EFFECT OF CATALYST THICKNESS AND BARRIER LAYERS ON PATTERNED VERTICALLY-ALIGNED CARBON NANOTUBE GROWTH

by

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ABSTRACT

EFFECT OF CATALYST THICKNESS AND BARRIER LAYERS ON PATTERNED VERTICALLY-ALIGNED CARBON NANOTUBE GROWTH

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We investigated the role of sub-catalyst barrier layers in Vertically-aligned carbon nanotube (VACNT) growth and explored its effect on VACNT structures. Al_2O_3 and several alternative barrier layers including native SiO_2, thermally grown SiO_2, and Ti were deposited on silicon wafers prior to Fe layer deposition. The effect of the barrier layers on VACNT growth characteristics, specifically: VACNT growth rate, carbon nanotube (CNT) size, density, and dimensional control of patterned vertical structures were examined. VACNT forest growth was characterized by scanning electron microscopy (SEM). The effect of the barrier layer on the Fe catalyst after both pre-growth annealing and CNT growth was characterized by atomic force microscopy (AFM) and transmission electron microscopy (TEM). TEM revealed that the Al_2O_3 barrier layer both reduced diffusion of the Fe into the Si substrate and played a significant role in particle formation resulting in small Fe nanoparticles. Ther-

mal SiO_2 provided a significant barrier to diffusion into the substrate but did not result in Fe nanoparticles as small as those on the Al_2O_3. Thinner Fe catalyst layers resulted in faster, denser, and better-aligned growth.

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Chapter 1

Introduction

1.1 Motivation and applications

Carbon nanotubes (CNTs) have garnered much attention for their unique mechanical and electrical properties. CNTs are entirely composed of carbon double bonds. Because of this they are extremely strong along their axis as well as flexible in all directions. Electrically, CNTs can be either metallic or semiconducting. The difference in electrical properties depends on their chirality and diameter [1].

Vertically-aligned carbon nanotube (VACNT) growth has also received significant attention. Possible applications for VACNT forests include nanoprobes, field emission displays [2], and scaffolding for the deposition of other materials [3]. The purpose of this research is to optimize VACNT growth for high-aspect ratio scaffoldings.

VACNTs have great potential as an alternate method for forming high aspect-ratio structures. Most current methods involve etching deep into a substrate. These etching processes limit the aspect ratio of the features and are slow and expensive. Current etch rates for silicon (one of the most commonly etched materials) are less than 10 nm/s [4]. However, it is quick and inexpensive to grow carbon nanotubes vertically from a patterned substrate. We have demonstrated VACNT growth rates of over 10 μm/s. These VACNT features can subsequently be coated through Chemical Vapor Deposition (CVD) with silicon, carbon, or a number of other materials.

1.2 Growth reactions

VACNT forests are usually grown from a Si substrate covered with a barrier layer of alumina and a layer of Fe catalyst [5]. VACNTs are grown on these layers through CVD. The samples are annealed at temperatures ranging from 500 °C to 900 °C. While annealing at these high temperatures the thin layer of Fe balls up into discrete particles. It is hypothesized that barrier layer of alumina assists in the formation of Fe nanoparticles. After the pre-growth anneal, Ethylene (or a similar carbon gas) flows over the sample. With certain temperatures and gas ratios, the ethylene reacts with the Fe and CNTs are formed. Under unfavorable conditions, the ethylene decomposes and covers the sample and Fe particles with layers of amporphous carbon, stopping the CNT growth. It is hypothesized that flowing H_2 along with the ethylene prevents the buildup of amorphous carbon and enables the catalyst particles to continue functioning. For our growths we used a flow of 125 sccm Ar, 500 sccm H_2, 620 sccm C_2H_4, and a temperature of 750 °C. We investigated how different barrier layers and Fe catalyst thicknesses affect growth of VACNT structures.

