

DEPOSITION OF CARBON NANOSTRUCTURES BY SURFATRON GENERATED DISCHARGE

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ABSTRACT. Various carbon nanostructures were deposited by surface wave discharge from an Ar/CH₄/CO₂ gas mixture. The type and the form of the carbon nanostructure were controlled by the gas mixture and the gas inlet. The nanostructures that formed were investigated by scanning electron microscopy and by Raman measurements. The influence of the geometrical combination of the gas inlets (via surfatrons or via the gas shower system) into the chamber is found to be a crucial deposition parameter for the controllable growth of desired carbon nanostructures.

KEYWORDS: surfatron, carbon nanostructures, microwave plasma, PECVD.

1. INTRODUCTION

Plasmas are extremely successful in many industrial thin-film applications, e.g. in the production of micro-electronic devices and solar cells [1] and for biomedical applications [2]. Many of these thin-film materials have been successfully developed using mainly empirical methods. Microwave (MW) plasma is frequently used in so-called plasma-enhanced chemical vapor deposition (PECVD). In MW PECVD, the feed gas mixture is ionized and excited by microwave radiation in a reaction chamber. Ionized and excited neutral atomic and molecular components from plasma, generally of low fractional ionization, in which radicals and neutral react and/or recombine and finally condense onto the substrate as a thin film [3]. The commercial and technical value of low temperature plasmas is well established.

Among the broad range of plasmas, surface wave discharge (SWD) is nowadays considered promising as a low-temperature process for depositing various coatings. SWD is widely used in the engineering industries as a source of reactive radicals and for depositing ZnO thin films, SiO_xC_yH thin films, semiconductive SiGe films, and some others [4–7]. However, deposition of carbon nanostructures by SWD is not broadly used. SWD is characterized by the transport of energy toward an active plasma area by an electromagnetic wave that is spread along the plasma column [7]. The so-called surfatron waveguide can operate both in a continuous regime and in a pulsed regime employing a microwave generator.

Low-temperature MW plasma is a strongly non-equilibrium system generating an exotic physical and chemical environment through free electrons at low gas temperatures. This unique environment allows the treatment of temperature-sensitive materials at molecular precision.

In the present work we investigate the growth of var-

ious carbon nanostructures by surface wave discharge. The influence on the deposition process of gas flow rate, gas mixture and the geometrical combination of gas inlets (via surfatrons or via a gas shower system) into the chamber is discussed here.

2. EXPERIMENTAL DETAILS

2.1. DEPOSITION SYSTEM

Figure 1 shows the experimental set-up of a modified plasma-enhanced CVD reactor [7]. The plasma system consists of 4 independent nozzles (surfatrons) which form a single SWD. The nozzles are connected to the microwave source (2.45 GHz). The MW generator used here can be operated both in continuous mode and in pulsed mode, with averaged absorbed power of about 300 W per surfatron and with repetition frequency $f = 60$ Hz.

The process gases were introduced into the vacuum chamber via surfatrons (1 or 4 nozzles) or via a gas shower. The distance between the sample and the surfatron outlet(s), i.e., the quartz tube, varied in the range from 1 to 3 cm.

2.2. DEPOSITION OF CARBON NANOSTRUCTURES

The deposition of the carbon nanostructures comprised three steps:

- (1.) A catalyst fabrication step, which employed thermal evaporation of an Ni layer (6 nm in thickness) on 10×10 mm² Si/SiO₂ substrates. The thickness of the Ni was monitored by *in situ* measurements, using a quartz-crystal-based thickness monitor (INFICON XTC/2).
- (2.) A thermal treatment step, during which the Si/SiO₂ substrates covered with a catalyst layer were thermally treated in hydrogen plasma using the large area pulsed linear-antenna microwave plasma

