

Controlled CVD-Growth of Multi-walled CNTs

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Abstract. Many applications of carbon nanotubes (CNTs) require a material with defined properties, however most synthesis routes yield CNTs of varying purity, structure, diameter, and length. Chemical vapor deposition (CVD) allows a good control over the CNTs synthesis and leads to promising results, however the effect of many parameters remains unclear. In order to improve this situation a comprehensive study was carried out under highly controlled conditions. The used CVD reactor was capable to perform deposition processes with temperature deviations smaller than 1°K. The substrates were patterned Fe films with a thickness below 10 nm on silicon/siliconoxide. The effects of the conditioning of the catalyst prior to growth, growth temperature, and growth time were investigated. The synthesis in a hydrogen/acetylene atmosphere yielded pure multi-walled CNTs with diameters between 10 – 20 nm. The length of the CNTs was accurately controlled by the growth time. The density of the CNTs can be varied by the preconditioning of the catalyst. The controlled synthesis allows an integration of CNTs into technologically relevant structures for microelectronics and elucidates the mechanism of the catalysed CNT growth.

INTRODUCTION

The unique electrical properties of carbon nanotubes make them promising candidates for future nanodevices. Logical circuits, sensors, and actuators, using CNTs have been demonstrated, and first prototypes for field emitting displays on the basis of CNTs already exist [1]. For applications, however, the availability of CNTs with defined dimensions, properties, and purity remains a crucial problem. In addition, the CNTs have to be placed in defined positions. The CVD synthesis has turned out to be a promising method for this task and a large number of studies are undertaken to achieve a controlled CVD growth of CNTs [2, 3]. The type of catalyst material, its thickness, growth conditions like temperature, and gas pressure have influence on the purity, diameter, alignment, and quality of the CNTs [4]. Thus the numerous parameters give the possibility to tailor the CNTs in a wide range according to the requirements, however, at the same time they have to be controlled accurately to achieve reproducible results.

In this study we present new insights into the CVD growth of CNTs. The CNTs produced are highly pure, well graphitised, and vertically standing on Si-wafers. In addition, the tube diameter distribution is very small and the length can be controlled via the growth time. The CVD synthesis presented here is highly reproducible and can be carried out on a large scale. This resembles a step towards the implementation of CNTs in to the existing process flow of silicon based microelectronics.

EXPERIMENTAL

The synthesis was carried out in a programmable process furnace (ATV-PEO 603). It consists of a quartz chamber which can host up to 25 6-inch wafers. The furnace is heated resistively and can be actively cooled by a speed regulated air blower. Programmable, exact temperature profiles with heating and cooling rates up to 100°C/min can be applied. For CNT synthesis the substrates are heated to 700°C in pure hydrogen atmosphere and conditioned for 5 min. Afterwards additional C₂H₂ is injected for variable time periods. The substrates are full 6-inch silicon wafers or 15 x 15 mm chips with a 500 nm SiO₂ layer and a 1.25 μm resist layer. I-line lithography was employed for patterning the resist with feature sizes down to 0.35 μm. Iron as catalyst was deposited onto the wafers with a target film thickness between 2 - 10 nm by e-beam evaporation. After lift off the exact height of iron films was estimated with SFM (DI-Nanoscope III).

RESULTS

After CNTs growth the substrates appeared black at regions where the catalyst was applied. SEM investigations revealed that this stems from vertically standing blocks, which consist solely of multi-walled CNTs. In Fig 1a a CNT pattern on a silicon wafer is depicted.

