RAMAN SPECTRA AND MORPHOLOGY OF CARBON NANOTUBES IN DEPENDENCE ON TEMPERATURE OF DEPOSITION BY CAPACITIVELY COUPLED RF PLASMA PROCESS

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Introduction

Specific interest has been focused on carbon nanotubes (CNTs) [1] as possible wiring elements in the nanometer range. Since 1991, many methods have been developed for the synthesis of single and multi-wall carbon nanotubes [2,3]. These techniques vary not only in their chemical principle (thermal or plasma enhanced process) but vary by the deposition system itself. Common feature of all these processes is using of transitions metals like Ni, Co, Fe as the catalyst. However, up to know only few works focus on detailed study of CNT growth at different substrate temperatures.

In the present work we investigate the influence of temperature on the growth of CNTs by a radio frequency glow discharge PECVD system. CNTs are synthesized on Si/SiO_2 substrates from the gas mixture of methane and hydrogen and using nickel as the catalyst layer. The morphology and the structure of grown nanotubes are investigated by scanning electron microscopy (SEM) and Raman spectroscopy.

Experimental

Carbon nanotubes synthesis was realized by rf (13.56 MHz) PECVD reactor, shown in Fig. 1 [4].

Si wafers (10x10 mm) coated with 1,4 μm thick SiO_2 layer were used as the substrates. The SiO_2 layer acts as a diffusion barrier between Ni and Si precluding the formation Ni silicide. The Ni layer (thickness 5 nm), used as the catalyst, was deposited by the thermal evaporation method. The thickness of Ni was monitored by *in situ* measurement using a quartz-crystal-based thickness monitor (INFICON XTC/2). Next, the Si/SiO2 substrates covered with catalyst layer were thermally treated in H_2 atmosphere using an ellipsoid microwave plasma reactor (AIXTRON P6). The process conditions were as follows: gas pressure 30 mbar, H_2 flow 300 sccm, microwave power 1300 W, and temperature was in range 750÷800°C, treatment time 5 min.

After the annealing process, set of CNT growth experiments was carried out at different substrate temperatures ranging 250 ÷ 560°C. Gas mixture of methane and hydrogen was used as the source gases and the flow rates were 20 and 60 sccm, respectively.

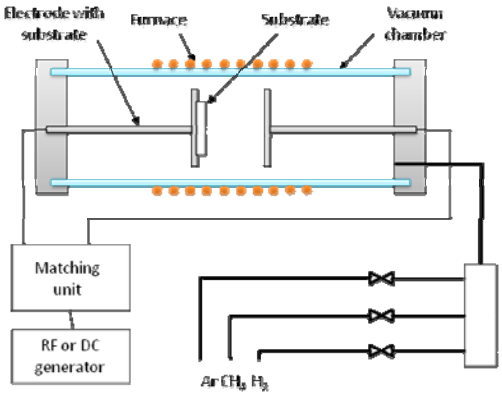

Fig. 1: Schematic diagram of the radio frequency PECVD reactor

After stabilizing the substrate temperature, the depositions were carried out for 15 min in stable discharge at power of 450 W.

CNTs were characterized by Scanning electron microscopy (SEM, Raith *e*_LiNE). Raman measurements were performed using an ISA DILOR-JOBIN YVON-SPEX Labram confocal system with 632.8 nm radiation from a He-Ne laser.

Results and discussion

Influence of the deposition temperature on the growth of CNT was studied for three different temperatures ranges: low temperature (250°C), medium temperature (400°C) and high temperature (560°C). Other deposition parameters like total gas mixture, total power, etc. were kept at constant for all samples deposited.

