

CVD GROWTH OF CARBON NANOTUBES WITH A Ni CATALYST IN A POLYIMIDE TRENCH

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Carbon nanotubes (CNTs) are ideal candidates as electrode materials for neuronal stimulation and monitoring devices such as microelectrode arrays (MEA). They provide a high charge injection limit without significant Faradic reactions and carbon nanotube electrodes have a high surface area to volume ratio. Flexible MEAs typically consist of thin conductors buried in a flexible insulator such as polyimide, where the actual contact areas have been opened by dry etching of the polyimide. CNTs are positioned in these contact areas by a low temperature (350 °C) chemical vapour deposition process from a catalyst which was deposited on the contact in the polyimide recess. To overcome poisoning of the catalyst by outgassing from the sidewalls of the polyimide trenches even at such low temperatures, a pre-treatment of the catalyst in an ammonia atmosphere for 15 min at 40 mbar and 350 °C was introduced. CNT growth on identical structures made from polyimide and silicon is compared in order to identify the relevant issues affecting growth.

Keywords: Carbon nanotube, Synthesis, CVD, polyimide.

1. Introduction

Since the first report on carbon nanotubes (CNTs) by Iijima in 1991, CNTs are becoming more and more important for applications, e.g. as electrode materials, in field emitter devices or in sensors. Carbon nanotubes (CNTs) are ideal candidates as electrode materials for neuronal stimulation and monitoring devices such as microelectrode arrays (MEA). They provide a high charge injection limit without significant Faradic reactions [1] and carbon nanotube electrodes have a high surface area to volume ratio. Flexible MEAs [2] typically consist of thin conductors buried in a flexible insulator such as polyimide, where the actual contact areas have been opened by dry etching of the polyimide. The objective in this work is to fabricate CNT-carpets on the surface of such contacts in a polyimide recess such that the CNTs form the actual interface to the living matter.

CNTs are often grown by chemical vapor deposition (CVD) or plasma enhanced CVD (PECVD) processes, which typically require temperatures around 700 °C. Such growth temperatures are too high for polymers like polyimide. We and others [3, 4] have previously shown that it is possible to grow CNTs at temperatures below 400 °C on flat substrates, however, these processes failed when trying to grow CNTs in a polyimide recess. A prime candidate for the cause of this failure is the outgassing of carbonaceous gases [5–8] from the polyimide sidewalls of the recesses before and during growth, since in earlier experiments on flat substrates, it was already shown that this can poison the catalyst. Therefore, in experiments on nearly identical

recessed structures in polyimide and inert silicon we set out to identify the detrimental factors and to eliminate them.

2. Experiments

2.1. Sample preparation

Initially, a glass substrate was spin-coated for 30 s with an adhesion promoter (VM-652 or diluted VM-651 from HD Micro Systems). Afterwards the polyimide precursor (PI 2611, HD-Micro Systems) with a thickness of 5 μm was spin-coated (500 rpm for 5 s, then 4000 rpm for 30 s) onto it. The polyimide was then soft baked on a hot plate at 90 °C for 90 s, followed by 90 s at 150 °C. The final imidization process was performed under N₂ flow at a pressure of 0.4 MPa with a temperature ramp rate of 4 °C/min from room temperature to 330 °C – 350 °C. The final temperature between 330 °C and 350 °C was then held for 30 min. After that, the sample was gradually cooled to room temperature. These steps were performed twice in order to achieve a final polyimide thickness of 10 μm .

These polyimide substrates were cut into 1 cm \times 1 cm pieces and spin coated (2000 rpm/ramp 20/30s) with a photo-resist (ma-P 1275, Micro-Resist-Technology) with a total thickness of 11.1 μm . After a soft bake at 80 °C for 5 min, the sample was exposed for 150 s in a UV mask aligner (Karl Süss MJB3) and developed for 1 min (ma-D 331, Micro-Resist-Technology). As a pattern, an array of 30 μm diameter circular electrodes was used. Then, the polyimide was etched by reactive ion etching (RIE) with oxygen at 100 W plasma power and a pressure of 0.1 mbar. The resist could be used as an etching mask, because the etching rate of the resist was about 160 nm/min, while the etching rate of the polyimide was about 260 nm/min. The depth of these etched trenches was varied from 1 μm to 5 μm in 1 μm increments. Afterwards, the etching mask was removed with acetone in an ultrasonic bath for 1 min and rinsed with isopropanol.

