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Sandwich growth of carbon nanotubes

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Abstract

Direct formation of structures that comprise freestanding CNTs connected to two surfaces was, thus far, not possible. In this article we report a novel approach to grow structured, highly oriented carbon nanotubes that are vertically aligned between a substrate and a massive cover. Growth is feasible at pre-determined, e.g., lithographically defined sites on metallic, semiconducting, or glass substrates. A novel, sandwiched catalyst structure and microwave plasma chemical vapor deposition (CVD) led to the formation of freestanding, small diameter carbon nanotubes. Our new technology offers a simple and scalable pathway to create 3D structured nanotube-based two-terminal electronic devices, device arrays, sensors and corresponding electronic circuits.

1. Introduction

Over the past decade, growth of carbon nanotubes (CNTs) was achieved by a variety of methods [1–6] for a variety of interesting electronic applications, e.g. transistors [7,8], field emission devices [9,10], gas sensors [11,12], or biosensors [13,14]. Considerable efforts relate to controlled synthesis as well as patterned growth of CNTs from the vapor phase [15–19]. However, direct formation of structures that comprise freestanding CNTs connected to two electrical terminals was thus far not achieved. In this paper we report a novel approach of growing structured, highly oriented, vertically aligned carbon nanotubes that are connected to two surfaces, e.g., device terminals. Growth is feasible at pre-determined, e.g., lithographically defined sites on metallic, semiconducting, or glass substrates. A novel, sandwiched catalyst structure and microwave plasma chemical vapor deposition (CVD) is utilized to form small diameter multi-walled and likely even single-walled carbon nanotubes. The new technology offers a simple and scalable pathway to create 3D structured nanotube-based two-terminal electronic devices, device arrays and corresponding electronic circuits.

Growth of carbon nanotubes is feasible by a number of thermal and plasma-enhanced chemical vapour deposition (CVD) methods [1–6]. Similar to the growth of diamond from the vapour phase [19], 2.45 GHz microwave plasma chemical vapour deposition (MWPCVD) from a carbon carrier diluted by hydrogen gas is also capable of creating this allotropic form of carbon. MWPCVD-grown CNTs are generated free from substantial amorphous carbon contaminations. They can be grown structured, highly oriented and vertically aligned at predetermined sites, defined by the presence and structure of metal catalysts that foster CNT growth (e.g., Fe, Ni, or Co) [5,6,20,21]. Fig. 1a sketches the common CVD growth approach: a metallic thin film catalyst on a substrate is converted into catalyst nano particles at elevated temperatures in a reducing atmosphere [3]. With a carbon carrier present in the CVD gas phase, the catalyst initiates CNT growth with its particle size defining the diameter and structure (multi-walled, single-walled) of the resulting nanotubes [22,23]. On one end, the tubes are connected to the substrate surface. Contacting the second end of the tube in order to simply measure resistance or to form two-terminal electronic devices and sensor structures requires additional complex technology steps such as silica deposition, polishing, metallization. If bare CNT surfaces are required, subsequent etching and cleaning steps are required [15].

