

# MICRO CHEMICAL VAPOR DEPOSITION SYSTEM: DESIGN AND VERIFICATION

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## ABSTRACT

The conventional chemical vapor deposition system has been miniaturized to the micro scale, leading to several potential advantages for the synthesis of nanostructures. First, minute heat capacity leads to fast temperature stabilization. Second, tiny chamber volume helps for rapid gas species exchanges. Third, small Reynolds number ensures laminar flow for better control of deposition sources. Forth, small diffusion length near the chemical reaction surface enhances efficient gas mass transfer. As a demonstration of principle, high-quality single-walled carbon nanotubes (SWNTs) are synthesized while similar experimental parameters in a large scale system fail to construct good quality SWNTs.

## INTRODUCTION

Chemical vapor deposition (CVD) has been widely used in microfabrication processes to produce thin films on substrates and has been an important method in the synthesis of various nanostructures [1]. The thermal decomposition or reaction of gaseous compounds is the key deposition sources in CVD. Atmosphere pressure CVD (APCVD) is performed at atmosphere pressure. As the mean free path for gas molecules is quite small (tens of nanometers), high flow rates are usually required to ensure efficient mass transfer of reactant gas. LPCVD (Low pressure CVD) system, on the other hand, typically operates at 30 to 250Pa with much lower flow rate due to the increased mean free path for gas molecules. CVD reactions can also take place with the assistance of plasma. Formation of the plasma could usually lower the reaction temperature, which is a primary advantage of plasma-enhanced CVD (PECVD) processes.

APCVD is easy to set up and does not require vacuum equipment, so it is widely used in the synthesis of nanostructures. The process is usually performed by forcing the reactant gas to flow through a heated tube in a furnace, as shown in Figure 1. After entering into the tube, the gas temperature inside the tube gradually approaches external furnace temperature. CVD reaction takes place either with or without the assistance of catalyst. For example, carbon nanotubes (CNTs) have been previously synthesized with the assistance of iron nanoparticles with methane as the carbon source. [2]

One may identify several challenges, especially during the synthesis of nanostructures, for a conventional CVD system. First, large heat capacity means that both heating up and cooling down process will take a long time. Second, large volume also implies that it takes a long time to switch from one gas to another gas inside the reaction tube. Third, in APCVD, high flow rate is required to ensure efficient mass transport of reactant gases but the flow rate is also limited to laminar flow requirement for high quality thin film or nanostructures. High flow rate can cause turbulent flow, which has a non-stable flow

field which would greatly affect the quality of synthesized materials [1, 5].

We propose and demonstrate a Micro-CVD system to address the aforementioned challenges in a large CVD system. By shrinking the conventional CVD system from the scale of meters to the scale of tens of micrometers, one can take the advantage of scaling effects to address issues described above. Theoretical analyses are conducted with experimental verifications to show the scaling effects in the CVD process.

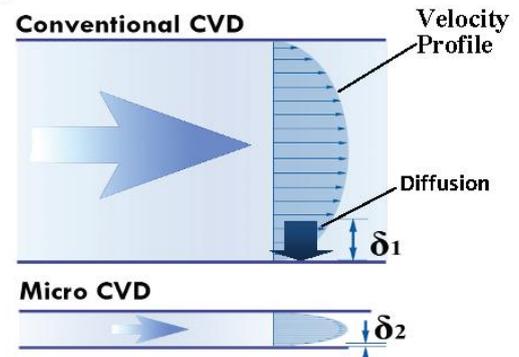


Figure 1: Comparing the conventional CVD system with the Micro-CVD system.

## THEORETICAL MODELING

The proposed Micro-CVD system replaces the quartz tube in the conventional CVD system with microchannels as illustrated in Fig. 1. The gas is heated up to the CVD reaction temperature by heating up the microchannels via joule heating. In short, micro-CVD is like a miniaturized conventional CVD system with only tens of micrometers in length and several micrometers in diameter. Several possible advantages are analyzed below.

