

# Atomic Layer Deposition-incorporated Catalyst Deposition for the Vertical Integration of Carbon Nanotubes

Sunghwan Jung<sup>†</sup>

**Abstract** – Carbon nanotubes (CNTs) are vertically grown inside high-aspect-ratio vertical pores of anodized aluminum oxide. A CNT catalyst layer is introduced by atomic layer deposition to the bottom of the pores, after which the CNTs are successfully grown from the layer using chemical vapor deposition. The CNTs formed a complete vertical conductive path. The conductivity of the CNT-vertical path is also measured and discussed. The present atomic layer deposition-incorporated catalyst deposition is predicted to enable the integration of CNTs with various challenging configurations, including high-aspect-ratio vertical channels or vertical interconnects.

**Keywords:** Atomic layer deposition, Carbon nanotubes, Catalyst, Vertical channel

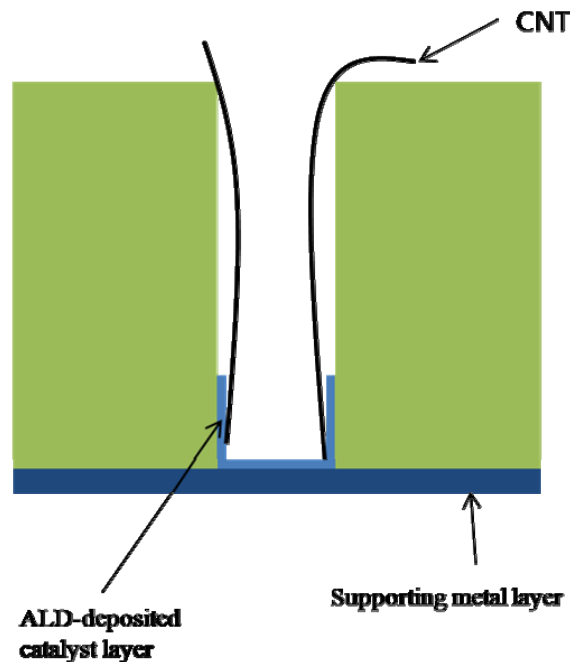
## 1. Introduction

The integration of carbon nanotubes (CNTs) into vertical channels has been extensively studied to achieve dense CNT arrangements required to properly exploit the outstanding properties of CNTs. Vertical integration typically involves vertical channels in an insulation layer, which guides the CNTs to grow vertically in the channels. The key to a successful vertical integration is to properly introduce the CNT catalyst layer at the bottom of the vertical channels. Physical vapor deposition and electro-deposition can be used for this deposition [1–3]. However, the layer thickness achieved by the traditional deposition techniques cannot be properly controlled inside the channels, thereby degrading the quality of the CNT synthesis. As an alternative approach resulting in better thickness control, a CNT catalyst layer can be buried underneath an insulation layer and exposed by physical etching which is to vertically channel the insulation layer [4–6]. In this approach, however, it is difficult to precisely operate in order to stop the physical etching on layers with thicknesses of only a few nanometers. To the best knowledge of the author, a reliable method must be designed to enable the deposition into the vertical channels of the nanometer thin layers with great control of thickness.

In this work, a novel concept incorporating atomic layer deposition (ALD) is proposed to address the challenge of achieving the deposition of the nanometer thin catalyst layer into the vertical channels. The ALD method is known to have great potential in producing conformal films with great control over the thickness at an atomic level within challenging configurations. In this concept, the CNT catalyst material is deposited by ALD into the vertical

