PATTERNED GROWTH OF SINGLE-WALLED CARBON NANOTUBES ON SILICON WAFER FOR ELECTRONIC DEVICES BY CHEMICAL VAPOR DEPOSITION PROCESS

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Abstract

The ability to controllably obtain ordered carbon nanotube architectures is important for fundamental characterizations and potential applications of electrical devices. Controlling the synthesis process applied chemical vapor deposition (CVD) has been an effective technique to order single-walled nanotubes (SWNTs) on patterned catalyst. In this paper, single-walled carbon nanotubes are synthesized by chemical vapor deposition of methane at positioned locations on a silicon substrate. This synthetic approach has allowed individual SWNT to be grown from appointed surface sites by catalyst patterning and has led to interconnecting SWNT electrical devices. The combined synthesis and microfabrication technique presented here enable the developing of many ohmically contacted nanotube devices that can be controlled the size . Base on TEM results, SWNTs are formed via an open-ended, base-growth mechanism (VLS mechanism).

Keywords: Electro Device, Interconnecting, Patterned Catalyst, Single-Walled Carbon Nanotubes

Introduction

The unique properties of carbon nanotubes offer extreme potential for various applications. One of the most promising applications of nanotubes is their use in nano-electronics devices such as a field effect transistor, nanotube interconnects and nanosensors [1-8]. The application of single walled carbon nanotubes in electronic devices system requires the controlled placement of nanotubes. Hence, developing controlled-synthesis methods to obtain well-ordered carbon nanotubes is important and a viable route to nanotubes based devices. Indeed, there are effective ways to control the growth of carbon nanotubes. Dai et al. [9] showed that self-directed growth of suspended nanotube networks on silicon tower tops using a liquid-phase catalyst precursor by chemical vapor deposition (CVD). Concerning this issue, Homma et al. [10] also demonstrated the fabrication of suspended carbon nanotube networks on 100 nm scale silicon pillar structures by simply depositing a catalyst film on the silicon substrate. However, additional efforts to build highly dense and organized nanotube networks connecting all designed locations even on a large scale are required for developing actual application of such self-assembled single-walled carbon nanotube networks.

In order to determine the growth sites of the SWNTs on the substrate, a resist pattern is defined by e-beam lithography process. The liquid catalyst material is brought onto the surface and calcinated, and then excess catalyst is removed in the lift-off step. In this paper, we present a systematic study to obtain high-yield growth of single-walled carbon nanotubes networks among patterned catalyst structures.

Experimental

Our research begins with the fabrication of marker, and pattern catalyst. A schematic of the process flow was shown in fig. 1 and fig. 2. The nanotubes were grown by a thermal CVD of methane at atmospheric pressure.

Materials

Silicon (100) wafer with surface oxide layer of thickness 1 μm was used as the substrate. All materials used in experiments are research grade materials purchased from different suppliers. $Fe(NO_3)_3.9H_2O$, and MoO_2(acetylacetone)$_2$ were purchased from Sigma Aldrich chemicals; Oxide C alumina from Degussa Inc; and high-purity methane and hydrogen from Air product Co..

Catalyst Preparation

Mixture of $Fe(NO_3)_3.9H_2O$, MoO_2(acetylacetone)$_2$, and 30 mg of alumina nanoparticles catalyst were prepared by impregnation in methanol. 40 mg of $Fe(NO_3)_3.9H_2O$, 3 mg of MoO_2(acetylacetone)$_2$, and 30 mg of Alumina nanoparticles are mixed in 30 ml of methanol and sonicated for ~ 1/2 hr.

Fabrication of Markers

In all experiments the thickness of the thermally grown oxide is typically ~*300* nm, and isolates the devices from the back gate. A set of markers is necessary for later locating the position of the nanotubes and the fabrication of the electrodes. These also include a set of electron beam lithography alignment markers (e-beam markers) and atomic force microscopy (AFM) markers. The fabrication of markers was depicted in fig. 1.

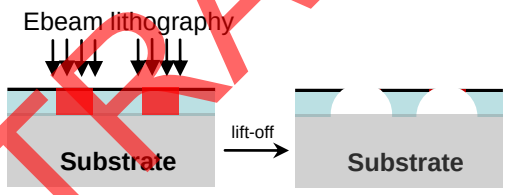

Figure 1. Fabrication of markers

Fabrication of Pattern Catalyst and Growth of Carbon Nanotubes

Substrates with markers were used as a substrate for this step.

