Catalyst patterning for carbon nanotube growth on elevating posts by self-aligned double-layer electron beam lithography

M. Häffner[a] and A. Heeren
Institute of Applied Physics, University of Tübingen, Auf der Morgenstelle 10, 72076 Tübingen, Germany

A. Haug and E. Schuster
Institute of Physical and Theoretical Chemistry, University of Tübingen, Auf der Morgenstelle 8, 72076 Tübingen, Germany

A. Sagar
Nanoscale Science Department, Max-Planck-Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany

M. Fleischer
Institute of Applied Physics, University of Tübingen, Auf der Morgenstelle 10, 72076 Tübingen, Germany

H. Peisert
Institute of Physical and Theoretical Chemistry, University of Tübingen, Auf der Morgenstelle 8, 72076 Tübingen, Germany

M. Burghard
Nanoscale Science Department, Max-Planck-Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany

T. Chassé
Institute of Physical and Theoretical Chemistry, University of Tübingen, Auf der Morgenstelle 8, 72076 Tübingen, Germany

D. P. Kern
Institute of Applied Physics, University of Tübingen, Auf der Morgenstelle 8, 72076 Tübingen, Germany

(Received 17 June 2008; accepted 2 September 2008; published 1 December 2008)

For gas-flow aligned growth of carbon nanotubes (CNTs), it is important to minimize interaction of the growing CNTs with the substrate. The authors present a method to fabricate thin catalyst films on top of protruding hydrogen silsesquioxane (HSQ) patterns. Self-alignment of the catalyst film with the HSQ pattern is achieved by exposing two layers of resist, polymethyl methacrylate (PMMA) on top of HSQ, simultaneously. By selecting appropriate development parameters for PMMA and HSQ, a common exposure dose can be applied. After a standard lift-off process HSQ is developed and CNTs are grown on the protruding HSQ patterns resulting in gas-flow aligned CNTs that can be further processed, e.g., for the fabrication of CNT based transistors.
© *2008 American Vacuum Society.* [DOI: 10.1116/1.2991516]

I. INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) in 1991 [1] and their first application as transistor channels,[2] a variety of methods for the alignment of CNTs have been reported.[3] Laminar flow-assisted growth techniques have been developed to grow aligned CNTs with no requirement of electrode fabrication or special substrate materials.[4–10] In order to achieve gas-flow alignment during chemical vapor deposition (CVD) growth of CNTs, it is important to minimize interactions of the growing CNTs with the substrate. One way of reducing the interaction is to elevate the catalyst above the underlying substrate.[11–13]

Thus, a method to fabricate thin metallic CNT catalyst films on top of a protruding support material is needed. Since the elevating posts underneath the thin metallic catalyst films have to act as a diffusion barrier for the catalyst during CVD growth, the cross-linked high-resolution e-beam resist hydrogen silsesquioxane (HSQ), resembling SiO_x, is an ideal candidate material.

A simple method to fabricate catalyst structures on elevating HSQ posts is to evaporate a thin layer of about 0.2 nm iron that acts as catalyst for CNT growth, on top of HSQ posts patterned on a silicon substrate. During CVD for CNT growth HSQ, resembling SiO_x, acts as diffusion barrier for the thin catalyst layer, whereas catalyst diffuses into silicon in the surrounding area that is not covered with HSQ. Thus nanotubes only grow on top of the HSQ pillars (Fig. 1). The advantage of this process is the possibility of using high resolution, high contrast HSQ lithography including vacuum drying and development of HSQ above room temperature[14] for accurate placement of CNTs.

However, if silicon is utilized as substrate for the HSQ patterns, the CNTs cannot be subsequently integrated in a transistor configuration, since the as grown CNTs lie on a

[a] Tel.: +49-7071-2976350; electronic mail: michael.haeffner@uni-tuebingen.de

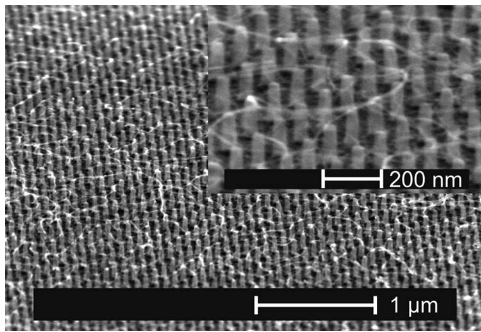

FIG. 1. High resolution HSQ pillars coated with 0.2 nm Fe, after CVD growth of carbon nanotubes.