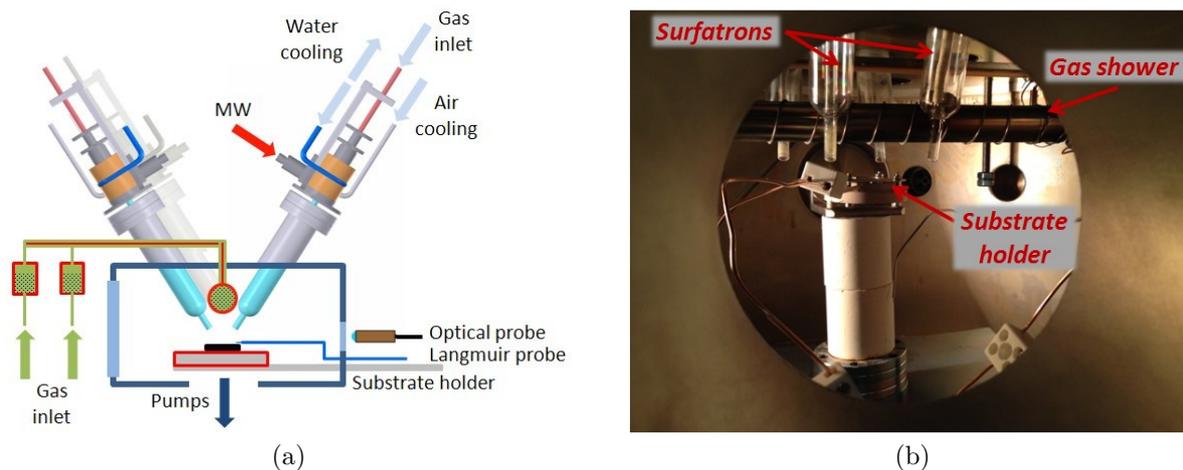


FIGURE 1. Schematic view of the modified plasma-enhanced CVD surface-wave discharge set-up used for depositing the carbon nanostructures (a) and the digital photography inside the vacuum chamber (b).