Figure 2 shows SEM images of grown CNTs at different substrate temperatures. The sample

deposited at the lowest temperature, i.e. 250°C, exhibits non-homogenous features (Fig. 2a). The surface looks like an amorphous carbon layer with isolated Ni particles which are partially embedded in the layer bulk. Figure 2b represents the sample grown at medium temperature, i.e. 400°C. First, the surface character changes substantially to the previous sample. A development of 3D-like structures is observed. However, poor density CNT is observed which indicates that this temperature range is still too low to obtain a CNT growth. On the other side, when the deposition temperature increased up to 560°C, a clear evidence of CNTs presence is observed (Fig. 2c). The nanotubes have been grown at relatively high density and they are partially ordered in vertical direction. The outside diameter of grown CNTs is in the range between 20 and 35 nm.

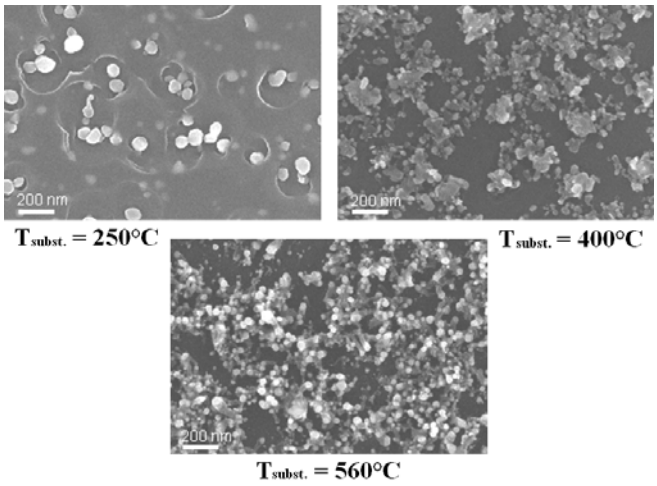

Fig. 2: Surface morphology of samples grown at different substrate temperatures of (a) 250°C, (b) 400°C and (c) 560°C.

Raman measurements of the deposited samples are shown in Fig. 3. For the first comparison, no significant differences among the spectra are observed. The peaks at 180 and 200 cm^{-1} are found for all the samples (Fig. 3a). These peaks are usually assigned to the radial breathing mode (RBM) of single-walled nanotubes [5]. This result indicates that should be presented also over sample grown at the lowest substrate temperature. We assume that due to their low density and low contrast we did not observed them by SEM measurements.

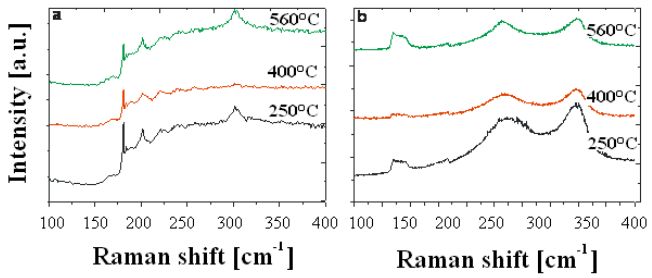

Fig. 3: Raman spectra of samples grown at low, medium and high temperatures: (a) the RBM region and (b) region D and G-bands.

The Raman spectra collected for higher wavenumbers reveal three broad bands for all temperatures studied, Fig. 3b. One is located at 1320 cm^{-1} (known as the D-band) and the second one lies at around 1580 cm^{-1} (known as the G-band). The D-band arises from amorphous carbon or defects in the nanotube walls while the G-band corresponds to the graphitic sheets of the CNTs. The third broad band centered at 970 cm^{-1} is assigned to the second order vibration mode of the silicon substrate [6].

Conclusions

Carbon nanotubes have been synthesized on Si/SiO_2 substrates by rf plasma-enhanced CVD system from a gas mixture of methane and hydrogen. The morphology showed a dependence of CNT growth on the substrate temperature. The presented study distinguishes between three regions: the low temperature range where poor CNTs growth was observed and layer-like deposition dominated, the medium temperature range where the transition in growth from two-dimensional to the complex 3D-like structures was observed, and high temperature range where CNTs dominated the CVD process. Raman measurements indicated presence of CNTs in the whole investigated temperature range. For our experimental setup, the minimum substrate temperature required for an effective growth of CNTs was 560°C.

Acknowledgment

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