Growth of Carbon Materials on Gold Substrate by Plasma Enhanced CVD

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1 Introduction

Carbon is a versatile building element of many interesting materials that have already find practical applications in the form of thin films (diamond, DLC) or potential applications in the form of nanostructures (fullerenes, carbon nanotubes, graphene). For electronics or sensors, it is important to provide a very good contact to the functional structures. Gold is the best choice taking into account its inertness, i. e. oxidation resistance. From this point of view the investigation of the growth of carbon materials on gold is important. The carbon-gold interaction plays an important role in different fields of electronics such as atomic force microscope lithography [1], bioelectronics [2] or semiconductor industry. Research in this field is developing rapidly e. g. the modification of interface structure and contact resistance between a CNT and gold electrode was recently modified by Joule melting and amorphous C-Au nanocomposite thin films were deposited by dc magnetron co-sputtering [3].

Herein we report on the preparation and characterization of the carbon nanocomposites which were synthesized on gold substrate from methane precursor using low pressure thermal chemical vapor deposition technique and two different plasma-enhanced chemical vapor deposition (PECVD) methods. The former one PECVD proceeded in microwave reactor at low pressure and the latter one was carried out using non-thermal atmospheric pressure plasma jet (ntAPPJ). Presented approach is based on the deposition of carbon material on gold instead of the deposition of gold on carbon material which is more common. Surprisingly, we didn't find similar studies dealing with the synthesis of carbon nanocomposites using direct deposition from hydrocarbon precursor on the gold thin film. The surface morphology was studied by high resolution scanning electron microscopy (HRSEM). Depth-structure profile including the film thickness was observed using the focused ion beam ablation. Energy-dispersive X-ray spectroscopy (EDX), infrared reflection absorption spectroscopy (IRRAS) and laser desorption-ionization time of flight mass spectrometry (LDI-TOF MS) were used to study the chemical properties. Gold and carbon related clusters were observed by means of mass spectrometric study.

2 Experimental section

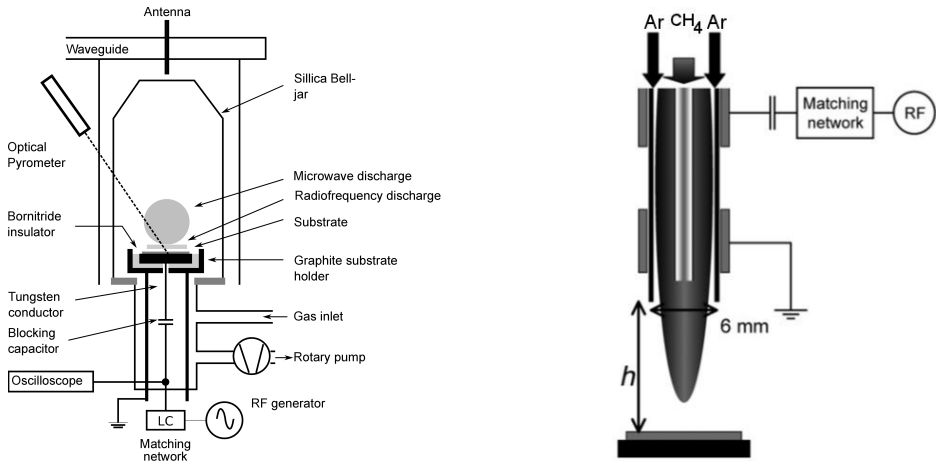
The silicon was covered with 100 nm thick gold layer using thermal evaporation. The substrate was then processed employing chemical vapor deposition using methane as precursor. Corresponding deposition conditions are listed in Tab. 1. The thermal CVD proceeded in the center of horizontal furnace inside quartz glass tube (1 m long, inner diameter 45 mm and hot zone length of 150 mm) terminated with flanges. The furnace deposition temperature was measured by K type thermocouple. The microwave low pressure PECVD proceeded in the conventional silica bell jar ASTeX-type reactor (Fig. 1a) operating at the frequency of 2.45 GHz. The power supplied to the plasma was 850 W. On the graphite holder of the substrate was applied 13.56 MHz RF 35 W power to ignite capacitively coupled discharge and to maintain negative self-bias voltage about 70 V on the substrate holder during deposition. The deposition started by the introduction of methane. The substrate temperature was measured using optical pyrometer and was about 900°C [4].

The radio frequency PECVD has been carried out by a miniaturized non-thermal atmospheric pressure plasma jet (Fig. 1b) [5]. The design of this plasma source features two outer copper ring electrodes (width $w = 4.0$ mm,

distance $d = 4.9\,\mathrm{mm}$) attached to the outer quartz capillary ($D_{out} = 6.0\,\mathrm{mm}$, $D_{in} = 4.0\,\mathrm{mm}$). The electrodes are RF shielded by a grounded metal enclosure. The upper electrode is capacitively coupled to the RF generator (27.12 MHz, DTG2710, Dressler) over a matching network and the power supplied to the plasma was 9 W. The lower electrode is connected to ground potential. Inside the outer capillary a inner capillary ($D_{out} = 1.85\,\mathrm{mm}$) is positioned to provide the thin film precursor during film deposition experiments. Downstream of the active plasma zone (between the electrodes) a chemically reactive effluent develops [6]. During the experiments reported here, the outer channel was fed with argon and the inner channel was fed with methan. The deposited area was a circle with the diameter of 6 mm.