1.3 Overview of VACNT structures

Large VACNT structures hundreds of microns in size have been demonstrated by many groups [6]. At this scale a variety of features can be obtained by patterning the Fe layer. However, at a smaller scale the VACNT's erratic growth direction blurs the edges of the features (see Fig. 1.1). Even when the features appear distinct, there are often stray nanotubes. These stray tubes become problematic when coated through CVD. A single nanotube a few nanometers in diameter becomes significant when coated with hundreds of nanometers of material. To make VACNT features on the micron-scale a dense and well-aligned growth must be achieved.

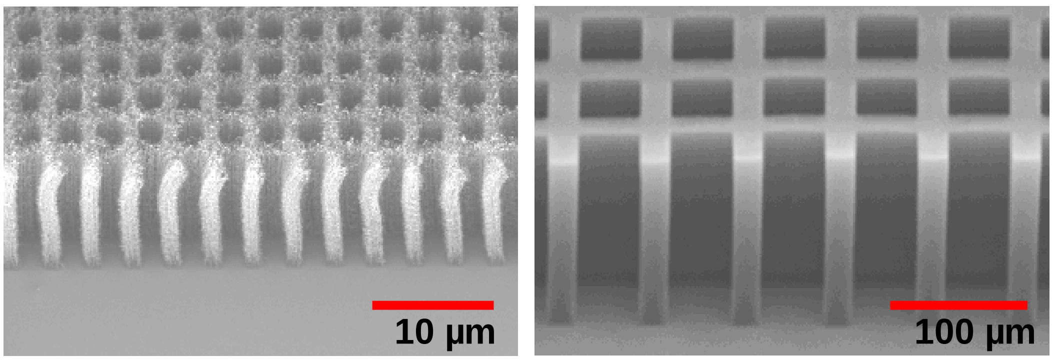

Figure 1.1 Comparison of small and large features.

1.4 Overview of experimental goal and procedure

To optimize the VACNT structures and learn more about VACNT growth we varied the barrier layer in one experiment and the Fe catalyst thickness in another. We studied these parameters at early stages of growth by analyzing nanotube and catalyst morphologies after very short growth times. This allowed us to optimize for small features and facilitated cleaner TEM sample preparation. Several barrier layers were deposited on silicon substrates and subsequently coated with identical, thin layers of iron. VACNTs were grown on these samples to determine the effect of the barrier layer. Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM) were all utilized to determine the barrier layer function and the resulting VACNT growth.

The effect of catalyst thickness was determined by similar experimentation. Samples were prepared with varying thicknesses of Fe on the standard Alumina barrier layer. These coatings ranged from 15 nm to less than 1 nm. VACNTs were grown on these samples and SEM and AFM were used to determine the effectiveness of the catalyst.

1.5 Summary of optimal parameters for VACNT structures

Alumina was found to be the most effective barrier layer. Native SiO_2 and Titanium showed significant Fe loss through diffusion and Fe-Silicide formation. Alumina was also the most effective in forming small and discrete Fe nanoparticles for dense VACNT growth.

It was determined that thinner layers of Fe grew denser, taller VACNT forests as well as increased the growth rate. These thinner Fe layers also were the most effective at forming stable structures. However, the sub-nanometer layers grew so fast that the height of the VACNT forest was difficult to control. A Fe thickness of 2 nm was determined to be optimal for stable, repeatable VACNT structures.

Chapter 2

Experimental Procedure

2.1 Barrier layer deposition

The first step in the preparation of the samples for both experiments was coating blank Si wafers with barrier layers. Our barrier layers were deposited or grown to form ∼30 nm blanket layers on the Si wafers. Alumina (20 nm) and titanium (34 nm) were deposited with a Denton Vacuum E-beam Evaporator. SiO_2 was thermally grown by annealing in a 6 inch tube furnace. A HF etch was then used to remove the oxide until a thickness of 26 nm was obtained. 1.2 nm of native SiO_2 was also used as a barrier layer. Barrier layer thickness' were determined by a combination of a Filmetrics F20 Film Measurement System and post-growth TEM imaging.