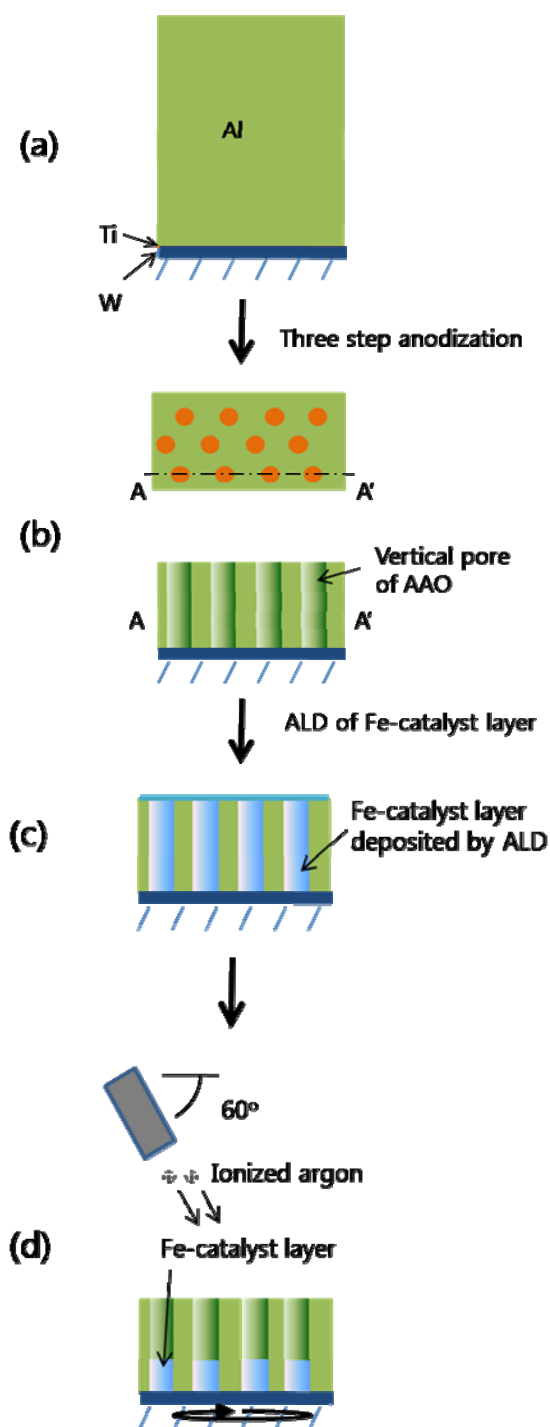
channels in order to produce a catalyst layer with well controlled thickness at the bottom of the channels. The schematic of this concept is presented in Fig. 1. Ion milling can be combined with this method in order to selectively remove the ALD deposited layer to the vertically defined regions where the CNTs will grow (Fig. 1).

In this work, an experiment was conducted to prove the concept. This involved the catalyst deposition and the CNT synthesis. In the experimental set-up, the pores of anodized aluminum oxide (AAO) were used for the vertical channel



**Fig. 1.** The conceptual configuration of the catalyst layer and CNTs integrated with vertical channels. The catalyst layer is deposited using ALD and vertically defined by ion milling

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**Fig. 2.** CNT template preparation: (a) Ti/W/Al layer; (b) aluminum anodization; (c) ALD deposition of Fe catalyst layer; (d) vertical definition of Fe-catalyst layer by ion milling. The template is revolved during the milling to equally mill the upper surface of the AAO

structures, in which the CNTs were to be synthesized and vertically integrated. Fe was chosen as the catalyst material for the CNT synthesis and deposited by ALD into the vertical pores of the AAO. Subsequently, a CNT synthesis

was conducted on the Fe layer. The CNTs synthesized from the layer were then inspected using scanning electron microscopy (SEM). Their quality was investigated using two-terminal I-V tests.

## 2. Experimental Details and Results

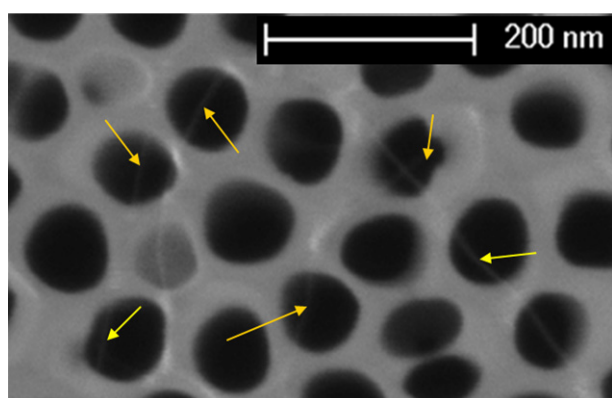
The AAO template was prepared as demonstrated in Fig. 2. First, a series of depositions of aluminum, tungsten and titanium with the thicknesses of 1.5, 20 and 5 nm, respectively, were undertaken, creating a multilayer stack on an Si wafer [Fig. 2(a)]. The aluminum layer was anodized in oxalic acid in order to create vertical nanopores [Fig. 2(b)]. Anodization was carried out using three steps to enhance the regularity of the pores in terms of their shape, size, and spacing. In the first step, the deposited aluminum layer was partially anodized with the application of a constant potential of 40 V; this anodization was then completely removed using chromic acid. The second step was a repetition of this process. In the final step, the remaining aluminum layer was fully anodized, and the vertical pores were produced. The vertical pores were then widened using phosphoric acid. In addition to the pore widening, the oxide barrier on the tungsten layer was removed, resulting in the exposure of the underlying tungsten layer. After the pore widening process, the resulting pores became ~80 nm wide and ~1000 nm high.