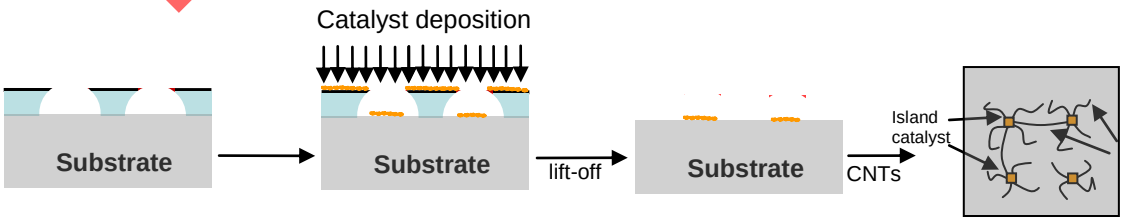

Figure 2. Fabrication of pattern catalyst and growth of CNTs

The obtained liquid catalyst is deposited onto the substrate (the size of substrate 5x5 mm) openings in the PMMA resist (patterned on specific identified locations by e-beam lithography) and blown dry. After lift-off in acetone, the substrate with patterned catalyst is placed in a 3-inch quartz tube furnace and the CVD is undertaken at 900°C with 250 sccm

H_2, 1000 sccm CH_4 for 10 mins. Argon is flown during heating up and cooling down. Methane and hydrogen flows are optimized to obtain long and clean single walled carbon nanotubes with very slightly amorphous carbon deposition.

Characterizations

Markers samples were fully characterized using SEM. The patterned catalyst and properties of SWNTs in methane CVD process was determined systematic by SEM, TEM, AFM and Raman spectroscopy. Using TEM grids as substrates for the growth of carbon nanotubes is considered a simple approach. The TEM grids are thin metal foils with punched holes. The grids have a diameter of 3.05 mm and a thickness of 12 to 15 μm. The melting point of the grids' metals is higher than 1000°C so that it is able to withstand high temperature in the growth process.

Results and Discussion

Fabrication of Pattern Catalyst Result

Our samples were characterized with GEREMI scanning electron microscope (SEM).

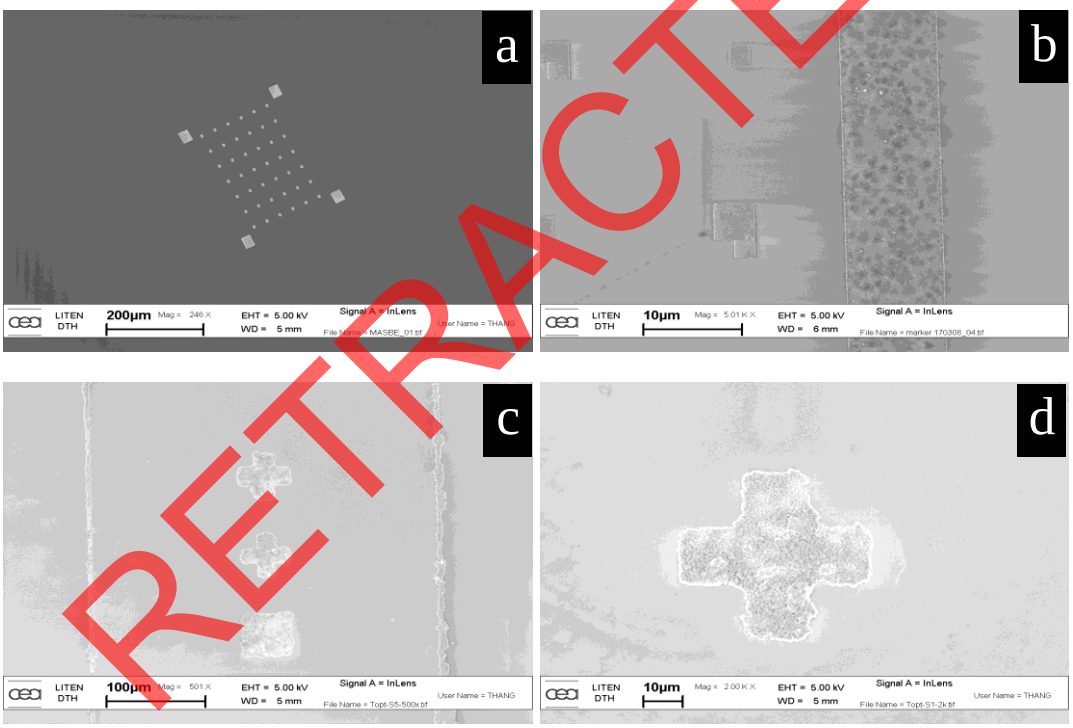

Figure 3. SEM images of markers (a) and patterned catalyst (b, c, d)

Fig. 3 shows SEM micrographs recorded on markers and catalyst islands on silicon substrate. The dark areas (fig 3a, b) are the markers and the white areas (fig 3c, d) are the catalyst islands. These SEM results indicate successes in fabrication the markers and obtained catalyst islands on silicon substrate.