2.2 Patterned Fe deposition

Once the samples were coated with a barrier layer a patterned layer of Fe was formed using photolithography. A 1 μm layer of AZ3312 photoresist was spun onto the wafers and then baked at 90 °C for 1 min. The photoresist was then exposed with

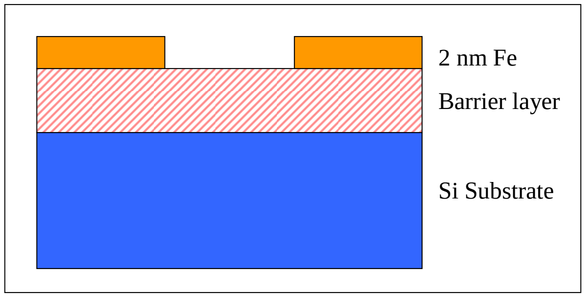

Figure 2.1 Pre-growth layer structure.

a pre-fabricated mask pattern using a Karl Suss Mask Aligner. The mask pattern consisted of 2.5 μm lines spaced 3.5 μm apart. The photoresist was then developed in an alkaline solution to remove the 2.5 μm lines.

For the barrier layer experiment, a 2 nm Fe film was deposited on the samples using a thermal evaporator. This covered both the exposed barrier layer and the photoresist. For the Fe catalyst thickness experiment, 1 nm to 15 nm of Fe was deposited on the samples also using a thermal evaporator. The remaining resist was lifted off with 1165 Microposit Remover and the samples were cleaned with acetone and isopropanol (see Fig. 2.1).

2.3 VACNT forest growth

The VACNT forests were grown in a 1 inch tube furnace. The same growth parameters were used in both experiments. Samples were heated to 750 °C under a flow of 500 sccm H_2 and 125 sccm Ar. When the furnace reached 750 °C ($\sim$10 minutes) a 620 sccm C_2H_4 flow was started. The C_2H_4 flow was controlled with a LabView program and solenoid valves. These allowed us to accurately repeat very short growth times. After a 2 s growth the C_2H_4 and H_2 were switched off and the samples were cooled to room temperature under 125 sccm of Ar. In the barrier layer experiment an identical set of samples underwent the same annealing procedure, but with no C_2H_4 flow. Additionally, a control set was left untouched after barrier layer deposition.

2.4 SEM, AFM, and TEM analysis

SEM was the primary tool for characterizing the VACNT growth. SEM was used to determine forest height, density, and alignment as well as CNT size and VACNT structural stability. While SEM and AFM were used for both the barrier layer and catalyst thickness experiments, TEM was used exclusively for the barrier layer experiment. AFM was used in tapping mode to characterize the Fe catalyst surface before and after annealing and to measure the thickness of Fe catalyst layers. TEM cross-sectional analysis was used to determine the Fe particle size distribution after growth.

Chapter 3

Results and Discussion

3.1 Effect of barrier layer on forest growth

3.1.1 Forest height, density, and CNT alignment

While all the tested barrier layers grew CNTs, there was a great variety in the height and density of the forest (see Fig. 3.1). In the short growth time, the alumina barrier layer grew an 11 micron forest and had the most vertically-aligned CNTs. Titanium grew a partially-aligned forest 1.5 microns high, native SiO_2 and thermal SiO_2 grew a sparse, randomly-oriented mat of CNTs on the surface. The VACNT forest on the alumina was the densest of all the barrier layers and grew the highest. Titanium was the next most dense followed by thermal SiO_2 and native SiO_2. Titanium also grew much thicker tubes than all other barrier layers. While all these trends held true for a 2 nm Fe catalyst thickness, it is possible that varying the Fe thickness could improve growth on native SiO_2, thermal SiO_2, and titanium.

