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A versatile plasma tool for the synthesis of carbon nanotubes and few-layer graphene sheets

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A technique is reported for the study of the combined growth process of carbon nanotubes (CNTs) and few-layer graphene sheets (FLGS) by means of microwave plasma-enhanced chemical vapour deposition. The carbon radical concentration is identified as the most important parameter for determining the morphology of the as grown carbon nanostructures, either tubular CNTs or plain FLGS. During an experiment, each position on the samples is exposed to a specific carbon radical concentration. Samples, composed of nickel particles deposited on silicon oxide substrates, catalyze the growth of CNTs only if the carbon radical concentration is low. A rapid transformation of morphology from tubes to flakes can be observed when the carbon radical concentration increases. The flakes, formed at the highest carbon radical concentration, are identified as FLGS, only a few atomic graphene layers thick but up to several micrometers wide. A possible growth scheme, based on qualitative analysis by electron microscopy is presented. It is further shown that the growth of FLGS does not require a catalyst by using plain silicon and quartz substrates without nickel for the FLGS synthesis.

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1. Introduction

The recent discovery of a fairly easy but elaborate synthesis route for the isolation of graphene sheets by micromechanical cleavage [1] has motivated many research groups to investigate graphene's properties and develop prototype applications. Room temperature quantum hall effect [2], massless dirac fermion transport behaviour [3], atomic resolution chemical detectors [4] and graphene oxide paper [5] are some of the exciting results that make graphene a popular and promising science topic with an ever increasing number of dedicated publications.

In order to make large scale graphene devices, a cheap mass production technique for the synthesis of few-layer graphene sheets (FLGS) is required. Current popular techniques like micromechanical cleavage of bulk graphite, chemical exfoliation [6] and epitaxial growth [7] are elaborate and not very likely candidates for mass production. Plasma-enhanced chemical vapour deposition (PECVD) has been put forward by many groups as a promising tool for the mass production of FLGS [8-12] but needs to be optimized in order to control the average number of atomic layers in each flake. Because the PECVD flakes are on the average approximately more than 10 graphene sheets thick and the extraordinary electronic properties of graphene quickly disappear when stacking more than three graphene sheets [13], the PECVD synthesized material is often considered nanostructure graphite and denoted with the name carbon nanowalls (CNWs) [8]. If so called CNWs can be shown to exhibit some of the exceptional graphene properties or if their production techniques can be optimized to limit the average number of sheets to a maximum of three, graphene based devices will be in sight. To be consistent in notation and since both FLGS and CNWs intrinsically denote the same material, only the former notation will be used throughout the manuscript.

We present microwave (MW) PECVD results of the combined growth of CNTs and FLGS. Both carbon nanostructures are synthesized during the same experiment by varying the carbon radical concentration, suggesting that the carbon radical concentration is the most important parameter for controlling the morphology of the as grown carbon nanostructures, either tubular or plain. The carbon radical concentration is varied by shielding the sample from the plasma in such a way that the corners of each sample are more exposed to the plasma than the centre regions. This way, a carbon radical concentration gradient is created from the centre to the edges of the sample without changing the process parameters. A clear transformation of morphology from tubes to freestanding sheets can be seen when analysing the sample from the centre to the edges. These results are used to develop a possible PECVD growth scheme for carbon nanostructures.

♣Awarded for the best oral presentation

The metal catalyst quickly saturates when exposed to abundant carbon radicals, thereby prohibiting CNT growth. Therefore, it is evident that the catalyst does not play an important role in the growth of FLGS, which are only synthesized in regions exposed to the highest carbon radical concentration. It is shown that the growth of FLGS does not require a catalyst by using plain silicon and quartz without nickel as substrates for the FLG synthesis.

2. Experimental methods

CNTs and FLGS were synthesized in a MW PECVD setup composed of an IPLAS Cyrannus MW plasma source mounted on top of a stainless steel vessel. The plasma source consists of a 6 kW, 2.45 GHz cylindrical MW resonator, which couples the MW power through five annular slots in a quartz tube. A stainless steel substrate holder is positioned in the centre of the quartz tube.

For the combined growth experiments, samples were prepared by molecular beam epitaxy deposition of a 1 nm thin nickel catalyst film on an oxidized 2 by 2 cm silicon wafer. The samples were annealed in H_2 environment at 750°C for 30 minutes. Because the synthesis of FLGS does not require a catalyst, various other materials like quartz and silicon were also successfully used as substrates.

