

A Generic Process of Growing Aligned Carbon Nanotube Arrays on Metals and Metal Alloys

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Abstract

Aligned carbon nanotube (CNT) arrays are integral toward the development of several applications such as field emission, interconnects in silicon technology, chemical and biological sensing. Even though the synthesis of CNTs has been described extensively in literature, there has not been significant success in growing uniform, well-aligned CNT arrays on pure metal surfaces other than metals that catalyze CNT growth themselves. In this letter, we describe a method of growing aligned CNT arrays on a variety of pure metals, metal alloys, and conductive ceramics using a bimetallic iron/alumina composite catalyst at low temperatures (550-700 °C). We believe the addition of alumina to the iron catalyst significantly reduces catalyst-metal underlayer interactions that have traditionally proven to be a barrier for growth of CNTs on metals. The alumina also minimizes surface diffusion of iron and allows the formation of a high density of uniformly dispersed catalyst nanoparticles to act as nucleation sites for well-aligned CNT arrays. Despite the presence of non-conducting alumina from the catalyst, the contact resistance between the CNTs and the metal underlayer was observed to be quite low, emphasizing the usefulness of this approach to practical applications. Our process was successful in growing aligned CNTs even on commercial steel plates and may be applicable for substrates of any shape or size.

1. Introduction

Since their discovery in 1991, research work on CNTs has increased exponentially over the years owing to their splendid physical, structural and electrical properties, which may be exploited for an extensive range of applications such as field emission, chemical gas sensing, nanoelectronics and bio-sensing [1-8]. There are distinct advantages of growing aligned CNT arrays on conductive substrate underlayers such as pure metals, metal alloys and ceramics, especially for field emission display screens, nanoelectrodes for chemical and electrochemical sensors and as interconnects in silicon technology [2-9]. Among the several CNT growth synthesis techniques, chemical vapor deposition (CVD) is the most versatile since the operating temperatures are considerably lower than arc discharge processes, making it amenable for controlled growth of CNTs in the form of well-aligned arrays over a variety of substrates.

Previously, growth of CNTs has been largely confined to non-conductive substrates owing to significant catalyst-metal interactions restricting availability of catalytic particles for CNT nucleation. Several groups have demonstrated the growth of aligned CNT arrays on silicon (Si) wafers either through sputtering or micro-contact printing of catalyst layers followed by CVD [10-11]. Ng et al. investigated the effects of several catalysts and underlayers deposited on Si wafers and observed that iron/nickel (Fe/Ni) and Ni catalysts on aluminum (Al) underlayers gave rise to aligned, oriented CNTs [12]. Wang and co-workers reported on the growth of aligned CNTs on metal sheets of Ni, titanium (Ti), tantalum (Ta) and Al-coated Si through pyrolysis of iron phthalocyanine at 950 °C [13]. However, this process was unsuccessful in growing CNTs on gold (Au), copper (Cu) or nichrome (Ni-Cr). Very recently, Talapatra and co-workers reported on the direct growth of aligned CNT arrays on a metal alloy, Inconel through a vapor-phase floating-catalyst CVD process but this technique is not suitable for direct growth of CNT arrays on metals such as Si or Au [14].

In this letter, we present a generic CVD process for the direct growth of well-aligned CNT arrays at low growth temperatures (550-700 °C) using a bimetallic iron/alumina (Fe/Al₂O₃) composite catalyst on a range of conductive substrates such as pure metals, metal alloys and ceramics.

2. Experimental Section

Several commonly used metals such as highly doped Si, Au, Ag, Cu, Al, tungsten (W), platinum (Pt), as well as metal alloys such as titanium nitride (TiN), nichrome (Ni-Cr) and steel were considered as substrates for the growth of aligned CNT arrays in our work. The metal films were either sputtered or evaporated (typically 100 nm thick) onto silicon dioxide (SiO₂) wafers except for W (TEM grids) and steel (hot-rolled steel plate). All substrates were ultrasonically cleaned in ethanol before CNT growth. The chemicals used for preparing catalyst solutions were acquired from a commercial vendor (Sigma-Aldrich).