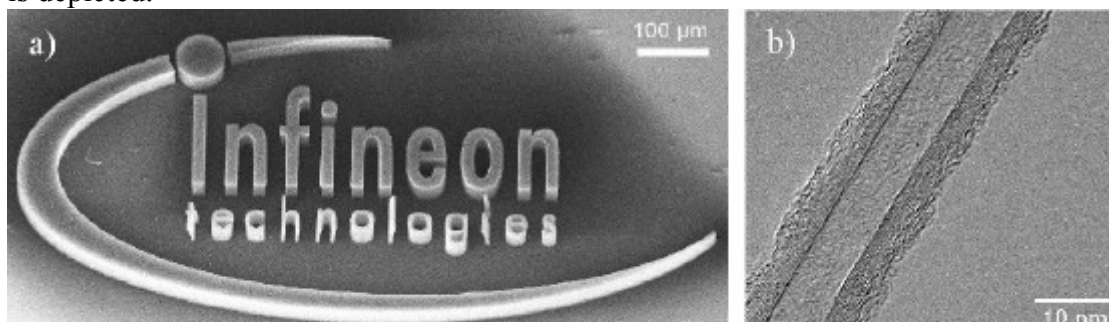


FIGURE 1. SEM (a) and TEM (b) image of CNTs synthesised on a silicon wafer. The CNTs are vertically standing, well aligned and have a low defect density.

HRTEM analysis revealed that the CNT diameter distribution is very small. Most of the CNTs consist of 8 – 10 well graphitised concentric layers with an outer diameter close to 15 nm while the inner diameter is approximately 5 nm, as seen in Fig 1b. This result is especially remarkable, since it was found for iron catalyst layers with different thicknesses. Only very small amounts of amorphous carbon can be seen on the outer shell of the CNTs. Other carbon structures, such as carbon onions, graphite particles, or fullerenes, were not found in our SEM and TEM studies.

The heights of the large CNTs blocks turned out to be uniform over the entire wafer within an error ±5%, as deduced from SEM measurements. The results for the heights of the blocks depending on carbon feedstock injection periods between 20 sec and 72 min are presented in Fig 2. A linear dependence of the CNTs length on the injection time is observed for medium growth times between 3 – 30 min. The growth rate here

is approximately 20 $\mu\text{m}/\text{min}$. CNTs longer than 1 mm can easily be synthesised under the described conditions, however for very long growth times ($t > 30$ min) the growth rate slows down. For very short injection times ($t < 3$ min) the CNTs length is longer than expected from the average growth rate. This is due to the large volume of the oven, which causes acetylene to remain with a considerable partial pressure in the reaction chamber even after the gas flow has been turned off. Thus, the effective growth time is higher than the injection time of acetylene.

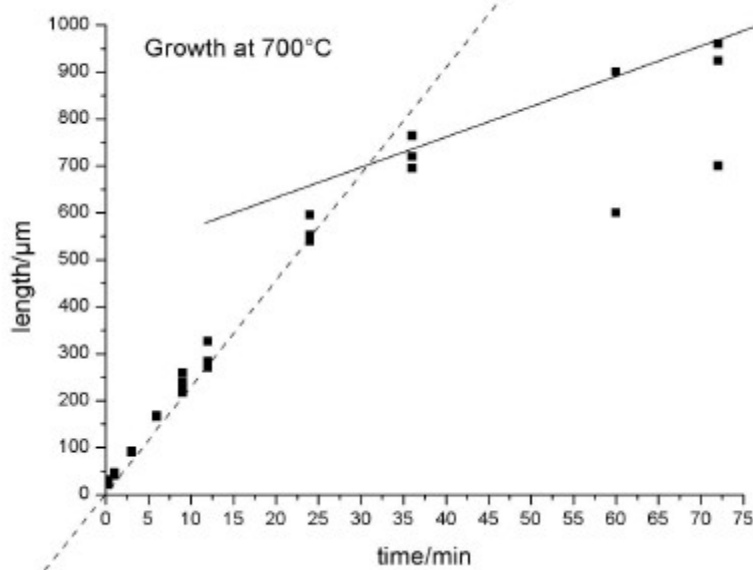


FIGURE 2. Height of the CNTs, depending on the injection time of the carbon feedstock gas. The CNT growth rate is constant for more than 30 min resulting in CNT longer than 0.5 mm.