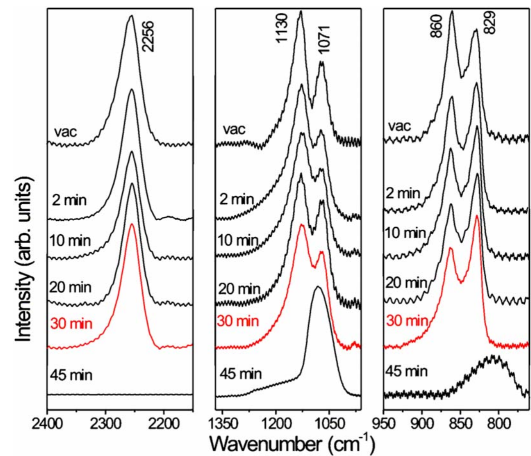

FIG. 3. IR spectra, showing that HSQ cross-linking increases with increased baking time at 150 °C after spin coating. Bands at 2256, 1130, and 860 cm^{-1} correspond to resist without cross-linking, bands at 1071 and 829 cm^{-1} to cross-linked HSQ.

conducting substrate. In the case of insulating substrates, like silicon oxide on silicon, catalyst has to be kept away from the space in between the posts. For this purpose a double layer approach has been developed. We perform a catalyst lift-off using polymethyl methacrylate (PMMA) e-beam lithography on top of an HSQ layer that is exposed simultaneously, resulting in catalyst layers on HSQ structures after HSQ development. The advantage of our process is that we can avoid a two-step lithography process[3] or the use of contact printing techniques[11] and precisely self-align the catalyst films homogeneously on protruding posts with diameters and heights in the tens of nanometers range.

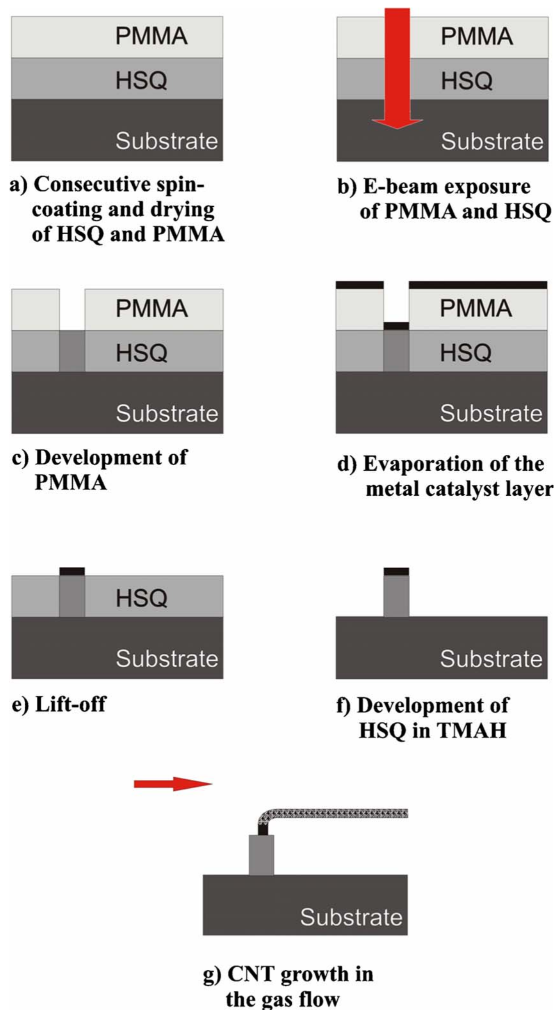

FIG. 2. Schematic fabrication process.

II. FABRICATION

In Fig. 2 the fabrication process is shown in detail. PMMA is spin coated on top of a spin-coated and baked layer of HSQ [Fig. 2(a)]. This step is critical, since the PMMA solvent will dissolve HSQ again, if it is not dried completely. On the other hand, drying of HSQ can significantly restrict resolution due to premature cross-linking.[14] The IR spectra in Fig. 3 show the increase in cross-linked HSQ with increasing baking time at 150 °C: The bands at the higher wave numbers (1130 and 860 cm^{-1}) can be related to isolated, cagelike HSQ, while the ones at the lower wave numbers (1071 and 829 cm^{-1}) can be related to cross-linked HSQ and thus network formation. Increasing relative intensities of network bands for the Si–O–Si stretching mode at 1071 cm^{-1} and H–Si–O bending vibration at 829 cm^{-1} with increasing baking time are observed. The relative intensity of the Si–H stretching mode (2256 cm^{-1}) decreases due to increased cross-linking of the cages $[(-\mathrm{Si-O-Si-H})_n \rightarrow (-\mathrm{Si-O-Si-O-})_n]$.

