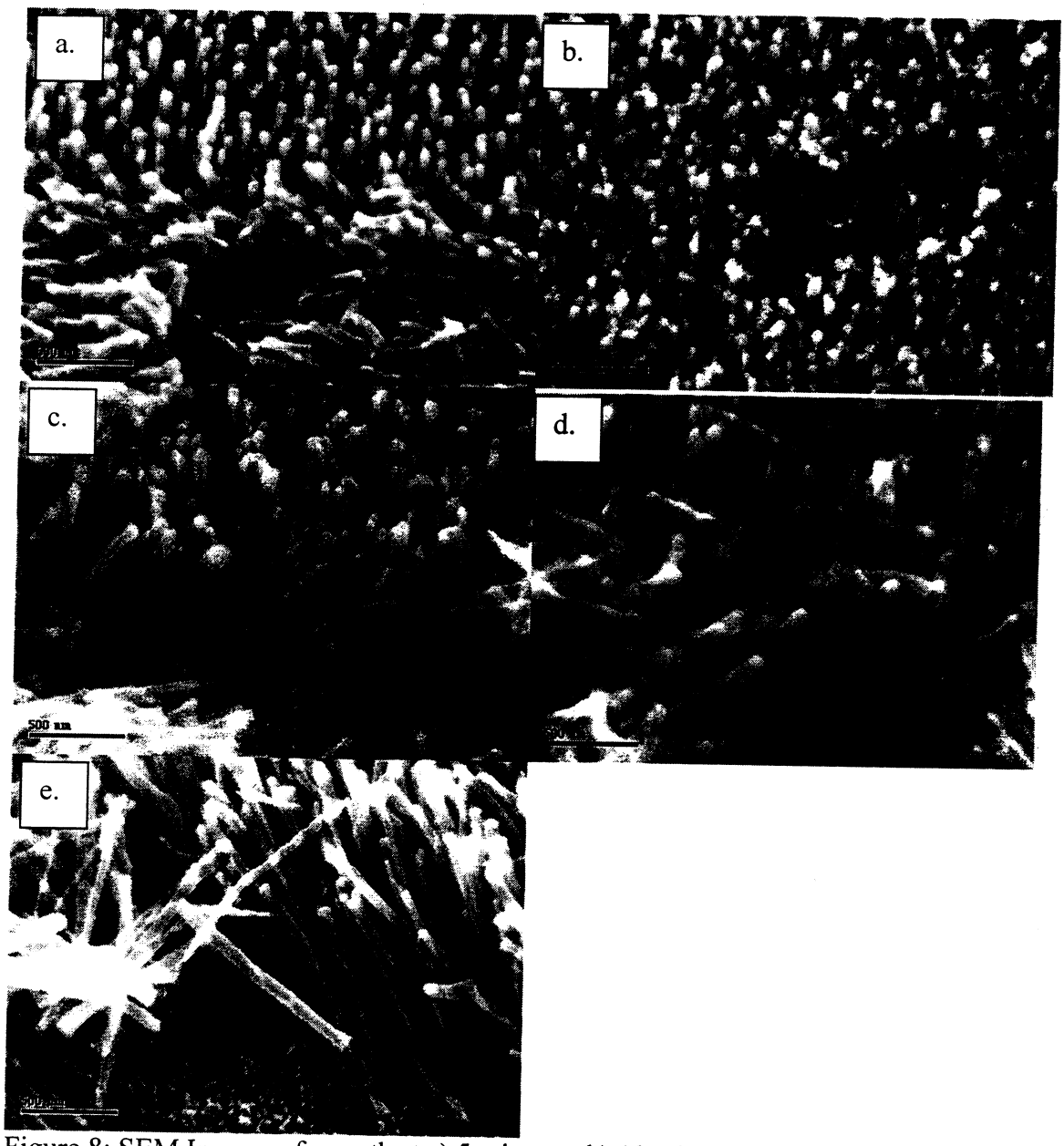

Figure 8: SEM Images of growth at a) 5 minutes, b) 10 minutes, c) 15 minutes, d) 20 minutes and d) 40 minutes, all under the same conditions.

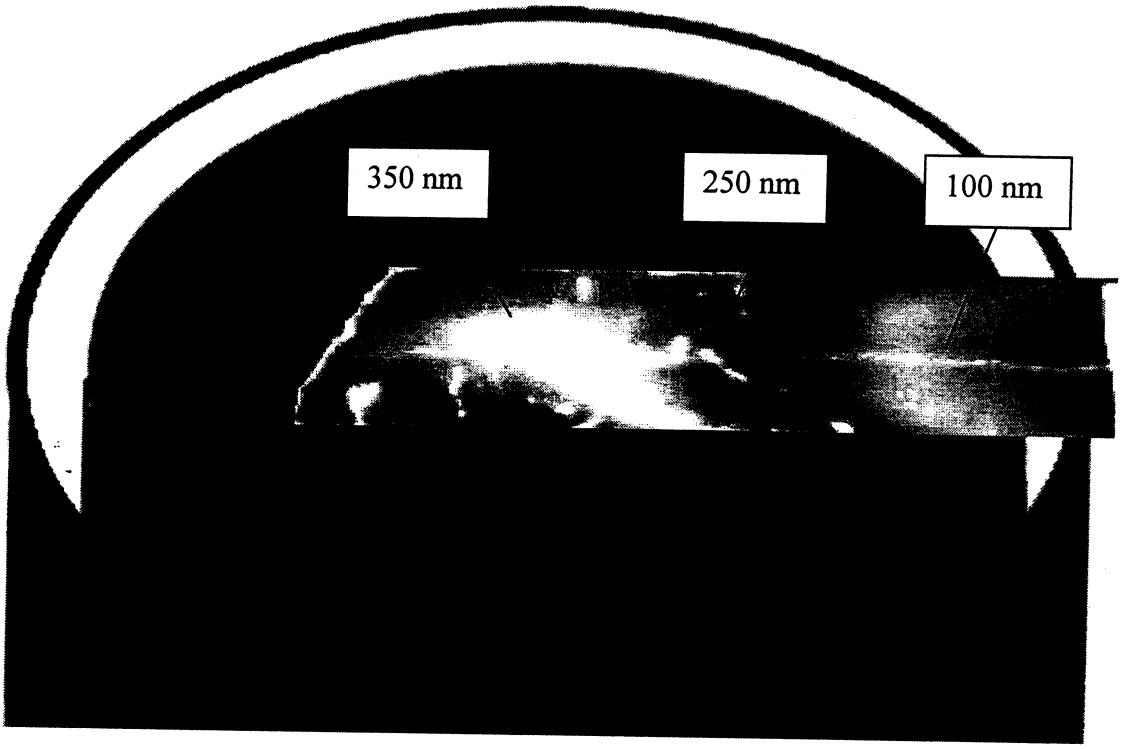


Figure 9: The lower electrode with the color and height profile of fibers. The height depends on the location on the lower electrode, and the color reflects the heights, as in a thin film.