A 10 mmol/L aqueous solution containing equal proportions of iron nitrate [Fe(NO₃)₃·9H₂O, ACS reagent, 98+%] and aluminum nitrate [Al(NO₃)₃·9H₂O, ACS reagent, 98+%] was prepared and employed as the catalyst solution for CNT growth. The solution was then applied onto the substrates using a micropipette and allowed to dry at room temperature. The substrates were then loaded onto an alumina boat and placed within a gas flow reactor consisting of a 1" quartz glass tube inside a temperature-controlled tube furnace. Under a steady gas flow rate of 200 sccm (standard cubic centimeters per minute) argon (Ar) and 45 sccm hydrogen (H₂), the furnace was heated to 625 °C. The substrates were typically annealed in this Ar-H₂ mixture for 10 min before the introduction of 5 sccm acetylene (C₂H₂) to begin CNT growth. CNTs were grown for 5 min, then the carbon precursor was shut off and the substrates were cooled down to room temperature in Ar. The morphology of the CNTs was examined using a Hitachi S-4000[#] scanning electron microscope (SEM) and a Jeol 2100F[#] transmission electron microscope (TEM).

3. Results and discussion

With the exception of Pt, the rest of the metal substrates considered in this work did not hinder the nucleation and growth of CNTs. The results of CNT growth on various substrates have been listed in table 1. SEM images of substrates of Si, Au, Ag, Cu, Al, Pt and W following CNT growth are shown in

[#] The identification of any commercial product or trade name does not imply endorsement or recommendation by the National Institute of Standards and Technology.

figure 1. On Si, Au, Ag, Al and W, the CNT arrays were uniformly aligned along the substrate normal. A closer inspection of the arrays indicated that the CNTs were approximately 10-20 nm in diameter and few tens of microns in length. Even though individual CNTs seemed to be bent, the overall CNT array structure exhibited excellent alignment, vertical to the substrate. In the case of Pt, the metal surface appeared to have swelled and restructured into platelets. On the other hand, CNTs on Cu were highly non-uniform both with respect to diameter (10-75 nm) and lacked any orientation ('spaghetti'-like).

Remarkably, even on metal alloys and conductive ceramics such as TiN, NiCr and steel, our growth process resulted in well-aligned CNT arrays wherever catalyst was dispersed (figure 2). Upon further investigation, we found that even in areas where the Fe/Al₂O₃ catalyst was not applied, CNTs as well as amorphous carbons and other carbon nanostructures appeared to have grown on the NiCr and steel substrates. The CNT arrays grown on steel were however very weakly adhered to the substrate and peeled off from the surface readily.

High-resolution TEM (HR-TEM) images of CNTs removed from an array grown on Au are shown in figure 3. An imaged 17 nm multi-walled CNT had ~ 16 concentric graphene sheets wrapped around a hollow inner core of ~ 5 nm diameter. An oblong catalyst particle could be found on a few of the CNTs suspended on the grid, indicative of tip-growth. We observed that CNTs grown on several other substrates also exhibited similar characteristics from our TEM analysis.

We believe that addition of Al₂O₃ plays a crucial role in reducing Fe-substrate interactions (acting like a diffusion barrier), resulting in the formation of uniform Fe catalyst nanoparticles for CNT nucleation into well-aligned arrays. Both Fe and Al nitrates undergo thermal decomposition into their respective oxides (Fe₂O₃ and Al₂O₃) above 250 °C [15]. Since the nitrates are well mixed at room temperature, well-distributed Fe₂O₃ particles in an Al₂O₃ matrix will be initially formed on the substrate. When this film is annealed in Ar-H₂ at 625 °C, the Fe₂O₃ is readily reduced to Fe while the Al₂O₃ remains quite stable in these conditions. During the CNT growth process, the carbon precursor C₂H₂ readily decomposes on the well-dispersed catalytic Fe particles confined within the non-catalytic Al₂O₃ matrix, resulting in the

growth of well-aligned CNT arrays. The alignment of the CNTs may be explained based on the “crowding effect” and van der Waal interactions, with each CNT being supported by a neighboring CNT [16].

