

TERMINATION OF CARBON NANOTUBE GROWTH: EFFECT OF SUBSTRATE STRUCTURE

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Introduction

Carbon nanotube (CNT) carpets have shown promise in a number of important applications such as membranes, Li ion batteries, supercapacitors, super hydrophobic surfaces, polymer-nanotube composites and “gecko” tapes [1]. For these applications to become commonplace reality, proper control of the collective properties and the uniformity of the single-walled CNT (SWNT) carpet are required. The preferred method for SWNT carpet growth is catalytic chemical vapor deposition (CVD) using a thin Fe film (<1 nm thick) catalyst supported on an alumina film with a hydrocarbon gas as the carbon feedstock [2,3]. CNT growth is currently limited by the catalyst. Yield, length, purity and growth rate are all critical to effective application of CNTs.

To fully achieve the promise of SWNT carpets, a rational approach for the design of catalysts with improved lifetime and activity is required. The successful design of catalysts will require a good understanding of the nucleation, growth, and termination mechanisms. Hitherto, our work has revealed that Ostwald ripening [4] and subsurface diffusion [5] of the catalyst during carpet growth are intimately connected to the growth termination process. Herein, we focus on the influence of the type of alumina on the evolution of the catalyst during carpet growth – particularly how the alumina type and porosity affect the Ostwald ripening behavior and the mass loss (or subsurface diffusion) of the catalyst, and how it impacts growth[6].

Experimental

The catalyst samples consisted of a 0.5 nm thick Fe film deposited by e-beam evaporation on 10 nm thick alumina films supported on p-type Si (100) wafers. The alumina films were deposited by atomic layer deposition (ALD), e-beam, and magnetron sputtering. Also used as catalyst supports were a 10 nm thick alumina film deposited by e-beam and thermally annealed at 800°C for 30 minutes and C-cut sapphire substrates. A total of five supported Fe catalyst systems were studied: (a) Fe on sapphire (sapphire/Fe), (b) Fe on sputter-deposited alumina (sputtered/Fe), (c) Fe on e-beam deposited alumina (e-beam/Fe), (d) Fe on thermally annealed alumina deposited by e-beam (annealed e-beam/Fe), and (e) Fe on

alumina deposited by ALD (ALD/Fe). In order to study the evolution of the catalyst on the different alumina supports, the samples were exposed to water-assisted growth conditions in the presence and absence of C₂H₂ for 1.5, 5, and 15 min. A detailed description of the CVD chamber, growth conditions for SWNT carpet is given elsewhere [7]. The catalyst samples were characterized by AFM, FESEM, XPS depth profile analysis, and variable angle spectroscopic ellipsometry (VASE). The experimental details of all the characterization studies performed are provided in ref 6.

Results and Discussion

There is a strong dependence of the catalytic behavior of alumina-supported Fe films on the type of alumina used as support. As presented in Fig. 1, the catalyst activity and lifetime, based on the carpet height after 5 and 15 min, increased in the following order: sapphire/Fe < annealed e-beam/Fe < ALD/Fe < e-beam/Fe < sputtered/Fe [6]. Sputtered/Fe shows the highest catalyst activity and lifetime followed by e-beam/Fe. Annealed e-beam/Fe shows an initial growth rate that is similar to e-beam/Fe, but results in early growth termination, evidenced by the constant carpet height after 5 min. ALD/Fe grows SWNT carpet reasonable well, but at a slower rate while sapphire/Fe did not support carpet (or aligned) growth at all.

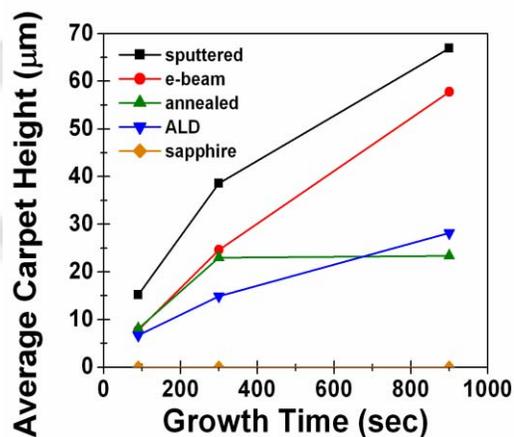


Fig. 1 Plots of average SWNT carpet height as a function of growth time for Fe catalyst supported on the various aluminum dioxide (sputtered/Fe, e-beam/Fe, annealed e-beam/Fe, ALD/Fe, and sapphire/Fe).