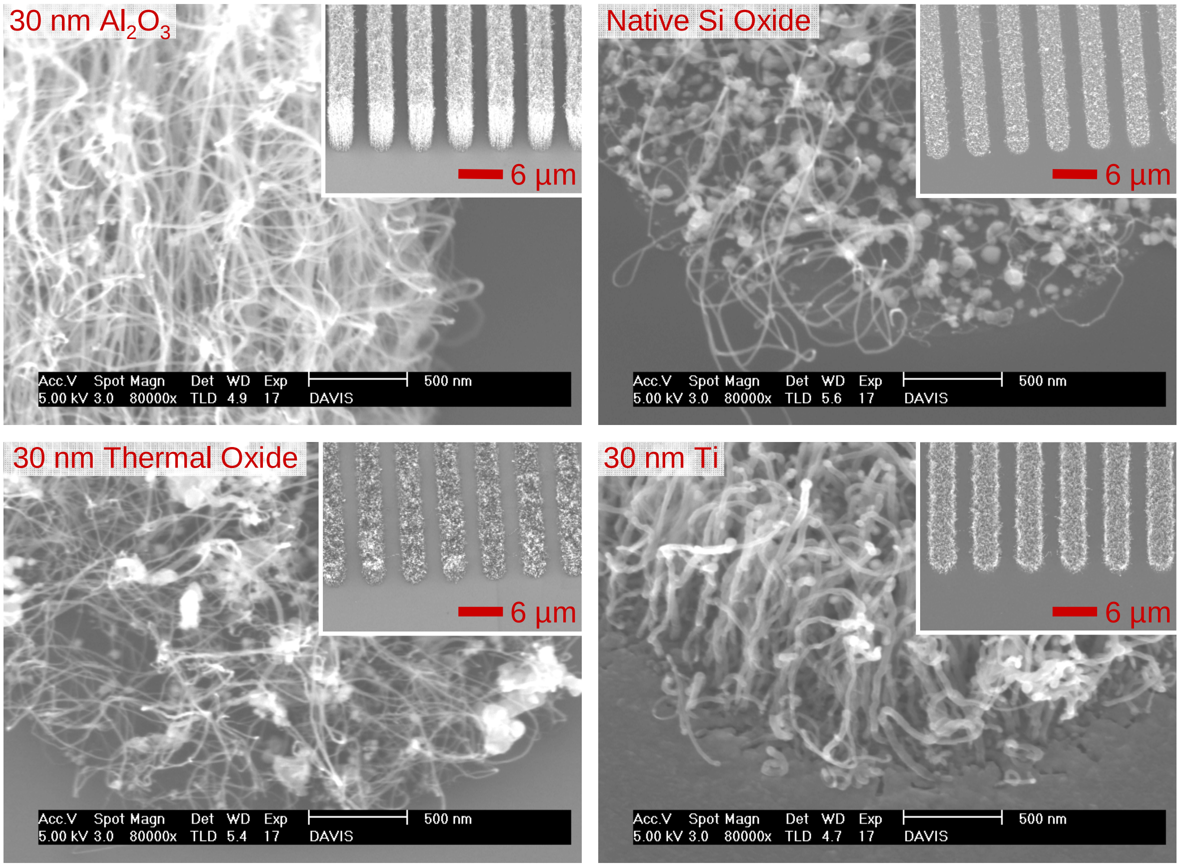

Figure 3.1 SEM images of the VACNT forest growth with different barrier layers. Each main image shows an 80,000X image of tube density and alignment. Each inset shows a 2500X view of the VACNT structures.

3.1.2 Particle size distribution

The size of Fe nanoparticles varied greatly with the different barrier layers (see Fig. 3.2). Using the cross-sectional TEM images we measured the size of all the Fe nanoparticles to determine the particle size distribution for each barrier layer (see Fig. 3.3). Alumina had the highest concentration of 1.5 and 4.5 nm particles. Thermal SiO_2 and native SiO_2 had similar overall particle distributions, with thermal SiO_2 having a greater concentration of 1.5 nm particles. Titanium formed much larger catalyst particles.