### Quick temperature stabilization

Due to the large heat capacity of the conventional furnace system, it takes half an hour or more for the system to warm up and cool down and lots of unwanted reaction can happen. For example, the synthesis of ZnO (Zinc Oxide) nanowires prefers fast temperature rise and fall to avoid the formation of ZnO thin film or microcrystals in low temperature region [3]. In order to analyze the time response of the system, we estimate the behavior of the system heat capacity  $C_h$  and the heat resistance  $R_h$  so that the time constant can be estimated by  $\tau_h = R_h C_h$ . The heat capacity of the system scales with volume or  $L^3$ , where  $L$  is the dimension of the system. The heat resistance, on the other hand, scales with  $L^{-1}$ . This is because the total heat flow

$$Q = k \oint_{system} dA \cdot \nabla T \sim kL^2 (\Delta T / L) \propto \Delta T \cdot L$$

where  $A$  is the area of heat flow,  $k$  is thermal conductivity, and  $T$  is temperature.  $\Delta T$  represents the temperature difference between the heating zone and the environment.

The heat resistance is then  $R_h = \Delta T/Q$  and scales with  $L^{-1}$ . Based on the previous analysis, the time constant of the system  $\tau_h = R_h C_h$  should scale with  $L^2$ . Shrinking the conventional CVD system from several meters in dimension down to tens of micrometers will result in an approximately  $10^{-8}$  reduction of response time. This means that the system temperature stabilization time will go down from tens of minutes to several microseconds and unwanted side reactions can be avoided by this super-fast temperature control.

### Rapid gas species exchange

To control a CVD process, switching from one type of gas to another is often advantageous for the process flexibility. In the example of CNT synthesis process, carrier gases (such as argon) continue to flow during the furnace heating up process. After the furnace temperature is stabilized, the carrier gas is switched to reactant gas (such as methane). During the switching process, the gas concentrations continue to change as the concentration of the carrier gas drops and that of the reactant gas rises gradually. It is desirable to minimize this gas exchange period as it may affect the quality of the synthesis process with lower concentration of the reactant gases to starting reacting in the early stage. The time needed for the gas exchange period can be estimated by dividing the total volume of the reactant chamber by the flow rate of the gas. For a conventional furnace, this time can be on the order of one minute (The volume is  $0.003 \text{ m}^3$ , assuming a 5-foot long, 2-inch in diameter tube, and assume a flow rate of 3000 sccm). This gas exchange period is undesired because one minute could readily grow CNTs up to  $10 \mu\text{m}$  long in a typical process [4].

The micro-CVD system provides fast gas exchange because of the reduced reaction chamber volume. If one continues with the dimensional analysis, the volume of the reaction chamber scales with  $L^3$ . Assuming the same gas flow speed, the flow rate scales with  $L^2$  due to the reduction of the cross sectional area. The gas exchange time should scale with  $L$  or about  $10^{-4}$  reduction due to miniaturization for the proposed micro-CVD system. Therefore, the gas exchange process will be  $10^4$  quicker and only takes several milliseconds.

### Small Reynolds number for Laminar flow

In a CVD process, laminar flow is often preferred. Reynolds number  $Re$  is often used to characterize different flow regimes. Laminar flow in a tube requires  $Re < 2000$  [5]. For a conventional CVD system, the Reynolds number is estimated to be

$$Re = \frac{\rho v_m D}{\mu} = \frac{\rho Q D}{\mu A} \approx \frac{1 \text{ Kg/m}^3 \times 3000 \text{ sccm} \times 0.05 \text{ m}}{1 \times 10^{-5} \text{ Pa} \cdot \text{s} \times 0.002 \text{ m}^2} = 125$$

where  $\rho$  is the gas density,  $v_m$  is the mean gas speed,  $\mu$  is the gas viscosity,  $A$  is the tube cross sectional area, and  $D$  is the tube diameter. Numbers are for methane (as it is used in the experimental section). We see that  $Re$  is already near the upper limit of laminar flow [6].

Reynolds number for the micro-CVD system, on the contrast, is as small as 0.01 assuming the same gas speed. With a small  $Re$  about 5 orders of magnitude away from the upper limit of laminar flow, we might increase the flow rate easily without worrying about turbulent flow.

### Enhancement on reactant gas mass transfer

Mass transfer is one of the most important issues in a CVD system. Fresh reactant gas is brought onto the substrate surface to produce the desired deposit, and the by-products are carried away by the flow of gas. As such, efficient gas transfer is necessary to produce high quality products from the CVD process. The mass transfer mechanism in an APCVD system is usually diffusion [1]. To understand this, we notice that the gas flows in parallel layers (laminar flow condition), and that the velocity of the layer at the substrate surface where the deposition happens is actually zero (due to the fluid viscosity, see Fig. 1). As a result, reactant gas does not directly flow onto the substrate surface, but the gas diffuses from the flowing layers through the stagnant layer to the deposition surface. The diffusion length  $\delta$  is therefore used to describe the distance over which the diffusion takes place. Short  $\delta$  is desired because the gas can easily diffuse in and out. Obviously,  $\delta$  is inversely proportional to the velocity gradient near the reaction surface such that a higher gas speed is preferred while no turbulence flow should be generated – a typical dilemma in the conventional CVD system.