By exposing both resists simultaneously, self-alignment is achieved [Fig. 2(b)]. In order to match the sensitivities of PMMA and HSQ, we adjust developing conditions for both resists. In the case of PMMA [Fig. 4(a)], the contrast curve shows decreasing sensitivity, i.e., increasing clearing dose for decreasing development time (left: 45 s, center, and right: 15 s) and more diluted solvent [metal isobutyl ketone (MIBK)] in isopropyl alcohol (IPA) (left and center: MIBK:IPA=1:3, right: MIBK>:IPA=1:5). In the case of HSQ [Fig. 4(b)], baking and decreasing development time increases sensitivity of the resist while maintaining sufficient

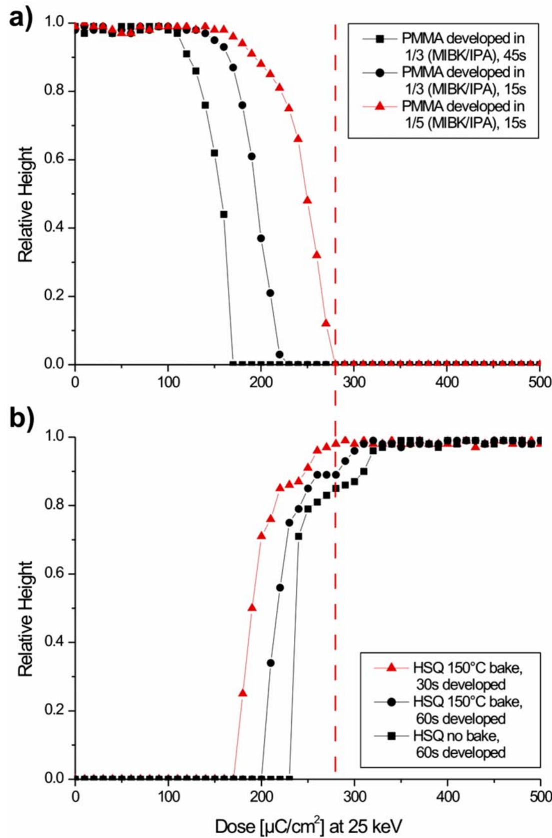

FIG. 4. Contrast curves of PMMA (a) and HSQ (b) for development under different conditions. The dashed line indicates the dose chosen for optimum development of both resists.

contrast. Development of PMMA in MIBK:IPA=1:5 for 15 s and development of HSQ for 30 s in TMAH after baking at 150 °C for 30 min are optimum conditions for full HSQ resist thickness and complete development of PMMA (dashed line) after exposing with a dose of 300 μC/cm^2 at 25 keV.

After a standard lift-off process [Figs. 2(c)–2(e)], HSQ is developed (f) and CNTs are grown on the protruding HSQ posts (g).

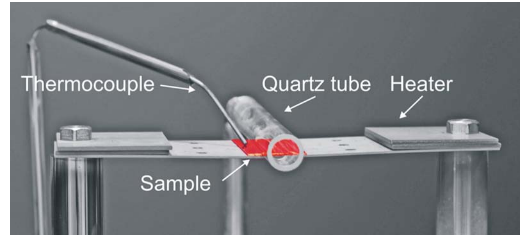

FIG. 5. Setup for CNT growth in gas flow through a quartz tube.

For gas-flow alignment a quartz tube with an inner diameter of 6 mm is placed over the sample in the CVD chamber (Fig. 5). A gas flow of ammonia and acetylene is applied to the sample that is heated by a graphite heater. Argon is used to adjust the velocity of the gas flow. A thermocouple allows for temperature measurement directly on the sample.