In the TEM images we saw silicides forming beneath the native SiO_2 and the

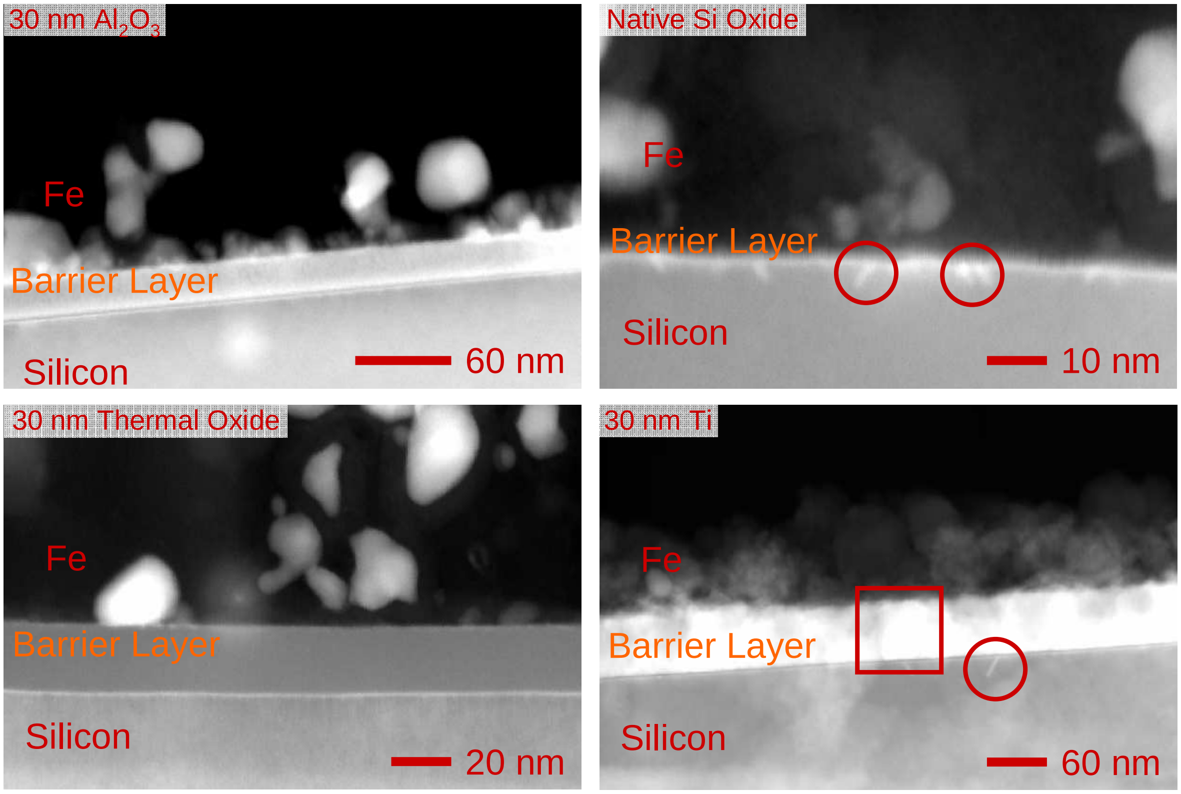

Figure 3.2 TEM cross section of the Fe particles after growth on different barrier layers. The circles highlight Fe silicide formation and the square highlights possible alloying in the titanium.

titanium barrier layers. By using Energy Dispersive X-ray Spectroscopy (EDX) and analyzing the growth orientation we concluded that they were Fe silicides. Also, some cloudiness is seen in the titanium barrier. This cloudiness could possibly be alloying between the Fe catalyst and titanium barrier layer (Fig. 3.2). While the alumina and thermal SiO_2 layers didn't show silicides forming after 2 s growths, longer growth times revealed that both eventually exhibit silicide formation.