In order to pattern the catalyst, a new layer of resist (ma-P 1215, Micro-Resist-Technology) with a thickness of 1.5 μm was spin-coated, soft baked at 90 °C for 90 s, exposed for 21 s and developed (ma-D 331) for 50 s. Afterwards, 10 nm Ti, 40 nm TiN as a diffusion barrier and 2 nm Ni as a catalyst were sputtered onto the sample and lift-off was performed in acetone. For this second exposure, the same electrode pattern was used, but it was aligned with an offset with respect to the first structure in order to produce catalyst areas inside the trenches as well as on the top of the polyimide surface. This was done in order to compare between the growth on the catalyst inside a trench and on the top surface.

In addition, nearly identical silicon structures were produced. To this end, ma-P 1275 with a thickness of 11.1 μm was again used as an etching mask. The silicon was etched in an RIE process with a gas mixture of 15 % O₂, 50 % SF₆ and 35 % Ar at 120 W plasma power with a pressure of 0.05 mbar. In this case, the etching rate of silicon amounted to about 230 nm/min. After removing the etch mask and cleaning the silicon samples in a 300 W oxygen plasma for 5 min, the catalyst dots were patterned the same way as on the polyimide structures.

2.2. Growth studies

In [4], we found that the optimum growing process had the following conditions: 5 mbar pressure, 5 min growing time, with a gas ratio of 1:1 (NH₃:C₂H₂). In addition, it was also found that the polyimide is outgassing carbon containing gases during the heating process, such as CO₂ and CH₄ [5–8]. This outgassing is poisoning the catalyst before CNT growth can start, so it is necessary to pre-treat the sample with NH₃ at 3.2 mbar as an etching gas [4]. Optimal pretreatment times were found to be 45 – 60 min at 450 °C and 75 – 90 min at 350 °C. In the

following experiments, growth on silicon samples was performed without any pretreatment, while the polyimide samples were pretreated according to the above-described procedure.

As presented in Fig. 1, no significant difference in the growth behavior on silicon was found, whether the CNTs grew on top of the surface or in the trench of the sample. The CNT height is shown as an average of 3 measurements with respective error bars.

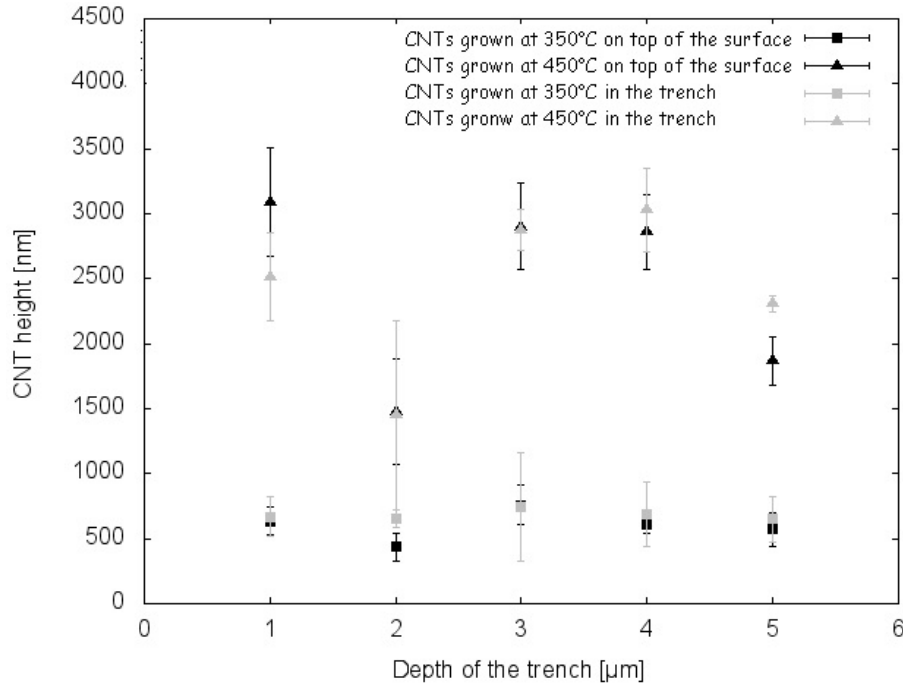


FIG. 1. CNT growth on Si. The grey dots are CNT heights in the trenches, the black dots are CNT heights on top of the surface of Si

CNTs grown on polyimide, however, showed a clear tendency to be shorter when growing inside a polyimide trench than when growing on the top surface (Fig. 2). No significant dependence of the CNT height on the depth of the trenches could be observed. It seems that the polyimide itself is influencing the growth process, as described in [4].