The micro-CVD system greatly enhances mass transfer by increasing the gas velocity gradient near the reaction surface. For gas flow in a tube with circular cross section, the velocity profile is given by [7]:

$$v(r) = 2v_m \cdot \left[ 1 - \left( \frac{r}{r_0} \right)^2 \right]$$

where  $r_0$  is the radius of the tube. This gives a parabolic velocity profile. The velocity gradient near the surface of the tube is

$$\left. \frac{\partial v(r)}{\partial r} \right|_{r=r_0} = \frac{4v_m}{r_0}$$

It is observed that the velocity gradient scale with  $r_0^{-1}$ , so there would be a  $10^4$  increase in velocity gradient following out prototype example if the gas has the same mean velocity  $v_m$ . This large velocity gradient can ensure an efficient mass transfer.

### Short gas warming up distance

One concern about the micro-CVD system is that whether the gas is fully heated up by flowing through such a short-distance in a microchannel. A simple heat transfer model is established to address this concern.

$$-v_m A \rho c_p \frac{dT(x)}{dx} + k_w A \frac{dT_w(x)}{dx} + h(T_w - T(x)) \pi D = 0$$

$$\Rightarrow T(x) = T_w - (T_w - T_0) e^{-\frac{x}{s}}$$

where  $s = \frac{2k_w}{v_m \rho c_p} \left( \sqrt{1 + \frac{16hk_w}{D(v_m \rho c_p)^2}} - 1 \right)^{-1}$ ,  $c_p$  is the specific gas heat capacity,  $T$  is the gas temperature,  $T_w$  is the temperature of the tube,  $T_0$  is the temperature of gas at the inlet, and  $h$  is the convection heat transfer coefficient. It is observed that  $s$  is a “temperature approaching length”, that is, after the gas flows a distance of  $s$ , the temperature difference between the gas and the tube goes to  $1/e$  of the previous value. Let’s estimate the value  $s$  for the Micro-CVD system. For laminar flow in a tube,  $h$  can be estimated by dividing the thermal conductivity of a gas by the diameter of the tube [7]. This gives

$$h \approx Nu \frac{k_w}{D} \approx 3.66 \times \frac{0.1 \text{ W/m}\cdot\text{K}}{5 \mu\text{m}} = 7 \times 10^6 \text{ W/m}^2\text{K}$$

, so

$$s \approx 1 \mu\text{m}$$

The “temperature approaching length” is so small such that within several micrometers, the gas temperature will reach that of the microchannels. This benefit comes from the great velocity gradient in the microchannels, which gives big convection heat transfer coefficient  $h$  (For ordinary forced convection,  $h$  only has a value between 50~250 W/m<sup>2</sup>K). Figure 3 is the temperature profile from the inlet into the microchannel with the assumptions based on the prototype synthesis conditions. It is found that within several micrometers, the gas temperature reaches that of the sidewall at 900°C. This is an important advancement in temperature control as compared with the previous “Local synthesis” demonstration from our group where temperature control is rather difficult using microheaters in a cold reactant gas chamber [8].

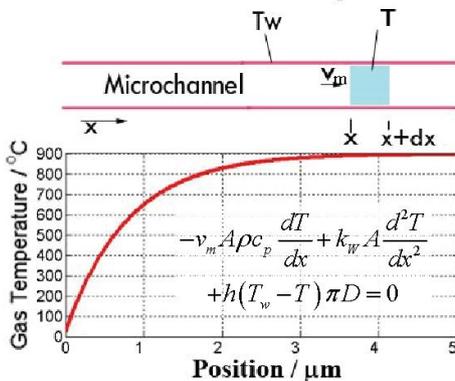


Figure 2: Analysis on the temperature profile of the gas within first several micrometers into the microchannel.

## DEVICE DESIGN AND FABRICATION

Figure 3 illustrates the cross sectional view of the prototype Micro-CVD system consisting of a suspended heating stage with built-in vertical microchannels as the chemical reaction chambers. These microstructures are constructed on a SOI wafer. The prototype dimension of the microchannel is 5μm in diameter and 50μm in length. Reactant gas is introduced through the backside hole (100μm in diameter and 400μm in length) etched by a through-hole deep reactive-ion etching (DRIE) step. A scanning electron microscope (SEM) image of the device can be found in Fig. 4. The stage is supported by a pair of flexible beams anchored to the substrate. These beams also function as the electrical heaters to provide the heating power to the stage.