3.1.3 Discussion

We found that the different barrier layers had a large effect on the VACNT forest growth. Alumina was by far the most effective barrier layer: it grew the tallest

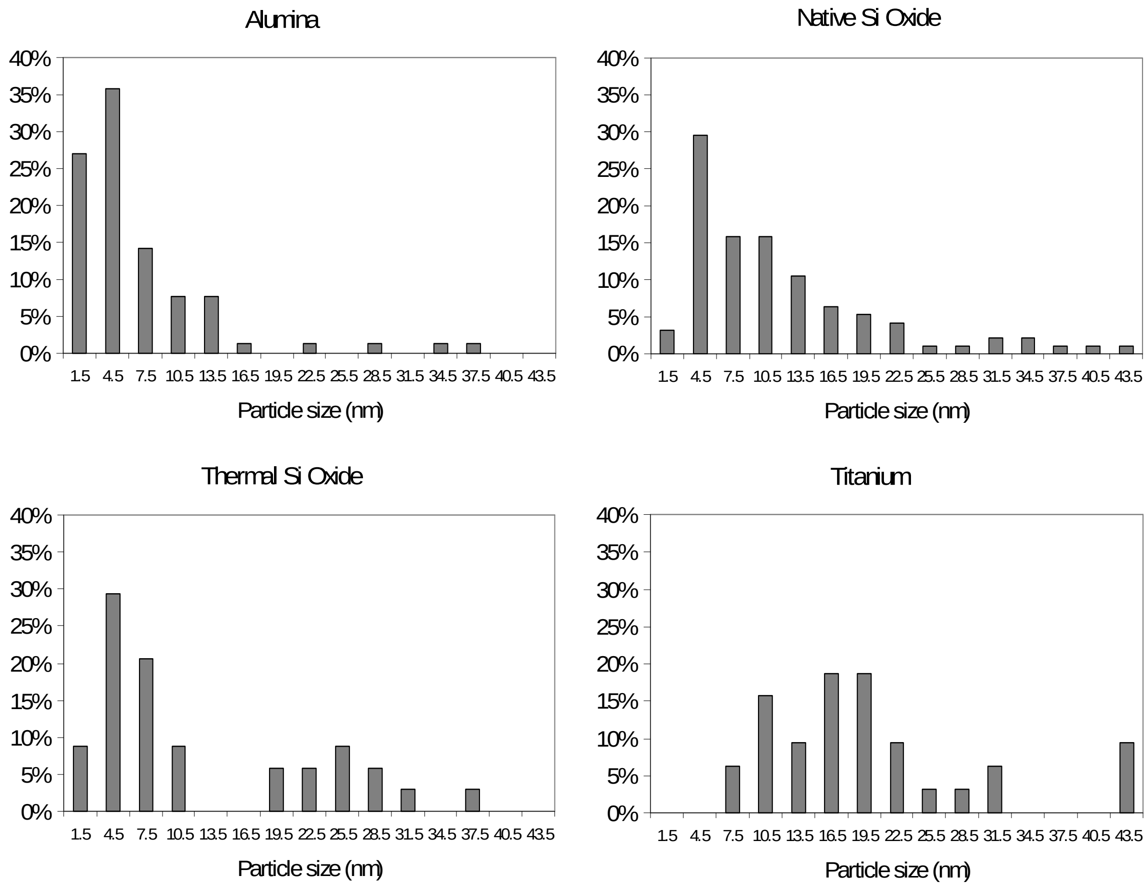

Figure 3.3 Histogram showing particle size distribution for the different barrier layers (bin size of 3 nm, values are normalized by the total number of particles).

and densest VACNT forest. Between the four barrier layers, the height of the forest correlated closely with its density (see Fig. 3.1).

The VACNT forest density is closely correlated with the size and density of the catalyst particles. Alumina, which has the highest percentage of 1.5 and 4.5 nm particles, grew the densest and tallest forest. Between the silicon oxide barrier layers, thermal SiO_2 had a greater concentration of 1.5 nm particles and consequently grew a denser and taller forest. Titanium formed much larger catalyst particles, peaking around 18 nm. We can see from the SEM image (Fig. 3.1) that the titanium barrier layer grew much larger CNTs as well.

It appears that the barrier layer is able to control the Fe particle size and subsequent CNT size and density. An additional function is the prevention of Fe loss through diffusion. Any Fe lost to silicide formation or alloying is unavailable to catalyze CNT growth. Comparing native and thermal SiO_2, we assume that Fe loss through the native SiO_2 correlates to fewer 1.5 nm Fe nanoparticles and lower CNT density.