Simulations of the gas flow using COMSOL MULTIPHYSICS show a laminar flow above the sample (Fig. 6). A gas flow of 300 SCCM (SCCM denotes cubic centimeter per minute at STP) NH_3, 300 SCCM C_2H_2, and 400 SCCM Ar, resulting in 1000 SCCM, i.e., a maximum velocity of 59 cm/s through the 6 mm tube, is applied [Fig. 6(a)]. The simulation shows a gas velocity of about 900 μm/s at 1 μm above the sample surface (b), resulting in an aligned growth of CNTs. At a gas flow of more than 5000 SCCM, i.e., 2.9 m/s through the 6 mm tube (c), turbulences appear, which are expected to prevent CNT alignment.

III. RESULTS AND DISCUSSION

CNTs growing from iron catalyst on top of HSQ can be seen in Fig. 7. In (a) and (b), dense aligned CNTs are grown from catalyst bars at 600 °C, applying the gas flow from the left side. Isolated CNTs on top of small patterned HSQ structures are obtained during growth at an increased temperature of 800 °C [(c) and (d)]. The growth time is 10 s for the CNT in Fig. 7(c) and 20 s in Fig. 7(d). From the length of the as grown tubes, we thus deduce a growth rate of about

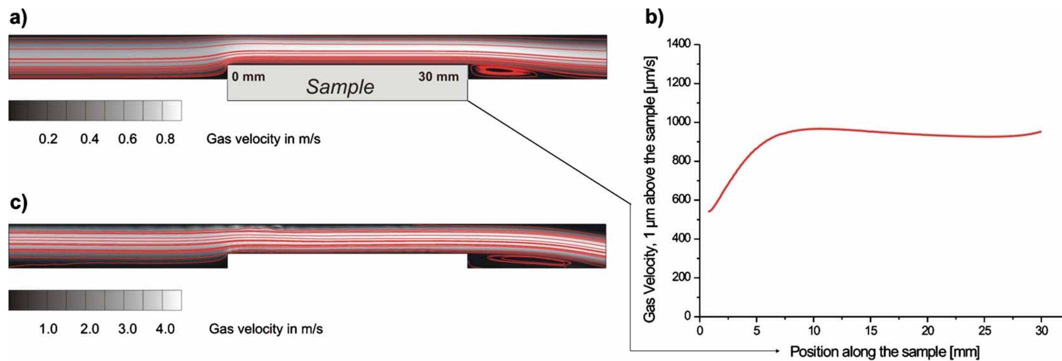

FIG. 6. Simulation of the gas velocity distribution for a gas flow of 1000 SCCM [(a) and (b)] and 5000 SCCM (c) through the quartz tube. (b) Gas velocity along the sample at the position of the CNT growth, about 1 μm above the sample.

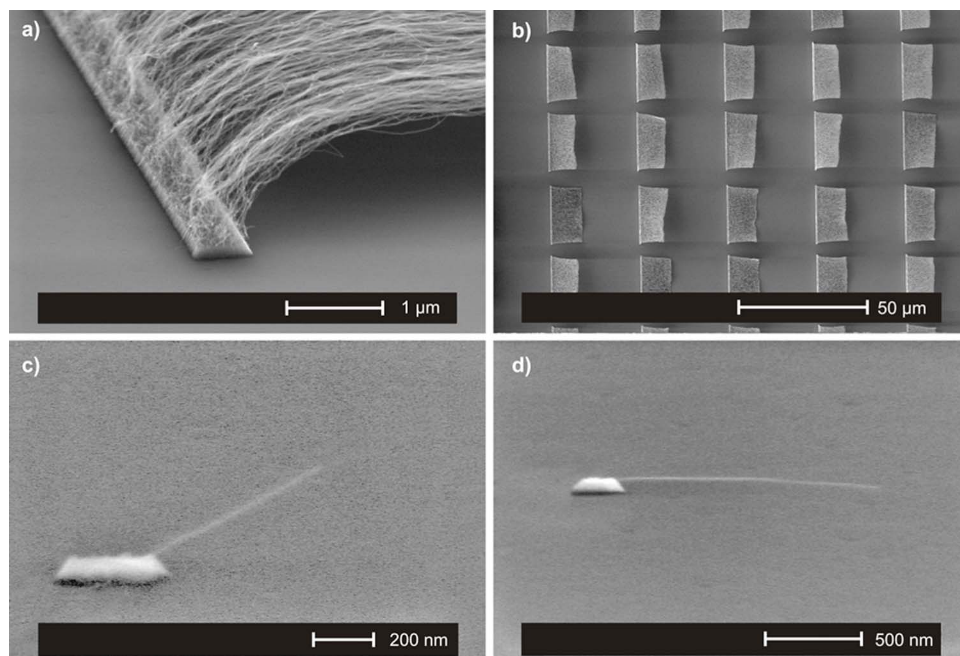

FIG. 7. Gas-flow aligned CNTs grown from catalyst bars at 600 °C [(a) side view; (b) top view] and from catalyst islands at 800 °C [(c) and (d)]. Gas flow is applied from the left side.