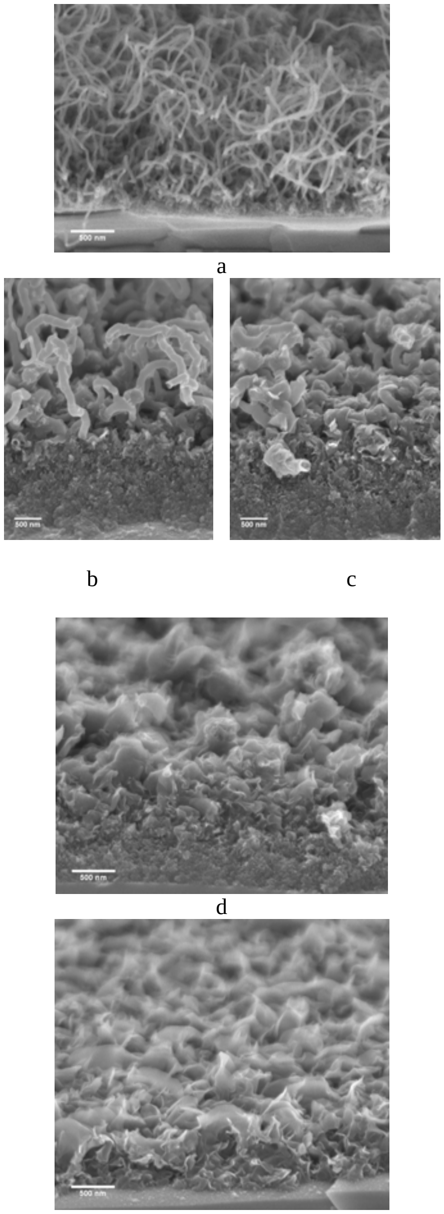
In order to shield the samples from the plasma and this way controlling the carbon radical concentration, the samples are put “up side down” on the substrate holder. This means that the nickel coated side of the sample is facing the substrate holder instead of the plasma, as would be the case in a regular experiment.

Previous to growth, the substrates are heated for 20 minutes in a 2 kW MW plasma at 40 Torr, using a H_2 flow of 200 sccm. This plasma is sufficiently powerful to heat the samples from room temperature up to 700° C as measured by a thermocouple embedded in the substrate holder. Immediately after the heating step, methane (CH_4) is mixed with H_2 with varying CH_4/H_2 ratio ranging from 1/4 to 1/8 at a total flow rate of 200 sccm. Keeping the plasma power and pressure at 2 kW and 40 Torr respectively, CNTs and FLGS are grown with these gas mixtures during various growth times ranging from 30 minutes to 1 hour.

The carbon nanostructures obtained in this way are analyzed with field emission scanning electron microscopy (FESEM, JSM-6340F) and transmission electron microscopy (TEM). Transmission electron microscopy was carried out using a Jeol 4000EX microscope operated at 400 kV.

3. Results and discussion

A possibility to study the influence of the carbon radical concentration on the morphology of the carbon nanostructures, without changing the PECVD process parameters, is to shield the sample from the plasma. This was done by positioning the samples “up side down” in the MW reactor. The nickel coated side of the samples makes contact with the substrate holder, which acts at the same time as a shield for the plasma. This way, the carbon radical concentration is very low at the centre regions of the sample in contrast to the edges, which are exposed to a much higher carbon radical concentration. Subsequent cross-section SEM micrographs were taken at intervals of 0.15 mm, scanning the sample from the centre to the edge. These results reveal a clear change in morphology of the as grown carbon nanostructures over a short distance of approximately 0.7 mm as presented in Fig. 1:



a

b c

d

e

Fig. 1. Subsequent cross-section SEM micrographs, taken at regular intervals of approximately 0.15 mm from the centre (A) to the edge of the sample (E). These results reveal a clear change in morphology of the as grown carbon nanostructures over a short distance of approximately 0.7 mm, due to an increase in the carbon radical concentration.