DISCUSSION

The presented CVD synthesis of the CNTs highly reproducible and scalable. It yields highly pure CNTs, with good graphitisation and a low defect density. In addition, the CNTs have a very narrow diameter distribution peaking at 15 nm. This qualifies the CVD synthesis as a potential candidate for the implementation of CNTs into semiconductor process flows.

The constant growth rate of approximately 20 $\mu\text{m}/\text{min}$ at 700°C allows the control of the CNT length up to 1 mm via the injection time of the carbon feedstock gas. However, with this huge growth rate the target accuracy for the CNTs length is limited to 10 μm . This is due to the control of the duration time of the carbon feedstock within the reaction chamber. The large volume of the chamber causes acetylene to remain with a considerable partial pressure in the chamber even after the flow has been turned off. This is also the reason, that for very short injection times ($t < 3$ min), the CNTs length is longer than expected for the given growth rate. At long growth times ($t > 30$ min), the growth rate slows down. Possible explanations are a rendered diffusion of the acetylene, a coverage of the catalyst particle with an amorphous carbon shell, or a

poisoning of the catalyst. Still, the highly stable conditions in the CVD chamber allow a undisturbed CNT growth in a reproducible manner with an accurate control of the CNT length.

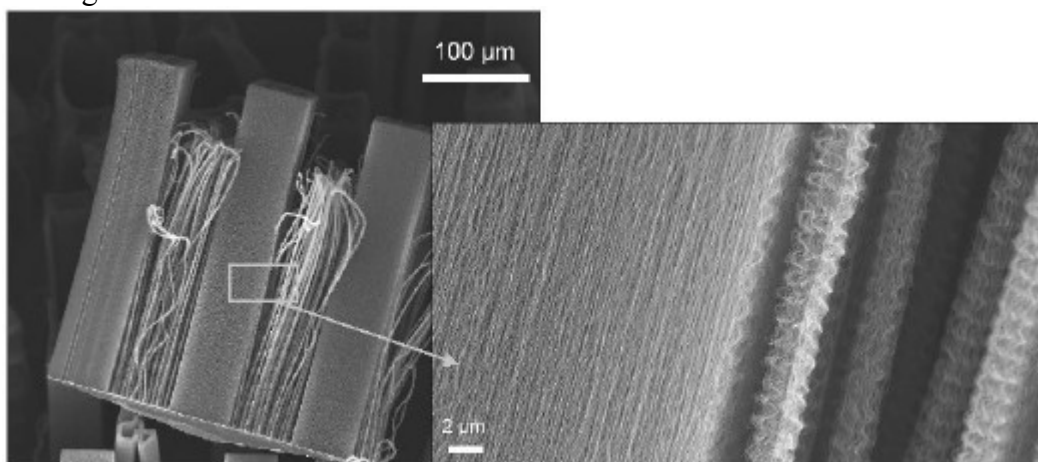


FIGURE 3. SEM images of blocks of CNTs with different widths lifted off the substrate. The higher magnification of the right image shows the better alignment of the CNTs in the wide block.

The degree of alignment of the CNTs in parallel to each other depends on the number of CNTs per unit area of the substrate. As seen in Fig 3, the alignment of the CNTs is higher in wide patterns (square blocks), than for smaller features. One explanation for this is that small patterns ($< 1 \mu\text{m}$) do have a thinner catalyst layer because of a shadow effect during catalyst deposition. As a result, a smaller number of active catalyst sites per unit area are formed. Thus, since the CNTs have more space during growth and are not forced to grow parallel, they are less straight and show a smaller degree of alignment.

CONCLUSIONS

The patterned growth on 6-inch wafers represents a further step to integrate CNTs into microelectronics. In this work techniques and set ups for a microelectronic compatible process flow were employed. The CNTs exhibit high uniformity, low impurity content and good alignment. The process time allows the control of the tube length.

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