3.2 Effect of Fe thickness on forest growth

3.2.1 Effect of thickness on forest density and CNT alignment

After alumina was seen to be the most effective barrier layer for dense, well-aligned growth, the Fe thickness was varied to determine its effect. We can see from SEM that the tube density and alignment varied greatly between the samples (Fig. 3.4). As we decreased the Fe thickness we saw denser VACNT forest growth and better aligned tubes. It also appears that the tube diameter decreased as well (though SEM is not the ideal tool for measuring CNT diameter).

3.2.2 Effect of thickness on structure integrity and growth rate

The integrity and growth rate of the VACNT structures varied greatly with Fe catalyst thickness (see Fig. 3.5). The thicker Fe layers resulted in many stray tubes and "floppier" VACNT features. Understandably, the structural integrity followed closely with CNT density and alignment. The rate of VACNT growth also increased dramatically with thinner Fe layers. While a fast growth rate is desirable, we found

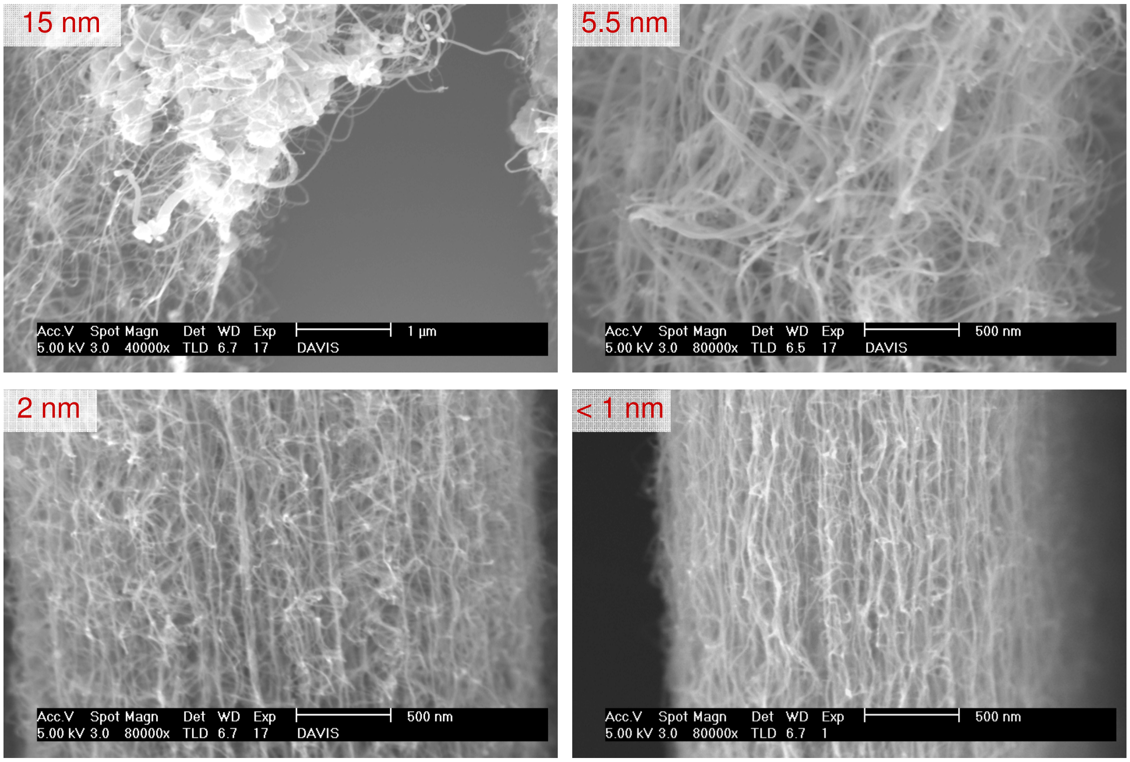

Figure 3.4 SEM image of VACNT forest growth density with different Fe thickness'

that the 2 nm layer was optimal. The 1 nm Fe layer grew so fast that in the 2 s growth period the structures exceeded the necessary height and began to flop over. Also, such a rapid growth is not desirable for repeatability and scaling up the process.