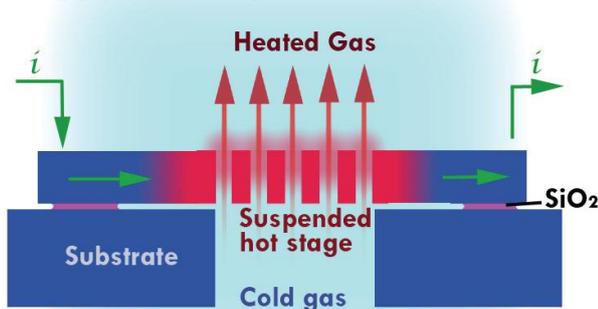


Figure 3: The concept and design of a Micro-CVD system.

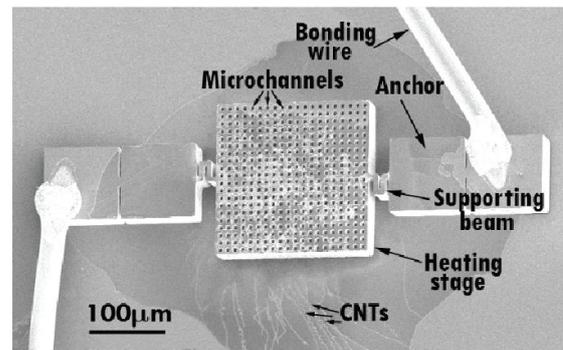


Figure 4: A SEM picture shows an overview of the device

Two pressure gauges are installed in the gas lines before and after the Micro-CVD chip to monitor the gas pressure drop along the microchannels. The flow speed of the reactant gas flowing through the microchannels can then be modulated by changing this pressure. Although the two pressure gauges are not mounted directly at the beginning and the end of the microchannels, the pressure drop mainly happens at the microchannels since it has the smallest diameter and thus the largest flow resistance. The flow speed  $v_m$  can be calculated by:

$$v_m = -\frac{r_0^2}{8\mu} \frac{dp}{dx} = \frac{r_0^2}{8\mu} \frac{\Delta p}{L_{mc}}$$

where  $p$  is the gas pressure,  $L_{mc}$  is the length of the microchannels. In order have a  $v_m$  on the order of centimeters per second (which is the typical velocity for conventional CVD system),  $\Delta p$  should be on the order of tens of pascals. The micro-CVD chip is then connected with electrical and gas interfaces as shown in Fig 5. By applying electric current through the beams, the stage can be heated up via joule heating.

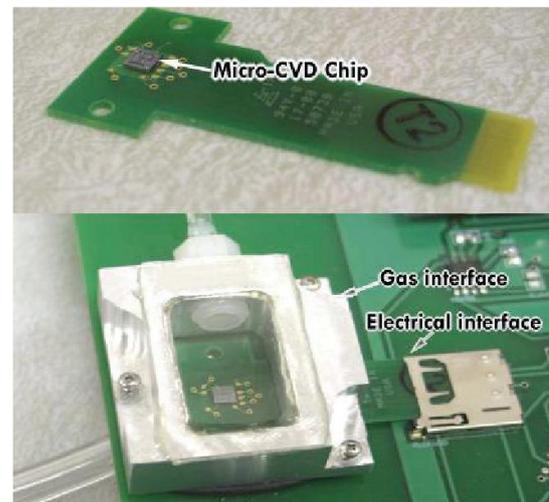


Figure 5: Electrical and gas interfaces.

## EXPERIMENTAL VERIFICATION

Figure 6 illustrates the process flow chosen for the verification of the concept of Micro-CVD by using the synthesis of single-walled carbon nanotubes as the demonstration example. A simple SOI process is conducted as stated previously to make the Micro-CVD platform with finished chips as illustrated in Fig. 3. A 0.5 μm-thick thermal oxide layer is grown as the barrier layer to prevent the iron nanoparticles (serving as the catalyst in CVD process) from diffusing into the silicon (Fig. 6a). A

photolithography is performed and the oxide on the contact pads is etched away to allow electric contact (Fig. 6b). Iron nanoparticles are then deposited onto it as the catalysts following reference [2] (Fig. 6c). The CVD process is then performed at approximately 750°C (by observing the glowing color of the heating stage under microscope). The voltage applied is 16.65V and the current is 128mA in the prototype experiment. Under the gas inputs of hydrogen and ethylene (volume ratio 20:3), and the pressure drop measuring 10KPa across the microchannels, SWNTs are expected to grow from the iron nanoparticles (Fig. 6d).