The above-mentioned discussion is applicable to describe the growth of CNT arrays on most metal substrates. Pt however, is well known for its catalytic properties in the presence of H_2 , which explains its failure to allow the nucleation of CNTs [17]. Even though the Pt film is covered entirely by the Fe- Al_2O_3 composite, the H_2 molecules tend to easily diffuse through the composite and interact with the Pt underneath, causing swelling and rendering the film unsuitable for CNT growth. We have observed that without the use of H_2 in our process, amorphous carbon tends to coat the catalyst surface following CVD of C_2H_2 . In the case of Cu, we believe that the tendency of Cu to alloy with a lot of materials including both Al_2O_3 and Fe tends to hinder uniform catalyst particle nucleation resulting in more randomly oriented non-uniform CNTs with a wide size distribution [18]. The vertically aligned CNT arrays grown on the rest of the metal substrates (Si, Au, Ag, W, Al) had very similar morphologies. The CNTs on every individual array were of uniform length with growth rates of $\sim 2-4 \mu\text{m}/\text{min}$. Unlike the previous attempts to grow CNT arrays directly on metals [10-14], we do not expect the underlying metal layer to exert any significant influence on the CNT morphology or growth behavior as long as the metal does not alloy with Al_2O_3 .

The generic nature of our process was reflected by the successful growth of aligned CNT arrays even on commonly employed metal alloys and ceramics such as TiN, steel and nichrome. We also observed that steel and nichrome also catalyze a variety of carbon nanostructures including randomly oriented CNTs, fibers, and particles in areas not covered with our Fe/ Al_2O_3 composite catalyst, due to the intrinsic presence of catalytic metals Fe and Ni on their surfaces. The growth results on all substrates were observed to be reproducible.

One of the key requirements for the electrical and electronic applications of CNTs such as interconnects, field emitters etc. is the need for a low metal-CNT contact resistance [19-20]. We measured the 2-pt resistance between the underlying metal and the top of the CNT array using a probe station

(contact tip size $\sim 25 \mu\text{m}$) and observed that the overall resistance inclusive of the contact resistance was under 400Ω for several samples (Au, Si, Ag, Al). We further investigated the exact contact resistance for CNTs on Au using a combination of 2-pt and 4-pt resistance measurements and calculated it to be $\sim 135 \Omega$. A more comprehensive study on the effect of varying process parameters on the properties of the CNT/metal interface prepared by this method on different substrates is currently underway and will be reported in future.

4. Conclusions

In summary, a simple, effective process for the growth of highly aligned CNT networks on a variety of bulk metal substrates as well as metal alloys has been developed. The growth process is based on the use of a bimetallic Fe/Al₂O₃ catalyst where the addition of Al₂O₃ is crucial in protecting Fe from reacting with the substrate underneath, and in dispersing them uniformly over the surface, resulting in the growth of well-aligned CNT arrays on most metal substrates. The contact resistance between the metals and CNT arrays was observed to be quite low in spite of the presence of Al₂O₃ facilitating their utility in electrical and electronic applications. Since the catalyst is dispersed from the solution, this approach is suitable for growth of uniform CNT arrays on substrates of all shapes and sizes.