From this difference in growth behavior between Si and polyimide, we conclude that the sample geometry is not responsible for the low CNT growth inside the polyimide trenches. The mean free path of acetylene at 5 mbar at 350 °C is around 40 μm, which is nearly 10 times more than the depth of the trenches and since we are only dealing with height/width aspect ratios of less than 1/6, there should be no significant geometry effect on the precursor supply. In order to investigate whether the open sidewalls in the polyimide trenches were responsible for the reduced CNT growth, new samples were fabricated where the sidewalls were also covered with catalyst. This was achieved by sputter-coating the sample with the Ti/TiN/Ni catalyst stack immediately after the first lithography and reactive ion etching step. Lift-off was then performed with the first photo resist mask which was left after the etching. After pretreatment in NH₃ at 3.2 mbar for 45 min, CNTs were grown using the process developed in [4], namely 5 min at 450 °C and 5 mbar pressure at a gas ratio of 1:1 NH₃:C₂H₂. Fig. 3 shows the result of such a growth experiment exhibiting regular growth of CNTs on the bottom of the trench as well as on the sidewalls.

This result indicates that the open polyimide sidewalls could be responsible for reduced growth in a trench with uncovered walls. While on flat substrates, catalyst poisoning by

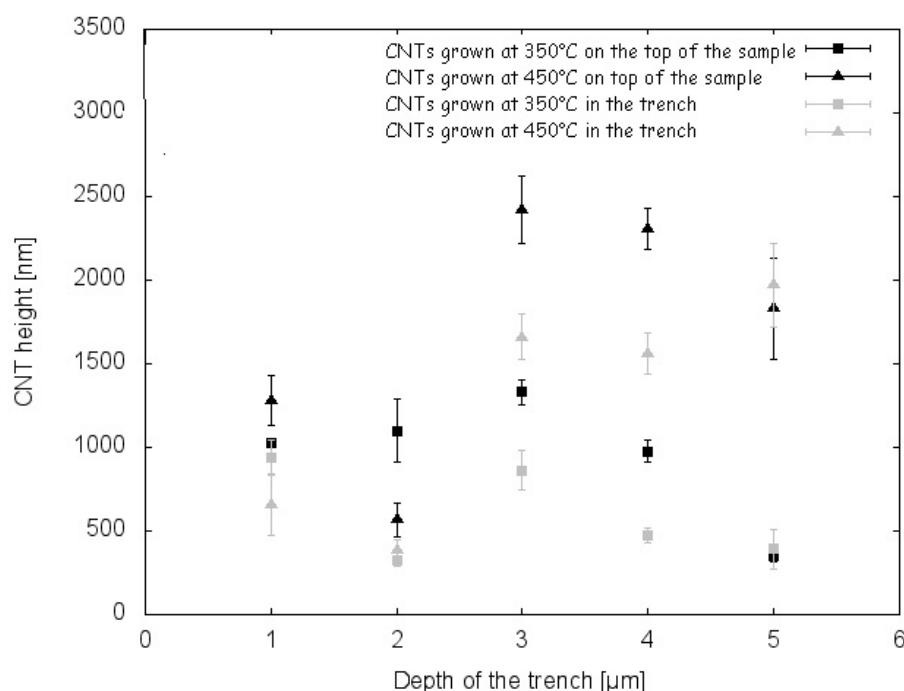


FIG. 2. CNT growth on Polyimide. The grey dots are CNT heights in the trenches, the black dots are CNT heights on top of the surface of Polyimide