- In the centre region of the sample, exposed to the lowest carbon radical concentration, CNTs are synthesized out of the nickel catalyst islands (see Fig. 1A). The tubes are approximately 50 nm thick and therefore clearly multi-walled. The tubes grow according to the tip growth mechanism, with the nickel catalyst particles visualised in the tip of the tubes, pushed upwards by the growing CNTs.
- Already a clear change in morphology can be seen in Fig. 1B., 0.15 mm away from the centre towards the edge of the sample. Due to an increase in carbon radical concentration, a 1 µm thick layer of amorphous carbon covers the roots of the tubes. The carbon nanostructures still have a tubular shape, but their thickness has doubled and the sidewalls are decorated with branches.
- Another 0.15 mm more to the edge in Fig. 1C, the carbon nanostructures are shaped in between tubular and plain sheets, with branches that are clearly visible as thin flakes, growing out of the sidewalls of the tubes. The amorphous base layer, covering the roots of the tubes has increased in thickness with approximately 50 %.
- As the carbon radical concentration continues to increase even more close to the edge of the sample, the tubular shape is completely transformed into planar sheets (see Fig. 1D and Fig. 1E), with FLGS growing vertically to the substrate surface. A contra-intuitive and remarkable fact is the decrease of the amorphous layer which even vanishes at the edges of the sample where the carbon radical concentration is the highest.

From the above results, we conclude that the carbon radical concentration is the most important factor in determining the morphology of the synthesized carbon nanostructures. CNTs can only be produced if a catalyst is present and the carbon radical concentration is low enough to prevent catalyst poisoning (see Fig. 1A). When increasing the carbon radical concentration, tubular shapes and amorphous carbon will be formed as long as the catalyst remains active (see Fig. 1B – Fig. 1D). At high carbon radical concentrations, a metal catalyst is useless since abundant carbon immediately saturates the metal and FLGS are formed (see Fig. 1E).

FLGS don't require a catalyst for the growth, any substrate and surface can be used, even the sidewalls of CNTs can be nucleation sites as evidenced from Fig. 1B and Fig. 1C. FLGS were grown on plain silicon and quartz substrates in the absence of a catalyst. A typical SEM micrograph of the results in presented in Fig. 2. The FLGS were further analysed by TEM to verify the internal structure. It is concluded from Fig. 3 that the flakes on the average consists of 13 atomic layers graphene, since the measured interlayer distance corresponds to the tabulated values for graphite.

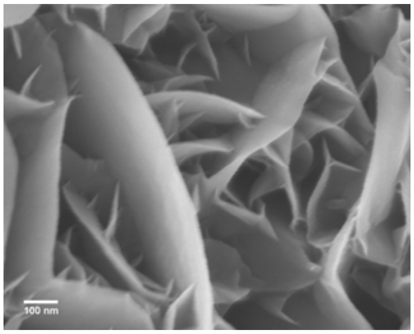


Fig. 2. SEM micrograph of FLGS grown on silicon substrates without the need for a metal catalyst.

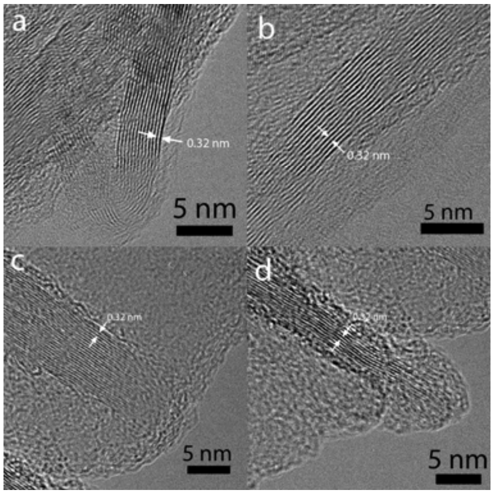


Fig. 3. TEM micrographs of FLGS show that the flakes on the average consist of 13 atomic layers with a typical interlayer distance of graphite.

4. Conclusions

In conclusion, a versatile MW PECVD technique is presented for the study of the combined growth of CNTs and FLGS. The FLGS can be synthesized together with the CNTs depending on the carbon radical concentration. We have identified the carbon radical concentration as the most important parameter for determining the morphology of the as grown carbon nanostructures, either tubular CNTs or stacked FLGS. Nickel particles only catalyze the growth of CNTs if the carbon radical concentration is low. A rapid transformation of morphology from tubes to flakes is observed when the carbon radical concentration increases. The flakes, formed at the highest carbon radical concentration, were identified as FLGS, only a few atomic graphene layers thick but up to several micrometers wide. A possible combined growth scheme, based on qualitative analysis by electron microscopy was presented. It was shown that the growth of FLGS does not require a catalyst by using plain silicon and quartz substrates without nickel for the FLGS synthesis.

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