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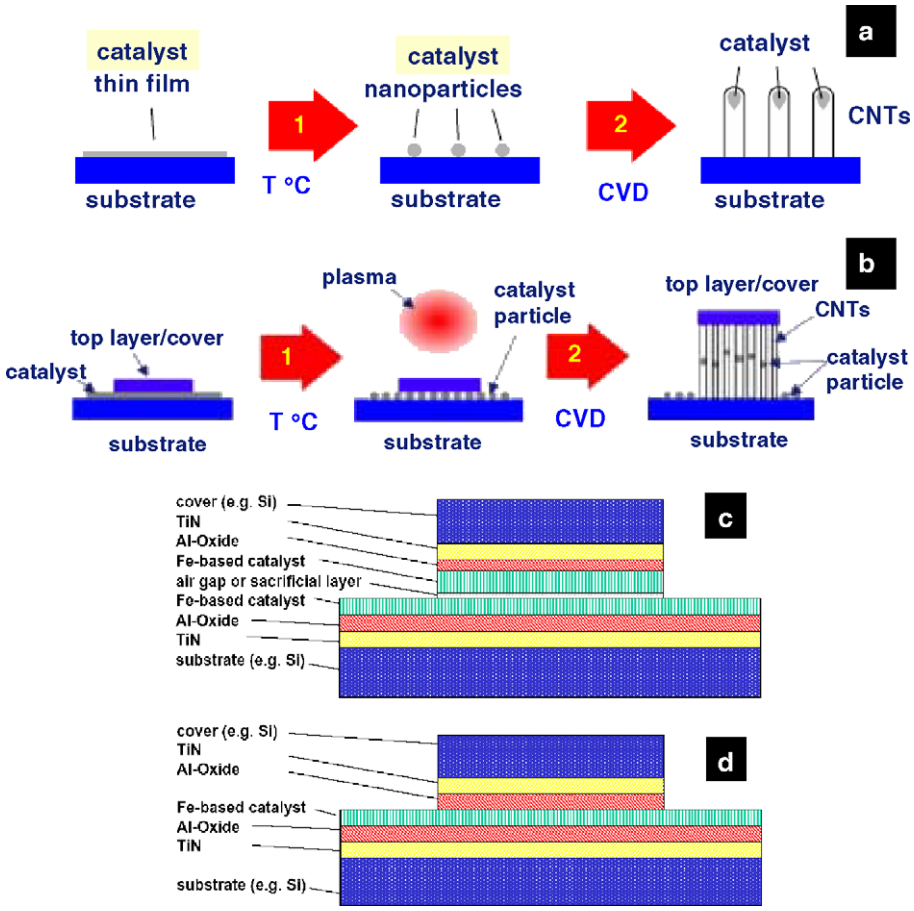

Fig. 1. Conventional (a) vs. sandwich (b) growth of highly oriented carbon nanotubes by microwave plasma CVD. Schematic of sandwiched catalyst stack structures with (c) and without (d) sacrificial layer/air gap.

The novel sandwich growth technology discussed here for the first time offers a greatly simplified approach to arrive at such structures. Moreover, it opens pathways to generate small and large footprint devices, device arrays and even 3-D device structures. The technology is simple to use and highly reproducible. Moreover, sandwich-grown CNTs exhibit substantially reduced tube diameters, thus putting microwave plasma grown single-walled CNTs within reach.

2. Sandwich structure and CNT growth

Fig. 1b outlines the novel growth technology and compares it to the conventional approach (Fig. 1a). The sandwich structure comprises a substrate, e.g. <100> silicon coated with a sputter-deposited titanium nitride (TiN) diffusion barrier layer to prevent reaction of the catalyst with the underlying substrate. TiN is followed by a thin (2–5 nm) aluminium oxide layer to minimize migration and aggregation of catalyst nano particles that form upon heating and exposure of the sandwich to a 2.45 GHz microwave plasma. Fig. 1c and d detail two options to create a sandwich: a 2 nm layer of thermally evaporated iron completes the bottom half of the stack. The same sequence of layers is repeated to create the top half of the sandwich with either an air gap or a sacrificial layer separating the two sections (Fig. 1c). Alternatively the catalyst can be truly encapsulated between top and bottom (Fig. 1d). Carbon access to the catalyst is only feasible from the sides of the stack structure. Fig. 1c and d also illustrate that catalyst is not only present in the sandwiched part of the structure but also across the entire plasma-exposed substrate surface.

A 2.45 GHz ASTeX microwave chemical vapor deposition (CVD) system [19] is utilized to grow CNTs. Microwave power levels of 1 kW, reactor pressures of 25 mbar and a CVD gas phase composed of 180 sccm of hydrogen and 20 sccm of methane gas are typical growth conditions. Most of our experiments were performed using the stack structures shown in Fig. 1c, although first experiments indicate that industrially more relevant use of the structure shown in Fig. 1d is indeed feasible. Preheating to the deposition temperature of approx. 600 °C is achieve by a radiofrequency-heater with the ignited hydrogen plasma as an additional energy source. After keeping the sample at a constant temperature of 600 °C for 5 min, methane is injected into the hydrogen plasma