OPTIMIZING THE PECVD-PROCESS FOR LOW TEMPERATURE GROWTH OF CARBON NANOTUBES

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Abstract

Carbon nanotubes (CNTs) are typically grown at temperatures above 700 °C. However, for many electronic and life-science applications, temperature sensitive substrates require the use of growth processes at temperatures below 380 °C. In order to grow vertically aligned CNTs at such low temperatures, optimized plasma enhanced chemical vapor deposition (PECVD) growth is applied with and without oversaturation of the catalyst with carbon before the PECVD-process. Optimization includes the variation of pressure, growth time, catalyst material and thickness. Quantitative results of CNT length and quality as well as optimal growth parameters for processes below 380 °C are presented.

I. Fabrication scheme

Catalyst dots were produced by electron beam lithography or by optical lithography. Silicon wafer were used as a substrate. On the substrate 600 nm TiN were sputtered by reactive magnetron sputtering as a diffusion barrier. Onto the diffusion barrier resist was spin coated: for e-beam lithography we spin coated PMMA, for optical lithography ma-P 1215. For a dot size below 300 nm e-beam lithography was used. After exposure the resist was developed. The dot sizes ranged from 10 µm down to 250 nm. After developing, catalyst with a typical thickness of 10 nm was sputtered onto the substrate by magnetron sputtering. Then the resist was removed with acetone. The CNTs grew from the catalyst dots. Our PECVD-process consists of four steps: first of all the chamber is pumped to a base pressure of 0.15 mbar. Then the sample is heated in ammonia atmosphere at 1.4 mbar for 5 min up to the designated temperature. The third step is to turn a 10 W DC-plasma on and let acetylene in the chamber. After the designated process time we turn the gases, the heater, and the plasma off, pumping the chamber to a pressure of 0.2 mbar, and then let nitrogen in to cool the sample. When the temperature of the sample reaches 160 °C, the chamber can be vented and the sample is removed.

II. Results

1. Variation of the gas mixture

A gas mixture of acetylene (C_2H_2) and ammonia (NH_3) was used for CNT growth in a PECVD-process. A DC-plasma with a power of 20 W was applied. The growth time was 15 min at different temperatures. Mixture ratios of 3:1 (NH_3:C_2H_2), 4:1, 8:1 and 11:1 were applied. The CNT height begins to increase for mixtures of 3:1 and 4:1 at 600 °C. We observed an initial increase of the CNT height in the 450 °C to 500 °C temperature range for a mixture of 11:1, but at higher temperatures NH_3 etches the CNTs back too fast. For the 8:1mixture the CNTs began to grow at temperatures around 400 °C, and the NH_3 did not etch the CNTs at 600 °C. The conclusion is that at lower ratios the catalyst is poisoning too fast at lower temperatures, at higher ratios the NH_3 is etching the CNTs. The optimal mixture turned out to be 8:1. [1]

2. Variation of the pressure

With the optimized gas mixture of 8:1, the process pressure was varied. The variation started with 1.2 mbar and ended with 2.8 mbar in 0.4 mbar steps for temperatures from 300 °C to 500 °C in 50 K steps. A 10 W DC-plasma and different growth times were applied. For comparison a growth time of 30 min was chosen. For 1.6 mbar a CNT height of about 100 nm at 350 °C was reached. At lower pressure we were not able to work at temperatures below 400 °C, since the plasma stability decreases with lower pressure. At higher pressures, e.g. 2.8 mbar, the height of the CNTs at temperatures around 350 °C and 400 °C shrinks rapidly. The conclusion is that at higher pressure the etching rate of the plasma at temperatures around 350 °C to 400 °C increases. At pressures lower than 1.6 mbar the plasma is not stable near the sample. The best growth rate was observed at 1.6 mbar. [2]

3. Variation of the catalyst

For CNT growth a 10 nm thick Ni, Co, Mo, or Fe catalyst was used. With Mo just a few experiments were made and then abandoned because the CNT growth began with the optimized parameters at temperatures higher than 600 °C. As Fe catalyst V2A, an alloy of 72% Fe, 18% Cr and 10% Ni, was used. For V2A the growth of CNTs started at 400 °C, which is a good result for an alloy. Another idea for an iron containing catalyst was ferritin: ferritin is an Fe^{2+}-ion in a protein shell. After removing the protein, using O_2-plasma, little clusters of nanometer size were left, consisting of iron oxide, which is reduced during growth. CNT growth with ferritin as catalyst set on at temperatures over 450 °C. Fe is not a well-suited catalyst, because it has a bcc crystal structure. This is not favorable for growing CNTs, whose structure is hcp. More closely related is Ni with a ccp structure. Co did not work too well as catalyst, because it oxidized too fast before CNT growth. The best catalyst was Ni for which the CNT growth started at 350 °C, followed by Co as a catalyst with CNT growth at 400 °C. [3]