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Tables and Figures

Table 1. CNT growth characteristics on various metals and metal alloys

Substrate	CNT characteristics
Si	Uniform, well aligned
Au	Uniform, well aligned
Ag	Uniform, well aligned
Cu	Non-uniform, random growth
Al	Uniform, well aligned
Pt	No CNT growth
W	Uniform, well aligned
TiN	Uniform, well aligned
NiCr	Uniform, well aligned
Steel	Uniform, aligned, not well adhered

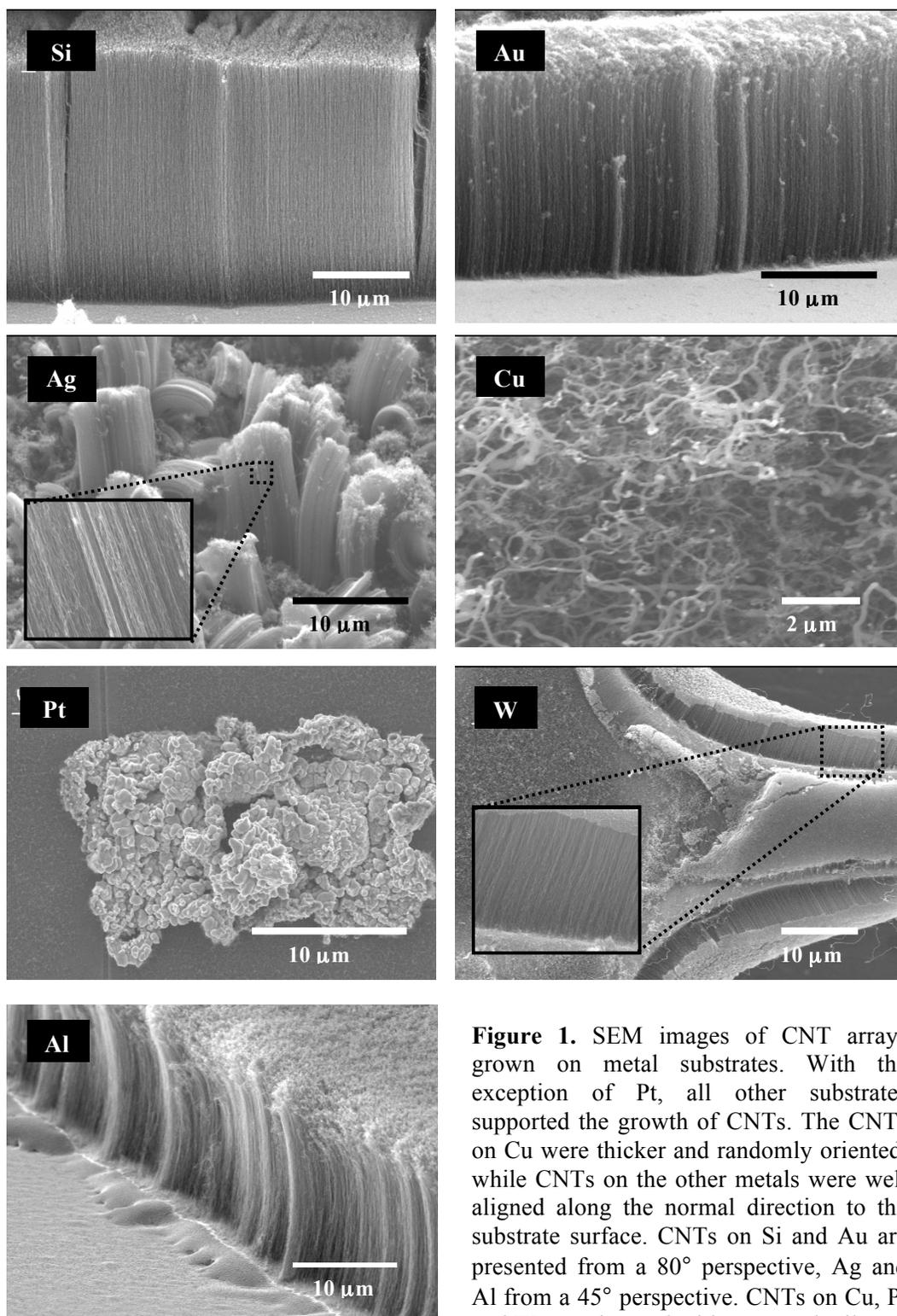


Figure 1. SEM images of CNT arrays grown on metal substrates. With the exception of Pt, all other substrates supported the growth of CNTs. The CNTs on Cu were thicker and randomly oriented, while CNTs on the other metals were well aligned along the normal direction to the substrate surface. CNTs on Si and Au are presented from a 80° perspective, Ag and Al from a 45° perspective. CNTs on Cu, Pt and W were imaged without sample tilt.