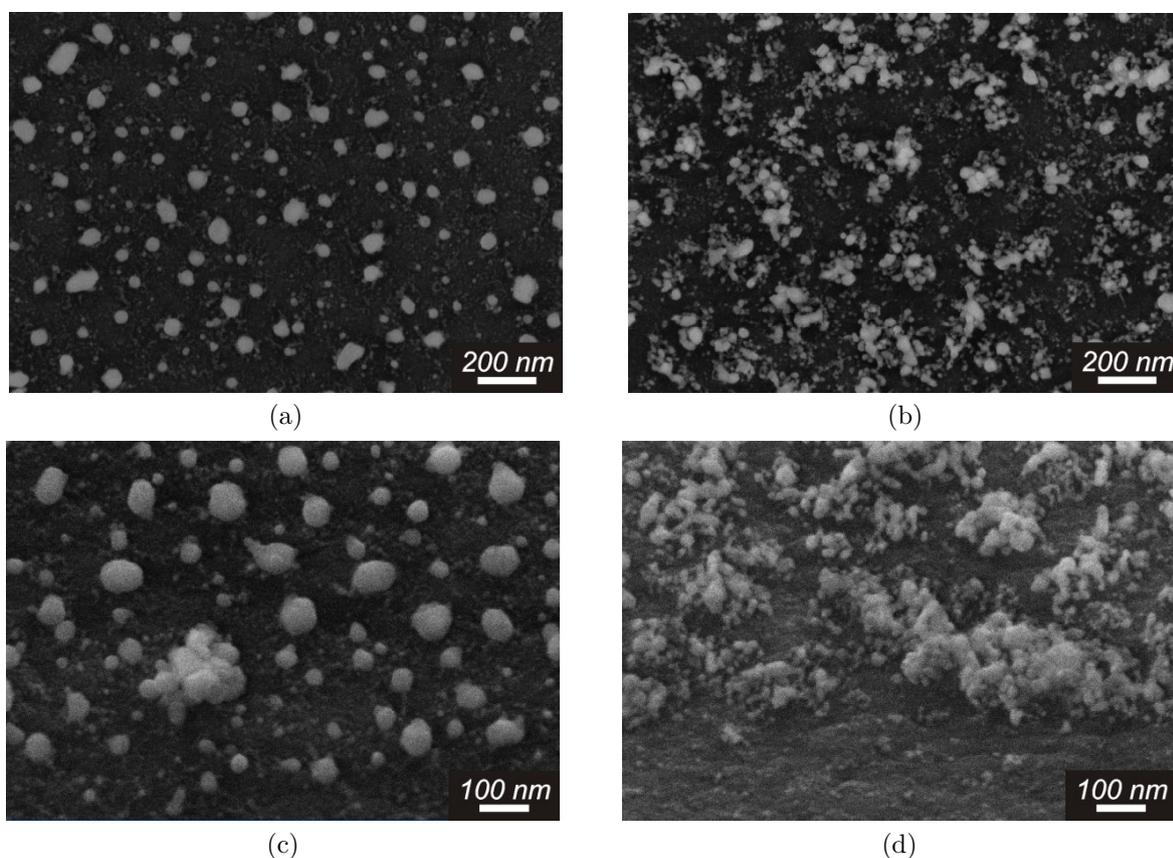


FIGURE 2. Surface morphology of carbon nanostructures deposited under various conditions: (a, c) Ar/CO₂ gases were injected through the single surfatron, and CH₄ was transported via a parallel surfatron, (b, d) Ar/CO₂ gases were injected via 4 surfatrons and CO₂/CH₄ gases were introduced through the shower head.

CVD process [8]. The process conditions were as follows: $P = 1700$ W, gas pressure 20 mbar, H₂ flow 300 sccm, substrate temperature $T_s = 650$ °C and treatment time 10 min. After the annealing process, the catalyst layer decomposed into small nickel clusters about 40 nm in diameter.

(3.) Deposition of carbon nanostructures, which was carried out using the modified plasma SWD PECVD system. The system was pumped to

a base pressure of 0.008 mbar and was then maintained at a pressure of 0.2 mbar by introducing an Ar carrier gas at a flow rate of 100 sccm and various ratios of CO₂ and CH₄. The flow of methane was changed from 60 to 90 sccm, while the flow of carbon dioxide was kept at a constant value of 30 sccm. A microwave power input of 300 W operated in the external modulation mode was used in all the experiments. Dur-

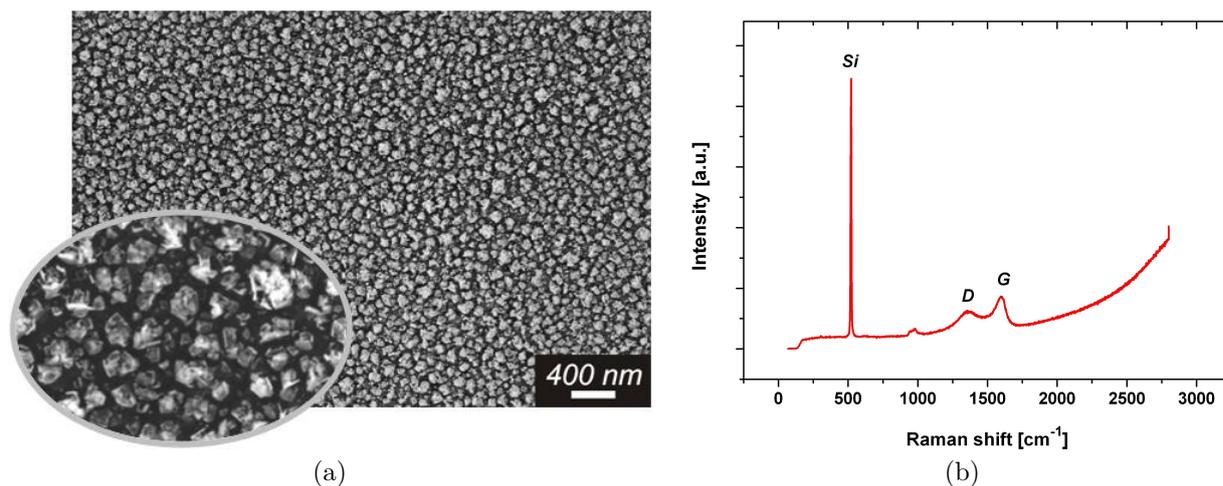


FIGURE 3. Top-view SEM image (a) and Raman spectrum (b) of carbon nanostructures deposited under the following conditions: Ar/CO₂ gases were injected through a single surfatron, and CH₄ gas flowed through parallel surfatrons.

ing the deposition process the substrate temperature was maintained at 650 °C and the deposition time was 15 min. The distance between substrate holder and precursor outlet was varied from 1 to 3 cm.