4. Variation of the growth time

The next step for optimizing all parameters was to vary the growth time for the best process. The growth time was changed from 15 min to 90 min in 15 min steps. During the first 60 min period CNT height increased with time. After 60 min etch back of the CNTs by the plasma dominates. In our case the growth optimum was 60 min. [2]

5. Variation of the catalyst thickness

Normally a 10 nm thick Ni catalyst was used. Changing the thickness to 2 nm, the optimized process at 350 °C was started. With a thickness of 10 nm a total CNT height of 400 nm was reached, with 2 nm thickness a total CNT height of over 1 µm was reached (see Fig. 1). The conclusion is that the height of the CNTs depends on the size of the catalyst particle: thin catalyst dots form smaller islands during the PECVD growth, so the catalyst particles diffuse faster during growth, so the CNTs are growing higher in the same process. [4]

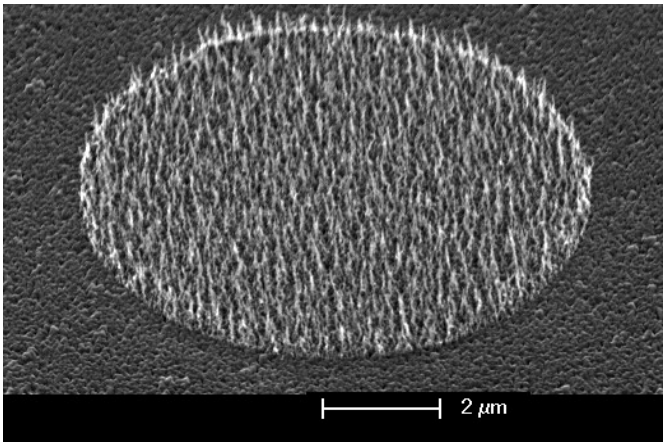

Fig. 1: CNTs grown on 2 nm thick Ni catalyst. CNT height: 1 µm.

6. Alternative PECVD process

Even with the optimized PECVD parameters we were not able to reach growth temperatures below 350 °C. According to the VLS-growth model it is necessary to oversaturate the catalyst particle with carbon. Therefore the sample was placed before the process in an acetylene atmosphere at 2 mbar for 5 min at 300 °C. After this catalyst preparation, we waited at 300 °C for 15 min and started then our normal optimized process for 60 min. With this process a total height of CNTs of 150 nm was reached (see Fig. 2), while without this initial oversaturation no CNT growth occurred.

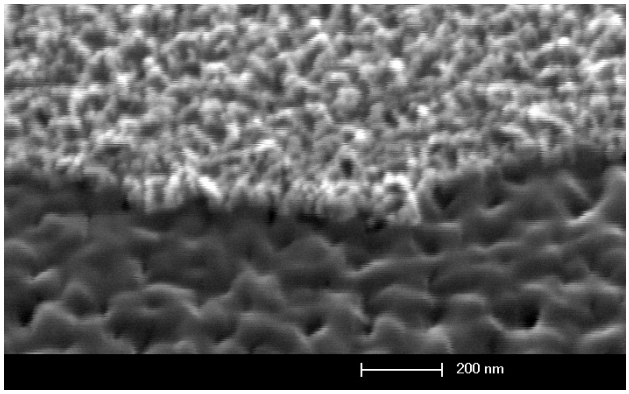

Fig. 2: CNTs grown at 300 °C by the alternative PECVD process on a 10 nm thick Ni catalyst with a diameter of 10 µm.

7. Raman-spectra

CNTs grown at 500 °C show a G-and D-peak of equal height in Raman measurements, which is comparable with CNTs grown at higher pressure and temperature. At lower temperature, the G-peak originating from ordered carbon shrinks, which means that the carbon is becoming more and more disordered. The conclusion is that the quality of the CNTs deteriorates with lower temperature.

Conclusions

We demonstrate the controlled growth of CNTs at low temperature on silicon with TiN as a diffusion barrier. The PECVD process was optimized and CNTs were obtained at 350 °C with a total height of over 1 µm. An alternative PECVD process was established to reach growth temperatures below 350 °C. With the alternative PECVD process we were able to grow at 300 °C with a height of 150 nm.

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