3.3 Summary of optimal parameters for VACNT structures

It was found that a combination of alumina and 2 nm of Fe were the ideal combination for the structures we desire. Alumina was found to be the best barrier layer for VACNT forest growth: it yielded the smallest Fe nanoparticles after annealing and the least loss of Fe through diffusion. Thinner catalyst layers resulted in faster, denser,

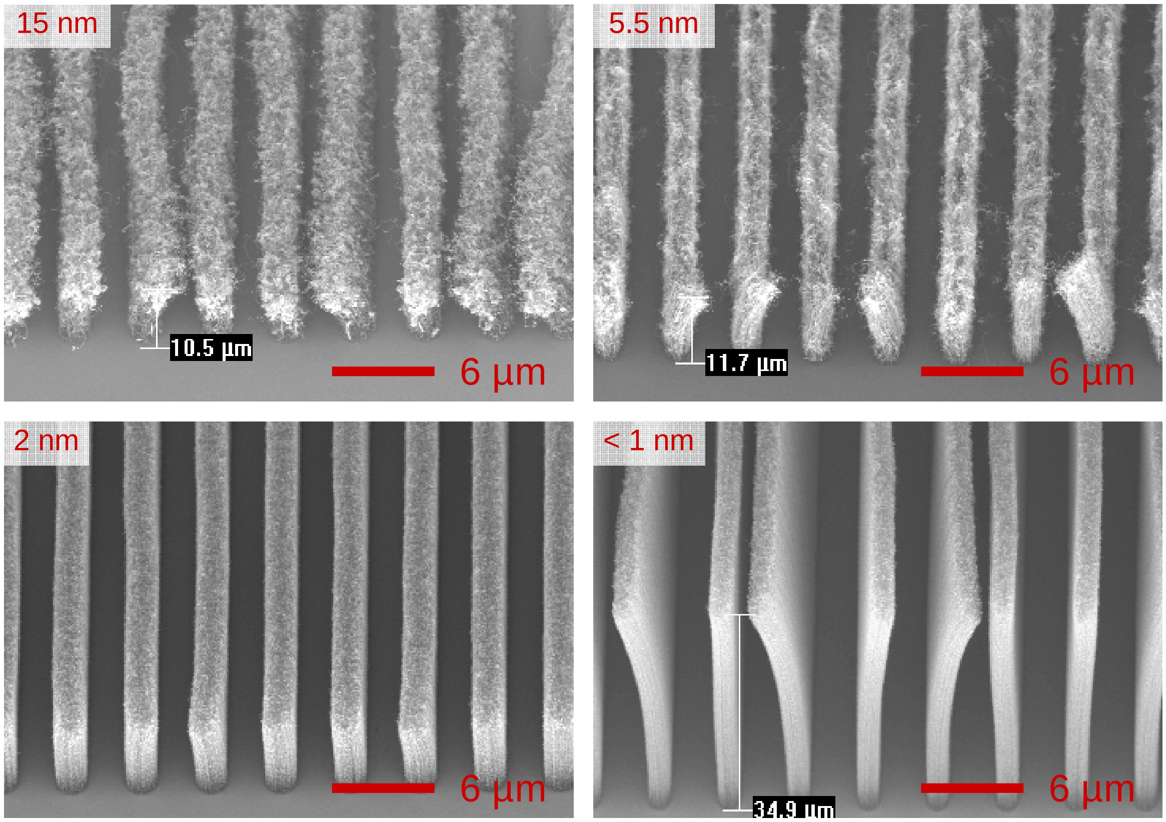

Figure 3.5 SEM image of VACNT structures with different Fe thickness'

and more-aligned growth. A 2 nm Fe layer resulted in a dense, well-aligned growth, as well as a reasonable growth rate.

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