2.3. MATERIAL CHARACTERIZATION

The surface morphology of the coatings (carbon nanostructures) was characterized by scanning electron microscopy (SEM *e_LiNE* writer, Raith GmbH) and was confirmed by UV-Raman spectroscopy (Renishaw InVia Reflex Raman spectrometer, 442 nm excitation wavelength).

3. RESULTS AND DISCUSSION

Figure 2 shows the surface morphology of carbon nanostructures deposited using various CH₄/CO₂ flow rates. The distance between substrate holder and quartz nozzle outlet was 1 cm. The SEM images clearly confirm that only isolated nanoislands were formed using an Ar/CO₂/CH₄ gas mixture (100/30/60 sccm) (Figure 2ac). The surface morphology changed considerably after the CH₄ gas flow was increased from 60 to 90 sccm (Figure 2bd). In this case, the SEM measurements indicate the development of nanotube-like structures. The Raman spectroscopy measurements did not reveal a reasonable signal of carbon phases.

Next we investigated the influence of sample position. The distance between substrate holder and precursor outlet increased to 3 cm. As in the previous case, a gas mixture of Ar/CO₂/CH₄ (100/30/60 sccm) was introduced to the chamber. The SEM image reveals the formation of a porous-like structure consisting of nanosized features (Figure 3a). The Raman spectrum (Figure 3b) is represented by three strong contributions: the silicon characteristic peak centered at 520 cm⁻¹ (Si-peak) and two broad bands centered at approximately 1350 cm⁻¹, which is attributed to the D band, and at approximately 1590 cm⁻¹, which

is attributed to the G band. The D band is usually assigned to the disorder and imperfection of the carbon crystallites, whereas the G band is one of the two E_{2g} modes of the stretching vibrations in the sp² domains of perfect graphite [9]. In addition, a weak broad band resolvable at 970 cm⁻¹ reflects the second-order peak of the Si substrate [10].

Increasing the methane flow from 60 to 90 sccm in combination with varying the gas inlet(s) resulted in the formation of vertically ordered carbon nanowalls (Figure 4ab). The distance between substrate holder and precursor outlet was kept at 3 cm. Figure 4c shows the Raman spectrum of the nanostructures that formed. Four basic features are recognized in the Raman spectrum: a sharp Si peak centered at 520 cm⁻¹, the D band (1369 cm⁻¹), the G band (1570 cm⁻¹), and the second-order D band (2D-band). The 2D band centered at 2720 cm⁻¹ is attributed to the typical symbol of graphitic carbon [11–13]. Moreover, it should be noted that the radial breathing mode (RBM) was not detected in any samples, i.e., absence of single or multiwall carbon nanotubes.

These results clearly confirm that various carbon nanostructures can be deposited by a surface wave discharge. The gas mixture and the working gas inlet to the process chamber were found to be the crucial parameters for the growth of various carbon forms/types. Increasing the CH₄ concentration and using the shower head for introducing working gases into the chamber led to the formation of carbon nanowalls (Figure 4ab). We found that reactive gases (CO₂ and CH₄) are optimally decomposed at the substrate by Ar plasma due to a set of plasma-chemical reactions which finally support the growth of carbon nanostructures. Moreover, we found that the optimal distance for deposition of carbon nanostructures is 3 cm for our experimental SWD process. These observations represent unique and, in certain cases, advanced features of the surfatron system.