Patterned Growth of SWNTs

The quality and the uniformity of the carbon nanotubes on the catalyst islands were characterized by SEM and Raman.

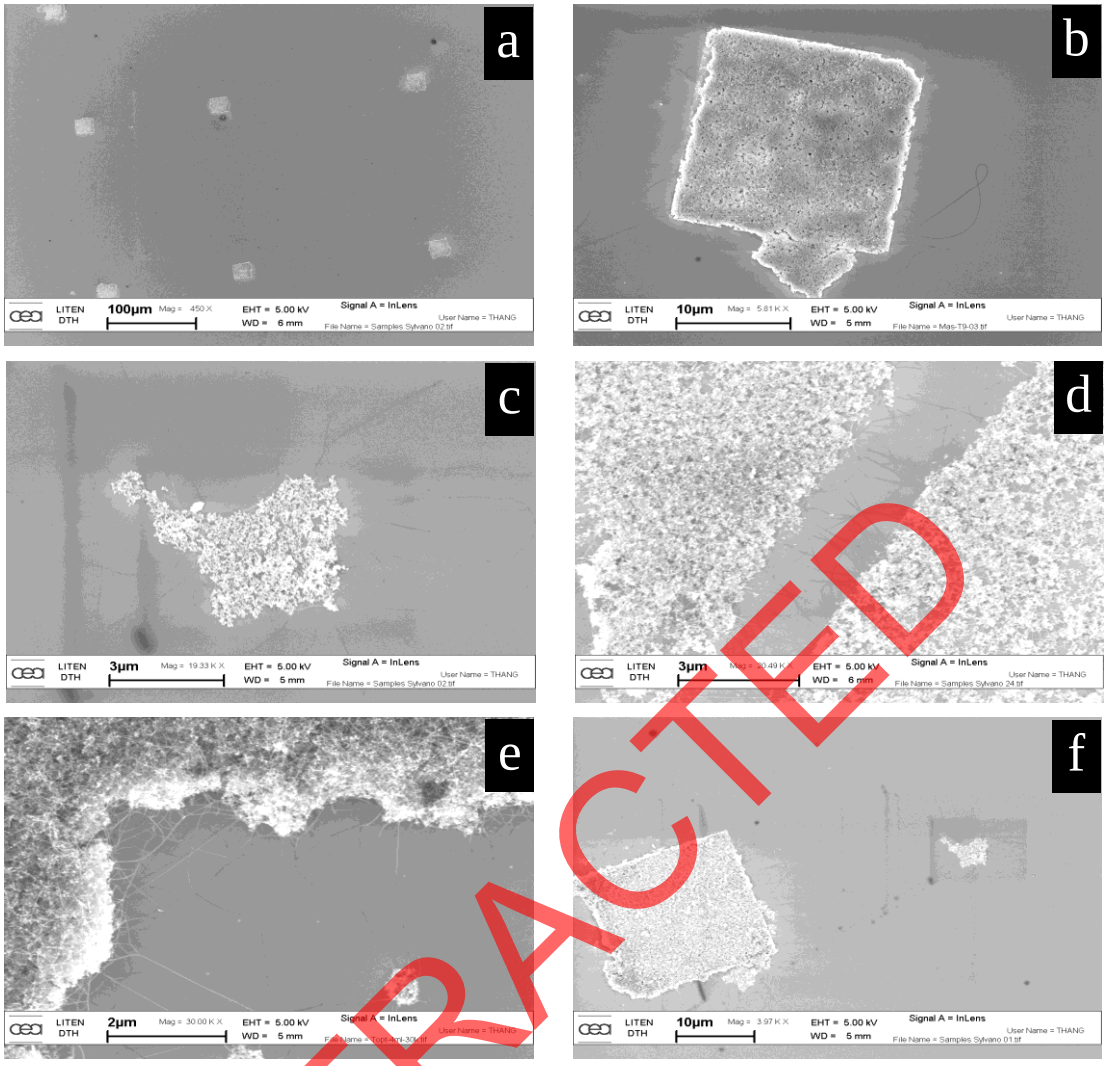

Figure 4. Scanning electron microscopy images of as-grown CNTs on/near catalyst islands

Fig. 4 shows the growth behaviour of carbon nanotubes on patterned catalyst. Using a low magnification of SEM instrument allows direct observation of the catalyst islands and as-grown carbon nanotubes.