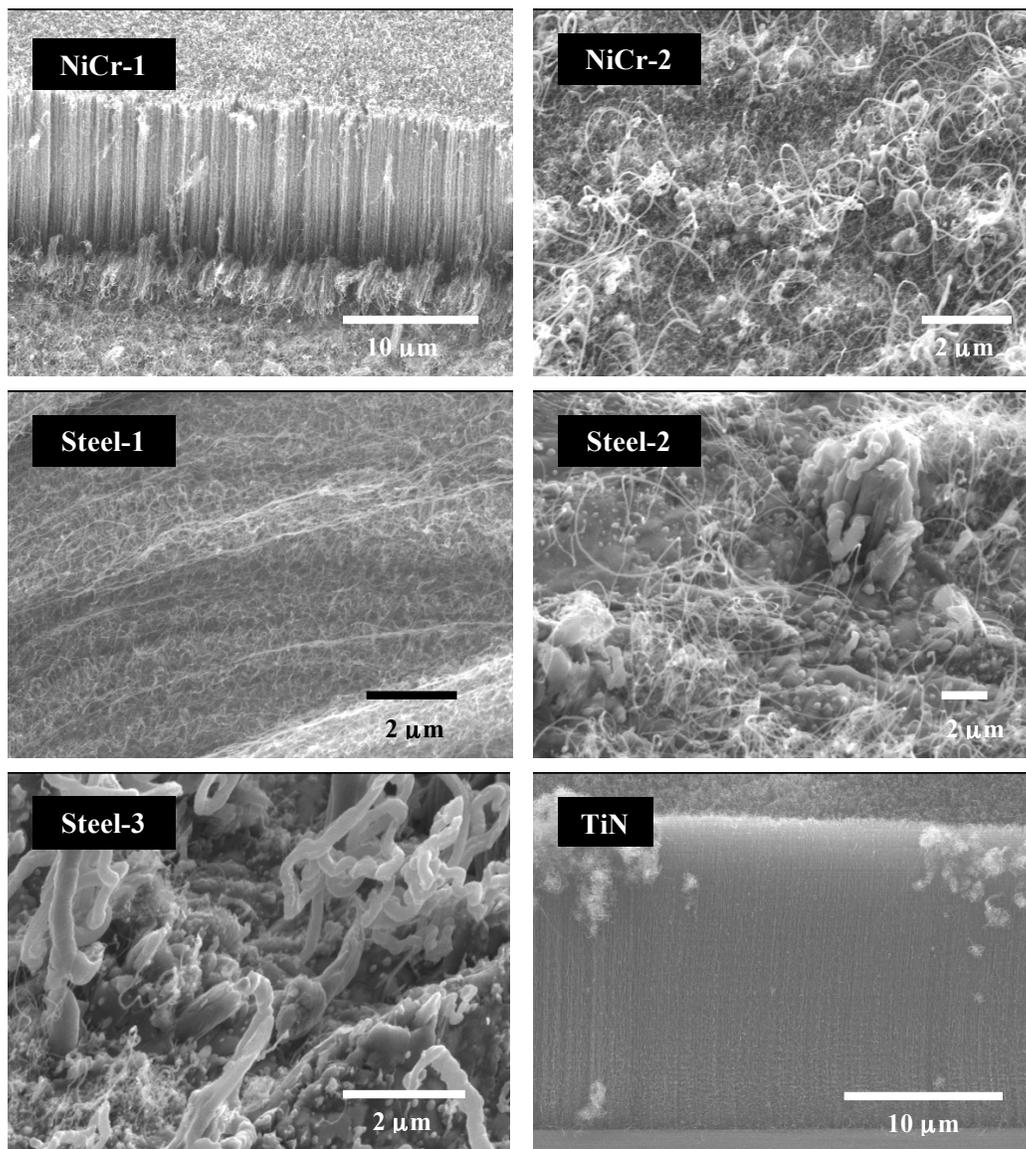


Figure 2. SEM images of CNTs grown on metal alloys nichrome (NiCr) and steel, and a conductive ceramic (TiN). The CNTs were vertically aligned wherever catalyst was deposited (NiCr-1, Steel 1, TiN). NiCr-2, Steel-2 and Steel-3 represent CNTs, fibers and amorphous deposits observed to grow in areas of NiCr and steel where the catalyst was not applied, due to the intrinsic presence of catalytic metals (Ni, Fe) on their surfaces. NiCr-1 and TiN are presented from an 80° perspective. NiCr-2, Steel-2 and Steel-3 are