In order to minimize the thermal stress after the anodization, the template was pre-annealed at 820 °C before the catalyst material was introduced. It should be noted that, generally, AAO straight from the anodization significantly contracts in size and reverts to a stable crystalline phase at elevated temperatures. Therefore, it was found that with the present CNT synthesis set to 820 °C, the AAO as anodized but un-annealed became severely fractured after the CNT synthesis due to the thermal mismatch between the Fe layer and the AAO structure at the high temperature, whereas the present AAO structure was preserved when it was pre-annealed.

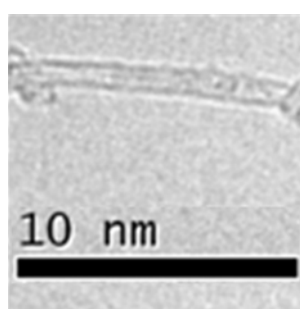
After the annealing process, Fe catalyst was deposited by ALD into the vertical pores [Fig. 2(c)].  $\text{Fe}(\text{Cp})_2$  was chosen as the precursor for the ALD. The ALD process was carried out based on a previous study [7] where the vertical pores of an AAO layer were filled with Fe oxide by ALD.  $\text{Fe}(\text{Cp})_2$  and oxygen were alternately supplied to an ALD reactor chamber, into which the AAO was placed in order to produce a Fe-oxide layer on the surface of the AAO template. The pulses of the  $\text{Fe}(\text{Cp})_2$  and oxygen were set to 20 seconds, which is assumed to be sufficient to allow the  $\text{Fe}(\text{Cp})_2$  and oxygen to fully diffuse and reach the bottom of the pores. The reactor chamber of ALD was set to a temperature of 450 °C where the ALD deposition was to take place. Between the pulses of the  $\text{Fe}(\text{Cp})_2$  and oxygen, argon was supplied to purge the preceding gas. This was done to prevent the direct engagement between the  $\text{Fe}(\text{Cp})_2$

and oxygen. The purge duration was set to 20 seconds; 10 runs of the  $\text{Fe}(\text{Cp})_2$ -argon-oxygen-argon cycle were done, which was assumed to produce  $\sim 2$  nm Fe-oxide; note that ALD growth rate was estimated to be 0.5 nm per cycle based on the observation that the pore width changed from 80 to 40 nm after 200 cycles were run.

After the ALD process, ion milling was used to vertically define the Fe-oxide layer and prevent any CNT synthesis from occurring in the upper region of the vertical pores [Fig. 2(d)]. The ion milling was conducted using an ion gun in the chamber of a metal evaporation system, which was set to the pressure of  $1 \times 10^{-5}$  Torr using an argon supply. The ion gun was angled to project an ionized Ar influx at  $60^\circ$  onto the substrate surface of the template in the chamber, as shown in Fig. 2(d). In addition, the template was spun by an electrical motor so as to ensure equal milling during the process. As a result of this ion milling, the upper portion of the Fe-oxide layer near the openings of the pores was removed in order to prevent CNT synthesis in this region.



**Fig. 3.** Vertical integration of CNTs. The SEM image of CNTs synthesized from the ALD-deposited catalyst layer emerging from the pores.