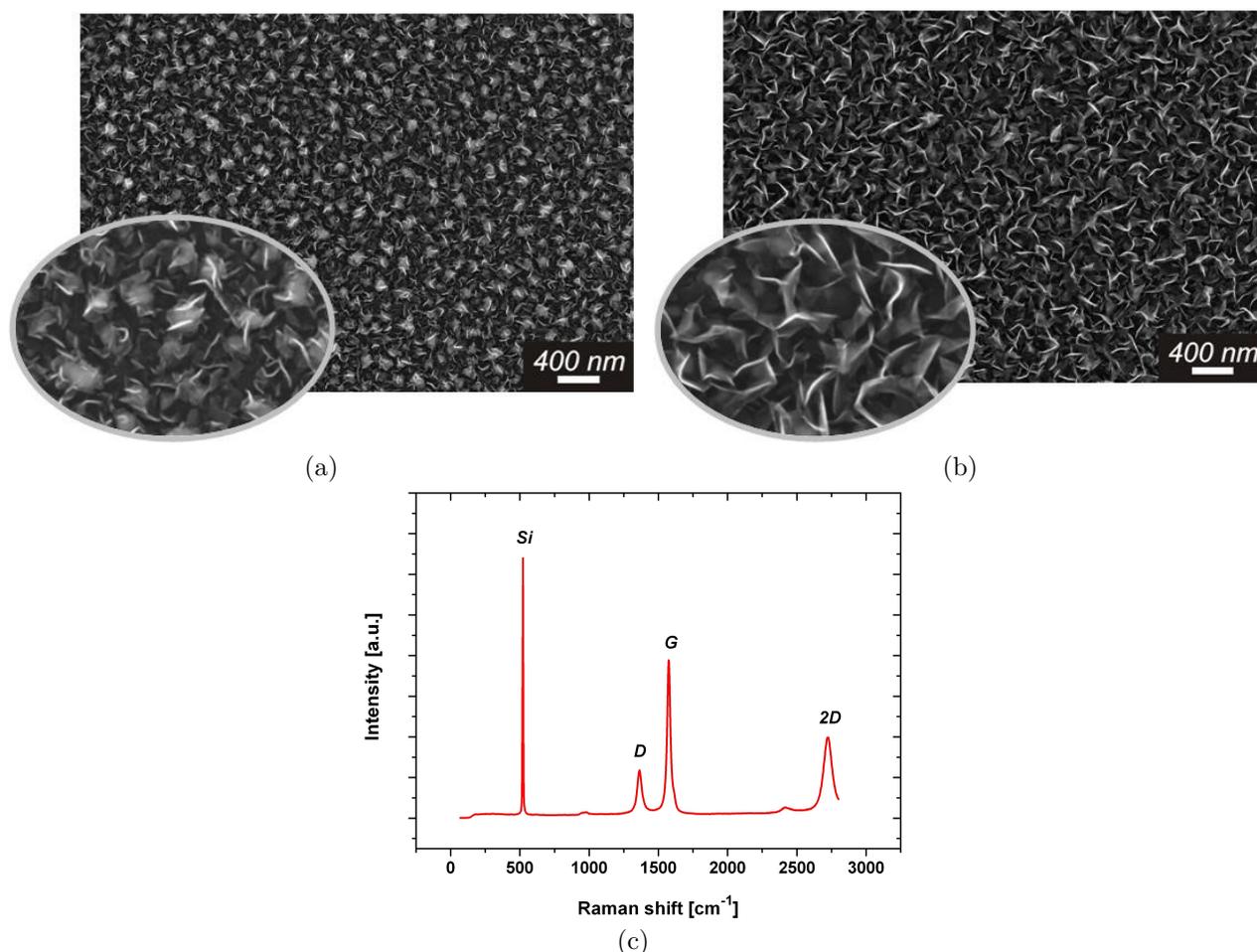


FIGURE 4. Top-view SEM images (a, b) and the Raman spectrum (c) of carbon nanostructures deposited under the following conditions: Ar gas was injected via 4 surfatrons, and CO_2/CH_4 gases were introduced through the shower head.

4. CONCLUSIONS

We have introduced the modified plasma enhanced CVD system working on the principle SWD as a versatile deposition system for the growth of various carbon nanostructures. We have shown that the carbon structures that are formed are significantly influenced by the gas mixture (i.e., ratios of CO_2/CH_4) and by the chosen gas inlet(s) for achieving the proper gas decomposition and/or plasma-chemically driven reactions at the substrate surface. The formation of carbon nanowalls was observed after the methane content was increased and its flow via the shower head was forced. We assume that the implementation of SWD will open new prospects in deposition of carbon allotropic forms, or even for gentle surface modification.

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