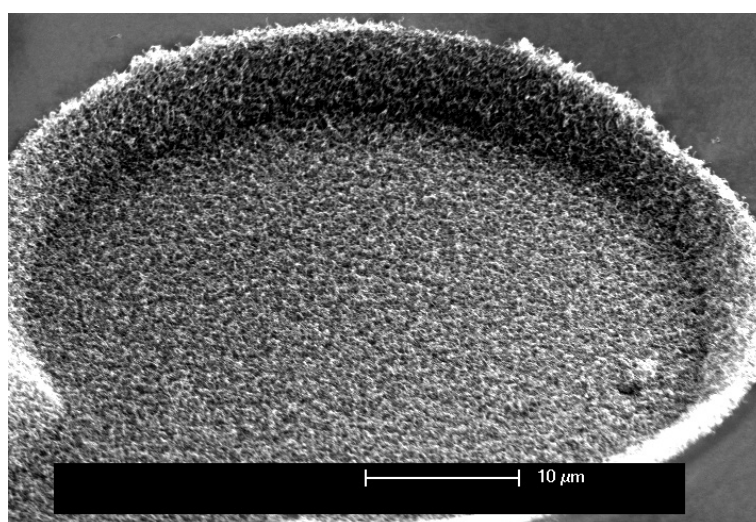


FIG. 3. A 3 μm deep trench in polyimide overgrown with CNTs

outgassing of carbonaceous gases such as CO_2 or CH_4 from the polyimide before growth was even started could be prevented by pretreatment in NH_3 for 45 min at a pressure of 3.2 mbar at reaction temperature. This procedure was obviously not sufficient in the case of polyimide trenches. Even increasing the pretreatment time to 2 h did not improve CNT growth. Therefore, the pretreatment pressure was increased to 20 mbar and 40 mbar. After a pretreatment at 20 mbar a slight improvement of CNT growth in the trenches was observed, but it was still significantly reduced compared to the top surface and rather long pretreatment times were necessary (see grey symbols in Fig. 4). At 40 mbar, the CNTs in the trenches have nearly the same height as the CNTs on the surface. In addition, at this higher pressure the pretreatment time could be

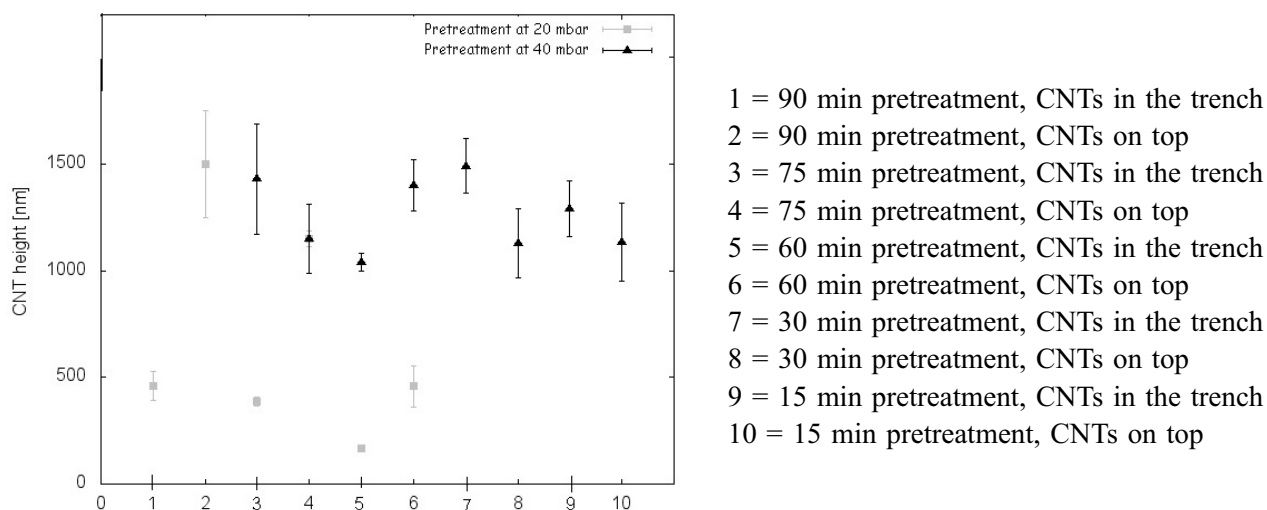


FIG. 4. CNT heights on Polyimide after different pretreatment times/pressures

reduced to 15 min at 350 °C. Obviously, a more efficient protection of the catalyst and possibly passivation of the sidewalls is achieved at this higher pressure.

2.3. Results

From the results of the growth experiments described above, we conclude that the difficulties in growing CNTs inside a polyimide trench were not caused by a too short mean free path of the acetylene molecules at 5 mbar, possibly resulting in a precursor depletion during the process, but rather by the behavior of the polyimide during the heating process itself, as described in [5–8]. The additional outgassing surface of the sidewalls can poison the catalyst in the trenches significantly more than on the surface. When the trench sidewalls were covered with the diffusion barrier and catalyst, no growth difference between the surface and the trenches was observed. Pretreatment for 15 min with NH₃ at an increased pressure of 40 mbar before CNT growth was sufficient to prevent catalyst poisoning at 350°C, also for open sidewalls, resulting in normal CNT growth.

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