Growth Control of Vertically-Aligned Single-Walled Carbon Nanotubes from Alcohol

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The vertically aligned single-walled carbon nanotubes (SWNTs) [1, 2] with film thickness up to 30 microns is grown on quartz or silicon substrates by alcohol catalytic CVD. The growth condition and growth mechanism of VA-SWNTs is discussed based on the *in-situ* growth monitoring by laser absorption [3, 4] during CVD. Film thickness L of VA-SWNTs film at various temperature, flow-rate, and pressure can be well fit by an empirical equation:

$$L = \gamma_0 \tau \left(1 - \exp(-t/\tau)\right)$$

where γ_0 and τ are initial growth rate and growth decay time, respectively. The initial growth rate γ_0 is linearly proportional to pressure up to the critical pressure which is determined by temperature [4]. This result indicates the first order reaction below the critical pressure.

The non-flow CVD [5] turned out to be very efficient, resulting a thicker film up to 100 μm. As shown in Fig. 1, effect of ethanol flow rate on the growth dynamics of VA-SWNTs is significant for lower flow rate. The peculiar growth curve for lower slow rate suggests the important role of small hydrocarbon molecules thermally decomposed from ethanol.

The predicted thermal decomposition process of ethanol based on the chemical kinetics model [6] is shown in Fig. 2. At 800 °C, original ethanol is almost completely decomposed after 2 s, leaving ethylene and water as main products. This thermal decomposition rate is about 15 times faster at 900 °C and 15 times slower at 700 °C. Because the reactivity of smaller hydrocarbon molecules can be very high as expected from the FT-ICR mass-spectrometer measurements [7], effect of some of decomposed molecule can be very important for low flow rate condition.

Effect of each decomposed molecules on CVD process is examined by mixing a fixed rate of hydrocarbon in the *in-situ* monitoring system. As shown in Fig. 3, drastic effect of acetylene addition was observed. Only about 1 percent of acetylene mixing to ethanol flow results 10 time fast growth rate. However, the decay time τ becomes much smaller with acetylene addition. Effect of ethylene is much less but considerable growth enhancement was observed when 25 % is mixed with ethanol. Further in-situ examinations revealed that small amount of acetylene itself is not effective to grow SWNTs but full amount of ethanol is always necessary.

The carbon conversion rate from ethanol to VA-SWNTs can be as high as 40 % with no-flow condition. Hence, isotopically modified ethanol can be employed to study the growth process to prove that the root-growth mechanism is applied to our VA-SWNTs [8]. The detailed chemical reaction process in gas-phase and on metal catalysts will be discussed based on CVD results using isotope labeled ethanol and acetylene as carbon source. Furthermore, control of diameter distribution is also discussed.

References:

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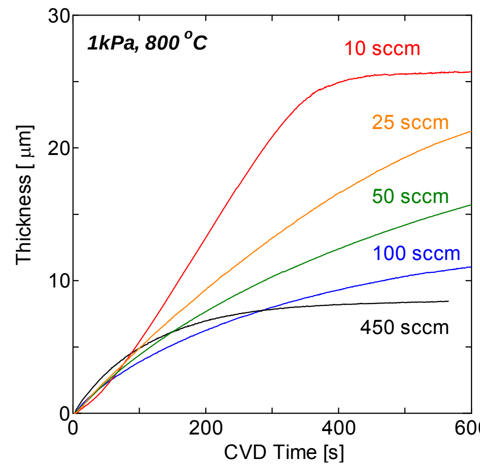

Fig. 1. Effect of flow rate on growth of vertically aligned SWNTs measured by *in-situ* laser absorption.

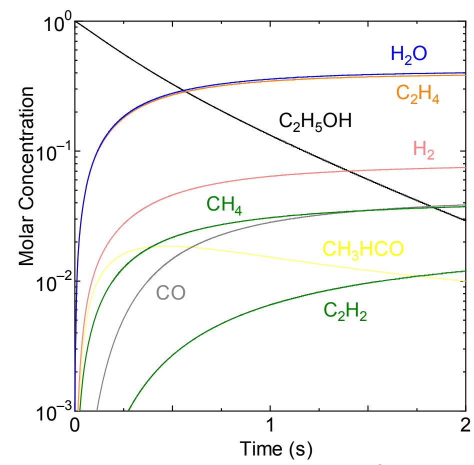

Fig.2 Predicted decomposition process of ethanol at 800 °C in a constant volume.

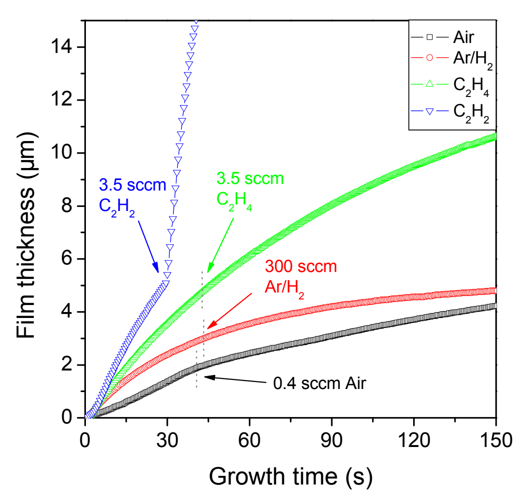

Fig. 3 Growth boost by addition of small amount of acetylene.