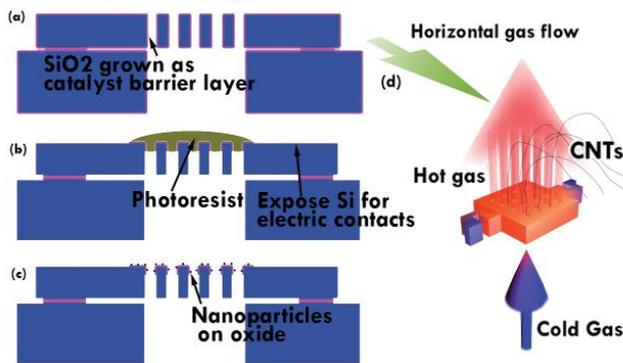


Figure 6: Process flow for single-walled CNT growth.

Figure 7a shows typical SWNTs synthesized by the Micro-CVD system. These SWNTs measure approximately 100 μm long and are grown in 5 minutes. It is suspected that these CNTs were floating in the gas environment during the growth process and later dropped onto the substrate as observed. It is also found that the CNT growth direction can be affected by a horizontal gas flow above the stage, which forces the CNTs to bend following the flow direction (Fig. 6d). The CNTs fall onto the substrate after the growth process, partially retaining this direction (Fig. 7b, indicated by arrows). These CNTs are verified by atomic force microscopy (AFM) measurements to be single-walled as their diameter is within 1~2 nm (Fig. 7c). They appear to be much thicker under SEM due to charge effects [9]. We believe that this is the first successful report to grow good quality single-walled CNTs using solution cast iron nanoparticles as catalysts, and hydrogen and ethylene as gas sources. A control experiment is performed using conventional thermal CVD with the same catalyst and gas under various temperatures between 600-850°C. Only short and curly CNTs are acquired as shown in Fig. 7d (growth temperature at 780°C). This is probably because amorphous carbon is formed on the iron nanoparticles due to the inefficient mass transfer of the conventional CVD system and the amorphous carbon blocks the CNT growth [10]. The good quality SWNTs acquired by the micro-CVD system is a direct verification of the superior operation of the Micro-CVD system as compared with the conventional one.

## CONCLUSION

The concept of micro-CVD system is proposed and verified experimentally with distinctive advantages as compared with the conventional atmospheric pressure CVD system, including agile temperature control, fast gas species exchange, steady laminar gas flow and efficient

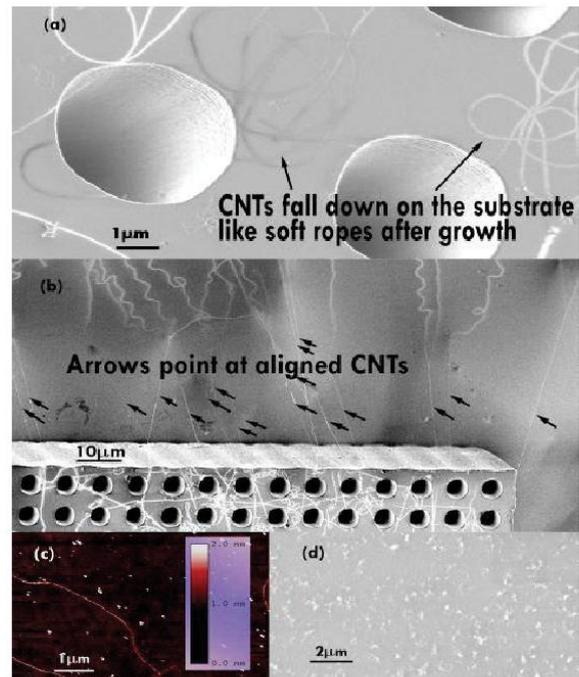


Figure 7: (a) CNTs grown by Micro-CVD. (b) Aligned growth. (c) AFM image. (d) CNTs by furnace growth.

gas mass transfer. Experimental results using a MEMS platform show the successful growth of good quality single-walled carbon nanotubes with approximately 100 μm in length and 1~2 nm in diameter. The control test using conventional furnace CVD system with the same setup was not able to produce high quality CNTs.

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