In order to account for the observed differences in the catalyst activity and lifetime, we performed a time-dependent study whereby the different alumina-supported Fe catalysts were exposed to water-assisted growth condition in the absence of C₂H₂. Ostwald ripening refers to the growth of larger particles at the expense of smaller ones to relieve the excess surface energy; it is generally characterized by (a) growth in mean particle size with time, accompanied by (b) decrease in particle number density. The influence of the alumina support on the mean catalyst particle height and the

catalyst particle number density after 1.5 and 5 min of exposure to SWNT carpet growth conditions was studied using AFM. The z-heights obtained by manual cross-sectional analysis and the number density of the catalyst particles were acquired from a $200 \times 200 \text{ nm}^2$ area. Fifty randomly picked catalyst particles from the same area were used in the determination of the mean heights.

First, the mean heights (Fig. 2a) of catalyst particles formed on the different substrates after 1.5 and 5 min of exposure to growth conditions in the absence of C_2H_2 reveal that there is severe coarsening of the catalyst nanoparticles especially in the case of sapphire/Fe and annealed e-beam/Fe. Based on the increase in the mean height of the particles, the Ostwald ripening rate decreases in the following order: sapphire/Fe < annealed e-beam/Fe < ALD/Fe < e-beam/Fe \approx sputtered/Fe.

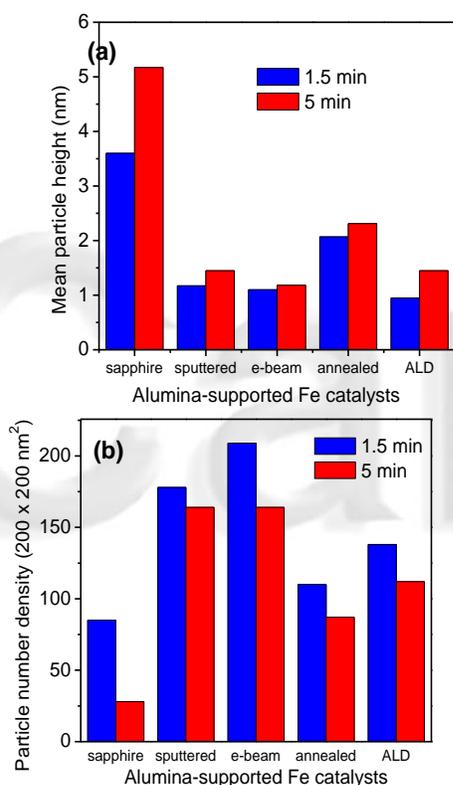


Fig. 2 Histograms of (a) mean particle height and (b) number density of catalyst nanoparticles as functions of the different alumina supports (sapphire/Fe, sputtered/Fe, e-beam/Fe, annealed/Fe, and ALD/Fe) formed after 1.5 and 5 min of exposure to water-assisted growth conditions.

Second, the number density of catalyst particles (Fig. 2b) formed on the different substrates after exposure to growth conditions in the absence of C_2H_2 reveal that the number density of particles decreases with time, which is one of the signatures of Ostwald ripening. On the basis of the percentage decrease in the number density, the rate of Ostwald ripening is lowest for sputtered/Fe and highest for sapphire/Fe followed

by annealed e-beam/Fe. The Ostwald ripening rates of ALD/Fe and e-beam/Fe are considerably lower and somewhat indistinguishable after 5 min of treatment. Interestingly, the Ostwald ripening behavior correlates well with the growth data in Figure 1. Since the Ostwald ripening behavior of catalysts is intimately connected to the growth termination process [4], we therefore postulate that the reduced ripening observed for e-beam/Fe and sputtered/Fe may actually be responsible for their high catalytic activity and lifetime.

As demonstrated in ref 6, the carpet height increases with increasing porosity. The Ostwald ripening rate increases with decreasing porosity while high catalytic activity is observed for samples with low Ostwald ripening rate. Further, the atomistic subsurface diffusion of Fe is highest for e-beam/Fe and is nonexistent in sapphire/Fe. Subsurface diffusion rate of Fe is reduced for alumina samples with low porosity. Interestingly, Sputtered/Fe that has the highest catalytic activity has subsurface diffusion rate of Fe that is intermediate between ALD/Fe and e-beam/Fe suggesting that mild subsurface diffusion is actually beneficial for carpet growth.

Conclusions

The catalytic activity and lifetime of $\text{Al}_2\text{O}_3/\text{Fe}$ is sensitive to the type of alumina used as support. Fe catalyst supported on amorphous alumina films deposited by magnetron sputtering, e-beam, and ALD showed different catalytic behavior. SWNT carpet growth is maximized by increased porosity of the alumina films, low Ostwald ripening rate, and mild subsurface diffusion rate as observed in sputtered/Fe catalyst. Ostwald ripening is higher when the surface is saturated with Fe and could result in growth termination as observed for sapphire/Fe and annealed e-beam/Fe. Our findings would benefit ongoing efforts aimed at developing a model catalyst for improved and controlled SWNT carpet growth.

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References

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