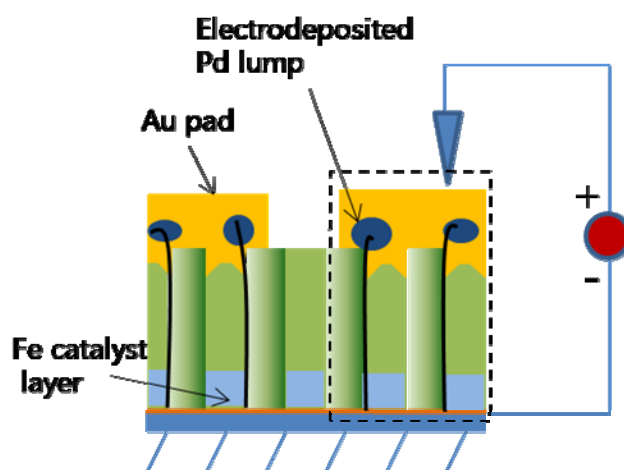


**Fig. 4.** The TEM image of the CNT grown from the ALD-deposited Fe layer showing the structure of a single-walled CNT.

After the ion milling, the CNT synthesis was conducted on the AAO template placed inside a CVD chamber. The temperature of the chamber was gradually increased to  $820^\circ\text{C}$ . When the temperature reached  $600^\circ\text{C}$ ,  $\text{H}_2$  was supplied to

reduce the Fe-oxide layer and prepare it for the activation when the CNT synthesis started. At  $820^\circ\text{C}$  and  $10^5$  Pa, the CNT synthesis occurred while 20 ccm of  $\text{C}_2\text{H}_4$ , 1000 ccm of  $\text{CH}_4$ , and 500 ccm of  $\text{H}_2$  were being supplied; the synthesis time was set to 3 minutes. After the synthesis, the AAO template was inspected using SEM. CNTs emerged from the vertical pores (Fig. 3). The observed CNTs appeared to be between 1–2 nm in diameter, which corresponded to single- or double-walled CNTs. Moreover, the TEM image of the CNT grown from the ALD-deposited Fe layer demonstrated the structure of a single-walled CNT and its diameter of  $\sim 1$  nm (Fig. 4).

A complete vertical conductive path of the CNTs was established using a Pd electrodeposition. In order to establish the complete vertical conductive path, the CNTs must be sufficiently grown to reach the top surface and also be in electrical contact with the underlying tungsten layer. Although some of the CNTs may have contacted the tungsten layer as they grew from the bottom of the pores, Pd electrodeposition was additionally conducted to ensure contact of the CNTs with the tungsten layer. Electrodeposition was conducted in a solution of  $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{NH}_4\text{Cl}$  with a current density of  $50 \text{ mA/cm}^2$  applied for 10 ms. After the electrodeposition, 5–10 nm wide Pd lumps were observed on the parts of CNTs extending out to the top surface of AAO, indicating that the vertical conductive path was established, thus allowing Pd deposition on the top AAO surface. Whereas a large quantity of Pd lumps appeared at the top surface, Pd filling inside the pores was scarcely present (as schematically shown in Fig. 5). The uneven distribution of Pd is due to the fact that, once the Pd deposition front reaches the bottom of a CNT in a pore, the CNT is then connected electrically with the bottom



**Fig. 5.** Set-up of I-V measurement for the CNT template. After electrodeposition, electrodeposited Pd lumps at the CNTs are observed at the top surface. Patterned Au pads are introduced using angled metal deposition to allow probe contact. Each I-V measurement engages the group of the CNTs underneath the pad (outlined by the dash line).

metal layer thereby making Pd deposit at the opposite end of the CNT, which is generally located at the top surface of the AAO structure.