Fig. 4b and 4c present the nanotubes grown around the islands catalyst. Fig. 4d, e, f shows the obtained-nanotubes across 3, 4 and 20 µm wide gaps, respectively.

In general, the growth of CNTs terminates upon touching another catalyst side (fig 4d-f), which allows us to control the length of CNTs by using the patterned catalyst with predefined gap. From our results, patterned growth method has proved valid for pattern spacing up to ~20 µm.

The SEM figures also reveal some unwanted features of catalyst pattern with micro-scale. These catalyst islands are not generally flat and uniform.

The SEM results are not strong enough and would be proved further by AFM technique. In our research, an AFM working in tapping mode was used to visualize the samples.

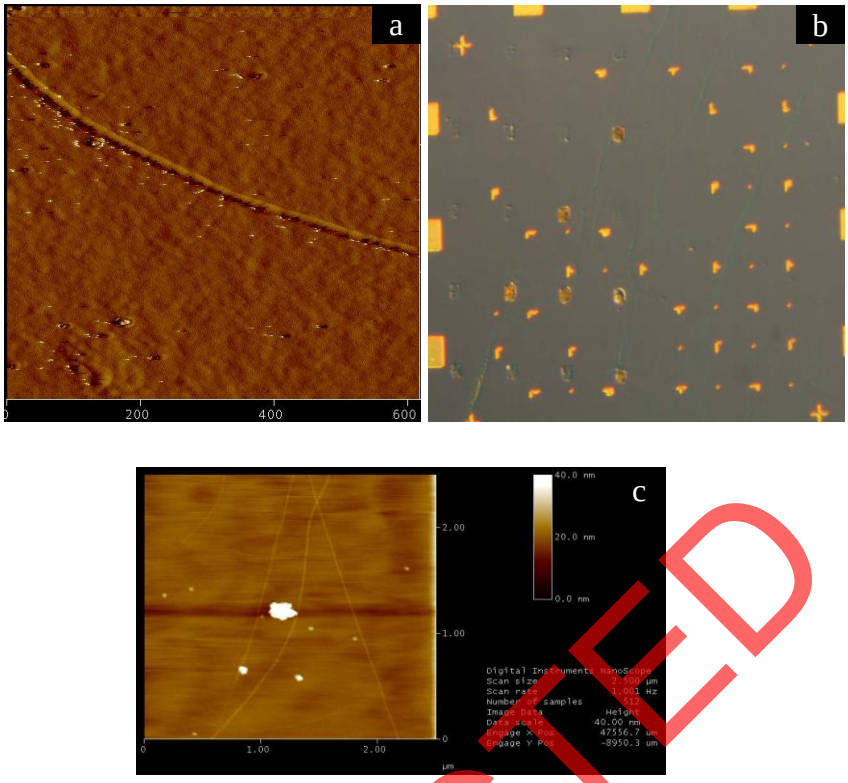

Figure 5. AFM images of as-grown CNTs from a patterned catalyst (with AFM markers)

Three representatives of AFM images are shown in Figure 5. The AFM results show an individual single wall carbon nanotube on the substrate's surface. Fig 5(b) illustrates the sample's surface after CVD process with the presence of the catalyst islands, AFM markers and the CNTs. The diameter of CNTs in Figure 5(c) is not greater than 1.8 nm, which is typical of as-grown carbon nanotubes.

In addition, some SWNTs are observed near island (fig 5c). These long SWNTs are desired for device integrations.

The produced-CNTs on catalyst islands are also characterized by resonant Raman spectroscopy to determine the conducting properties and diameters. Raman spectrum in fig. 6 shows some specific features of the as-grown carbon nanotubes on the catalyst islands.

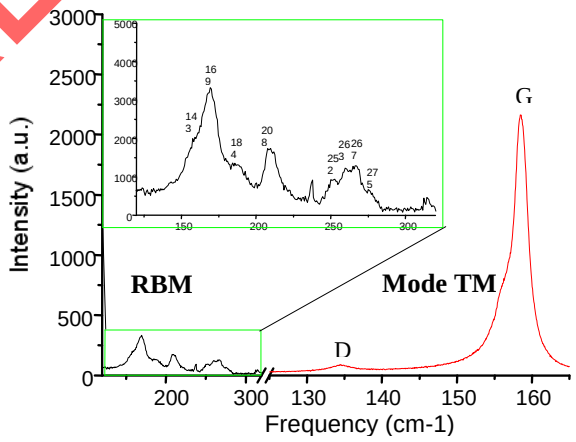

Figure 6. Raman spectroscopy of CNTs products

SWNTs properties were characterized by Raman microscope system (YVON) at an excitation wavelength of 514.5 nm.