presented from a 45° perspective. Steel-1 represents a portion of the CNT array that peeled off from the substrate.

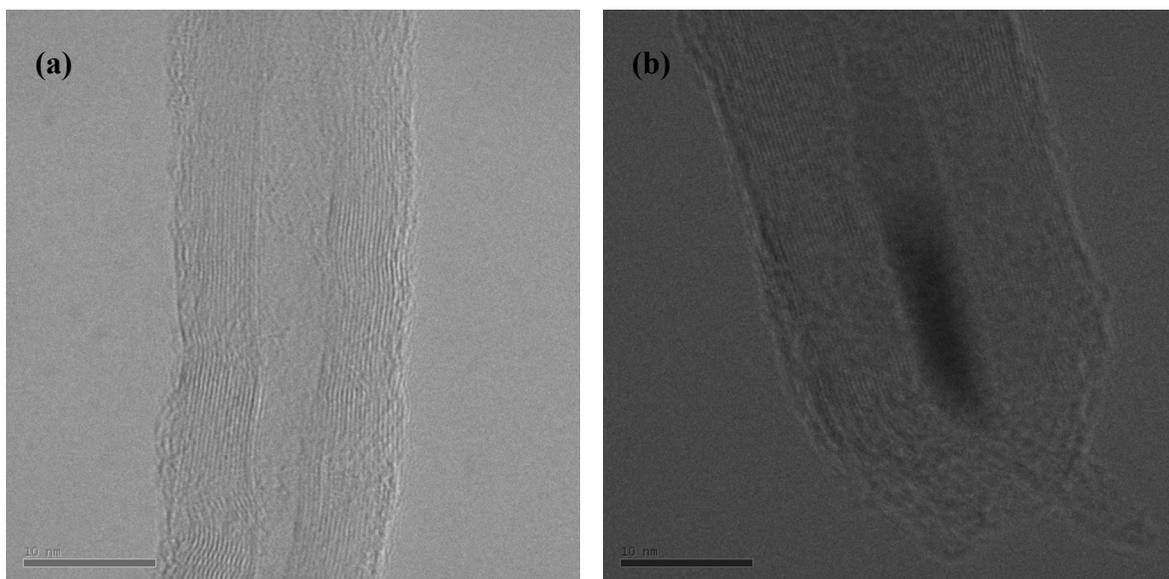


Figure 3. High-resolution TEM images of a single multi-walled CNT (grown on Au) clearly represent highly crystalline graphene sheets overlapping a hollow core. An oblong catalyst particle could be found on the tips of a few CNTs. The scale bars represent 10 nm. TEM analysis of CNTs grown on other substrates exhibited similar characteristics.

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