50 nm/s. Besides the density of CNTs after growth at different temperatures, the quality of the CNTs differs as well. The structural integrity of the obtained CNTs increases with rising growth temperature, as demonstrated in Fig. 8 which compares Raman spectra of nanotubes grown at 800 and 600 °C. Specifically, the higher temperature yields nanotubes displaying a lower $D(2D)/G$ peak intensity ratio which represents a measure of the defect content in the nanotubes.[15]

IV. CONCLUSIONS

A method is presented for the precise self-alignment of catalyst films on protruding nanostructured posts for gas-flow aligned carbon nanotube growth. In a catalyst lift-off process PMMA e-beam lithography is performed on top of a HSQ layer that is exposed simultaneously, resulting in catalyst layers on top of HSQ structures after HSQ development. From such structures gas-flow-aligned CNTs are grown under a variety of conditions.

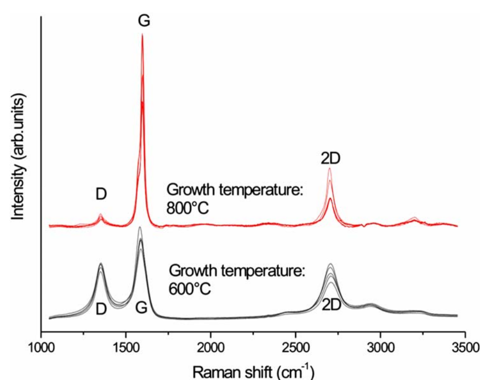

FIG. 8. Raman spectra (λ_{exc}=532 nm) of CNTs grown at 600 °C (lower spectra) and 800 °C. (upper spectra), in each case collected from five different locations. The relative ratio of the Raman bands assigned to ordered (G, 1597 cm^{-1}) and disordered (D, 1348 cm^{-1}; $2D$, 2703 cm^{-1}) grahite reflects the quality of the tubes.

[1]S. Iijima, Nature (London) **354**, 56 (1991).
[2]S. J. Tans, A. R. M. Verschueren, and C. Dekker, Nature (London) **393**, 49 (1998).
[3]L. Huang, Z. Jia, and S. O'Brien, J. Mater. Chem. **17**, 3862 (2007).
[4]B. H. Hong, J. Y. Lee, T. Beetz, Y. Zhu, P. Kim, and K. S. Kim, J. Am. Chem. Soc. **127**, 15336 (2005).
[5]L. Huang, X. Cui, B. White, and S. O'Brien, J. Phys. Chem. B **108**, 16451 (2004).
[6]S. Huang, B. Maynor, X. Cai, and J. Liu, Adv. Mater. (Weinheim, Ger.) **15**, 1651 (2003).
[7]S. Huang, M. Woodson, R. Smalley, and J. Liu, Nano Lett. **4**, 1025 (2004).
[8]S. Huang, Q. Fu, L. An, and J. Liu, Phys. Chem. Chem. Phys. **6**, 1077 (2004).
[9]S. Huang, X. Cai, C. Du, and J. Liu, J. Phys. Chem. B **107**, 13251 (2003).
[10]S. Li, Z. Yu, C. Rutherglen, and P. J. Burke, Nano Lett. **4**, 2003 (2004).
[11]A. M. Cassell, N. R. Franklin, T. W. Tombler, E. M. Chan, J. Han, and H. Dai, J. Am. Chem. Soc. **121**, 7975 (1999).
[12]Y. Homma, Y. Kobayashi, and T. Ogino, Appl. Phys. Lett. **81**, 2261 (2002).
[13]Z. Yu, S. Li, and P. J. Burke, Chem. Mater. **16**, 3414 (2004).
[14]M. Häffner, A. Haug, A. Heeren, M. Fleischer, H. Peisert, T. Chassé, and D. P. Kern, J. Vac. Sci. Technol. B **25**, 2045 (2007).
[15]M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, L. G. Cancado, A. Jori, and R. Saito, Phys. Chem. Chem. Phys. **9**, 1276 (2007).