The diameter (d) is determined by measuring the RBM frequency and applying the formula:

$$\nu_{RBM} = 224/d \text{ (nm)} \qquad \text{Eq.1}$$

Raman spectra show several RBM signals, suggesting that the grown SWNTs are bundles or individuals nanotubes. The frequency range for the observed RBM signals (120–300 cm^{-1}) corresponds to tube diameters from 0.8 to 2 nm.

In the high-frequency range of the Raman spectra, a prominent G-band (~ 1590 cm^{-1}) and the weak D-band (~1350 cm^{-1}) are observed. Commonly, the G-band intensity is approximately proportional to the density of SWNTs. The D-band is related to the structural disorder of sp^2 bonded nanocrystalline and/or amorphous carbon species. Its low intensity indicates that few defects are presents in these SWNTs. Another interesting feature is the very high ratio I_G/I_D (~24). This ratio confirms that high quality SWNTs are synthesized on the patterned catalyst.

The diameters and properties of produced-SWNTs are calculated and shown in table 1.

Table 1. Calculated Diameter from RBM Peaks of SWNTs on Patterned Catalyst

ω_{RBM}	d (nm)	CNTs properties
130	1.72	Semiconductor
140	1.6	Semiconductor
152	1.47	Semiconductor
170	1.32	Semiconductor
200	1.12	Metallic
270	0.83	Metallic, Semiconductor
290	0.77	Semiconductor

TEM Images of Carbon Nanotube on the Molybdenum Grid

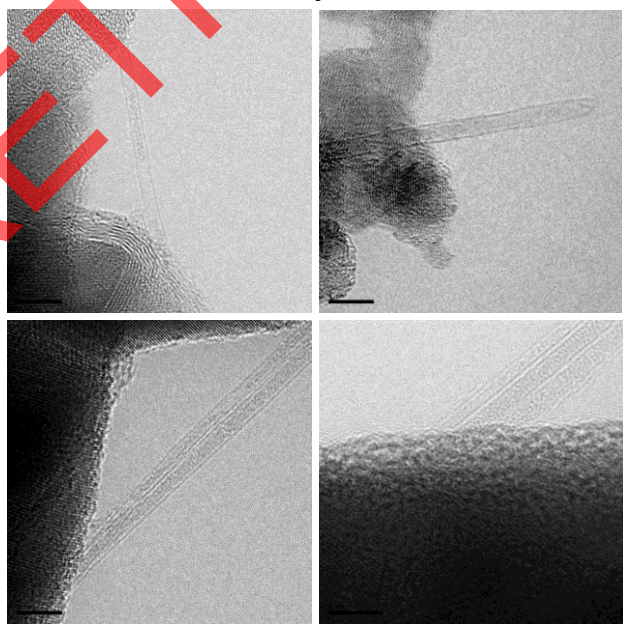

Figure 7. TEM images of individual SWNTs

TEM pictures show the bundles and individual (fig. 7) single-walled carbon nanotubes. These nanotubes have diameter of around 1.4 nm. The observed bundle SWNT includes some parallel tubes with diameter in the range of 1.3-1.6 nm.
Graphene layers covering the catalyst nanoparticles are seen together with catalyst particles in fig. 7. Besides, the TEM results confirmed that the MWNT and DWNT didn't grow on our process.

Conclusion

Outcomes the patterned growth of SWNTs on silicon substrate has been proved successful. A majority of single wall carbon nanotubes emanation from the catalyst sites are obtained. These CNTs emanation far away from the catalyst sites are of special importance for the device applications. Thanks to their long length, we are able to deposit metal electrodes on these CNTs. The research results will pave the way for patterned growth at the individual catalytic nanoparticle level, nanotube orientation control and device integration in a scalable fashion for future nanoelectronics devices.
The production of high-quality of single-walled carbon nanotubes by catalyst CVD method has been achieved. Normally, the produced-SWNTs are a mixture of the semiconducting and metallic SWNTs with the diameters in the range of 0.8-1.8 nm. Further research is required, since the position of nanotube is not under a precise control, and the orientation and chirality of nanotubes are out of control.

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