### 3. IV Measurements and Discussion

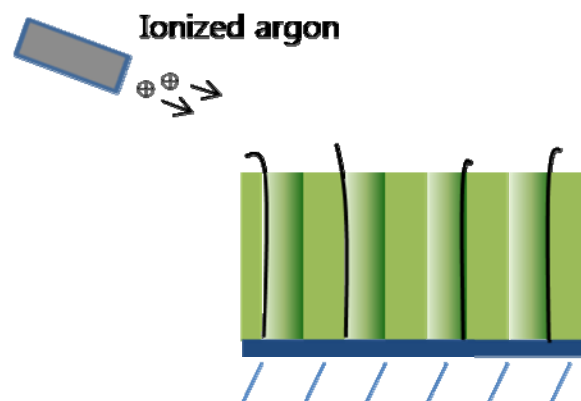
Two I-V measurements were performed to characterize the CNT vertical conductive path (Fig. 5). For the I-V measurements, Au pads were patterned with the angled metal deposition on the top surface of the AAO in order to allow probe contact. For the Au patterning, 5 nm of Ti was pre-deposited to promote adhesion on the AAO surface, after which 250 nm of Au was deposited. During the metal deposition of Ti and Au, (the normal direction to) the template was angled at  $60^\circ$  from the horizontal and was spun. The tilting angle of  $60^\circ$  was sufficient to ensure that no additional electrical path was introduced by the sidewall deposition. With the tilting angle of  $60^\circ$  and the pore diameter of 80 nm, the estimated sidewall deposition inside the pores was only 100–200 nm deep from the top surface of AAO, which was short of creating a full path to vertically cross the AAO structure whose thickness is 1000 nm. The pressure inside the reactor was set to  $10^{-6}$  Torr to allow long mean free path. After the Au deposition, the pores where Au was deposited were found completely close. Each pad was  $3 \times 3 \mu\text{m}$ , capping  $\sim 900$  pores.

Once the top pads were patterned, the suspended CNT “bridges” between the pads were removed by  $\text{O}_2$  plasma at 300 mTorr and 100 Watts in order to electrically isolate each pad. The pores underneath the pads were sealed, thereby safely protecting the CNTs inside the pores from the plasma. In the two-terminal I-V measurements, a probe was in contact with the top pad, and the other probe was connected to the tungsten layer (Fig. 5). The electrical resistance of each pad capping 900 pores was  $\sim 50 \Omega$  and thus, the resulting resistance per pore was  $\sim 45 \text{ k}\Omega$  ( $= 50 \times 900$  pores). Since the number of the pores successfully integrated with CNTs per pad is unknown, it cannot be directly assumed that the resulting resistance per pore truly represents the conductance of each individual CNT. Thus, in this paper, with the obtained results, details in the IV measurement set-up are presented below, which limit the conductance of the vertical path listed as follows:

- (I) The contact resistance of CNTs with the metals may not be ideal.
- (II) The “true” length of each CNT engaged for the vertical connectivity may be more than the height of the pores ( $\sim 1 \mu\text{m}$ ). As shown in Fig. 3, CNTs emerged out of the pores and extended to great length on the top surface. Since the length can be as much as  $5 \mu\text{m}$  considering the given size of the pad ( $3 \times 3 \mu\text{m}$ ), the true length of the CNTs engaged for the vertical path of the present configuration is likely to be greater than the ballistic length [8].

However, the extending parts of CNTs on the top surface of AAO can be removed using the angled ion milling technique used to vertically define the catalyst layer in the present study. Fig. 6 shows a proposed set-up of an ion milling gun to remove the extending parts of the CNTs, which are unprotected from the ionized gas.

In addition, a reference template was used in order to check the existence of other electrical paths than the CNT-integrated paths. The reference template was fabricated in the same manner of fabricating the CNT-integrated template, except that the  $\text{O}_2$  plasma treatment was conducted before the gold pads used for probe contact were patterned. Therefore, all the CNT-integrated paths were removed by the  $\text{O}_2$  plasma in the reference template before the gold pads were patterned, allowing the exclusive inspection of the existence of other electrical paths; the architecture of the reference template is same as that of the CNT template shown in Fig. 5, except that no CNTs are provided in the pores. Two-terminal I-V measurements were conducted on the reference template and no current was observed, confirming that the vertically-integrated CNTs comprised unique vertical current paths.



**Fig. 6.** Proposed ion milling set-up to trim the top parts of CNTs. The exposed parts of CNTs from AAO can be removed by angled ion milling.

### 4. Conclusion

A novel concept incorporating the ALD method was proposed and experimentally proven to properly introduce a catalyst at the bottom of vertical channels. The Fe catalyst was introduced to the bottom of the channel using ALD, and CNTs were successfully grown from the layer and properly integrated to form complete vertical conductive paths inside the vertical channels. No conductivity was observed in association with the Fe catalyst layer, proving that the CNTs comprised the unique vertical path.

Although the present work explicitly addresses vertical channels, the ALD-incorporated deposition is predicted to be an effective method in meeting the various challenging

configurations, in which the properties of CNTs can be efficiently exploited.

In future works, the present deposition technique involving other CNT catalyst materials, such as Co and Ni, can be explored.

### Acknowledgment

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