Sample	Method	I (sccm) CH4	I (slm) next gas	Pressure (bar)	Deposition time (min)
1	Thermal	7.6	0.3 H_2	0.08	20
2	MW	7.6	0.3 H2	0.08	40
3	AP	1.5	1 Ar	1	60

Table 1: Deposition conditions



(a) MW reactor (b) APPJ

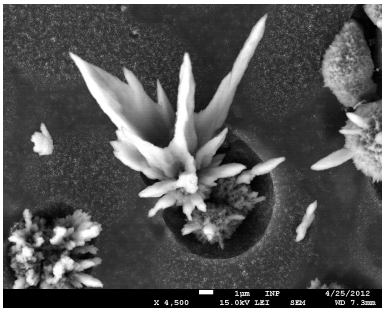
Figure 1: Deposition devices

3 Results

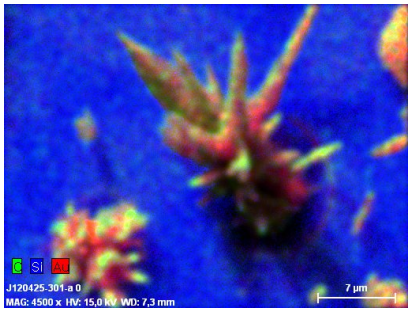
The 3D mesoscopic structures were prepared on the sample 1 using thermal low pressure CVD in CH_4/H_2 atmosphere. Figure 2a shows detailed SEM picture of one of these structures. Similar anisotropic gold mesostructures with complex shapes have been recently reported and are called mesoflowers [7]. Mesoflowers consist of a large number of stems, which are growing outward from the core making the mesoflower 3D. Their number is different for each mesoflower. Recently published mesoflowers were prepared through seed-mediated growth using oligoaniline-capped Au seed nanoparticles and were composed of pure gold [8]. In contrast to this, in the present study, the mesoflowers have been produced differently by thermal CVD. The spatially resolved EDX image of the mesoflower that is shown in Fig. 2a gives an evidence on the chemical composition of the mesoflower. The EDX signal shows that prepared mesoflowers are mainly composed of gold and partially of carbon.

The carbon layer on gold of the sample 2 which was synthesized during microwave low pressure PECVD in CH_4/H_2 atmosphere shows detailed SEM image (Fig. 3a). After high temperature annealing which takes place during this type of deposition process re-structuring of gold takes place. Spatially resolved EDX analysis in Figure 3b shows gold islands which were created by melting of the origin gold layer. The inner structure of this layer was estimated using FIB ablation. This method showed that about 120 nm thick carbon layer was deposited over gold. The island-formation of gold was also observed on the cross-section of this layer.

The thin homogenous a-C:H film was prepared on the gold surface of the sample 3 by means of ntAPPJ. Small spherical particles have been sporadically observed on the film (Figure 4a). The size (about one micron) of these particles is in agreement with carbon spheres that were prepared earlier in the radio frequency plasma [9]. Spatially resolved EDX analysis in Figure 4b demonstrates the chemical homogeneity of the distribution of carbon and gold on the sample. In this case, in addition to the formation of gold clusters, gold carbides and gold silicides were detected by LDI-TOF MS measurement and the stoichiometric formulas of gold carbides $Au_mC_n^+$ and other clusters identified are shown in Figure 5. Intensities of Au carbides and silicides reach about 20-30 percent of the intensities of Au-clusters. The results proof that the formation of carbides is significant. Recently, laser ablation synthesis of various gold carbides from the carbon obtaining materials has been published [10, 11, 12].

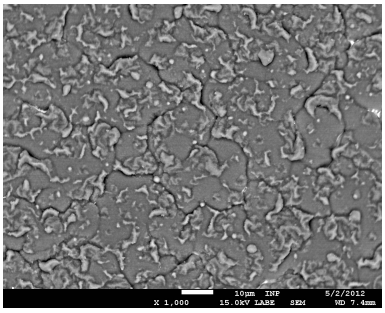


(a) SEM picture.

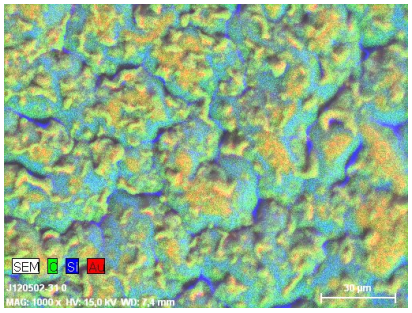


(b) Spatially resolved EDX.

Figure 2: Growth of the mesostructures during low pressure thermal CVD (sample 1).

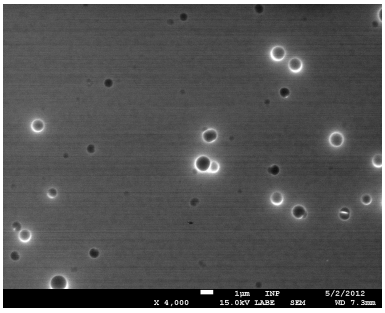


(a) SEM picture.

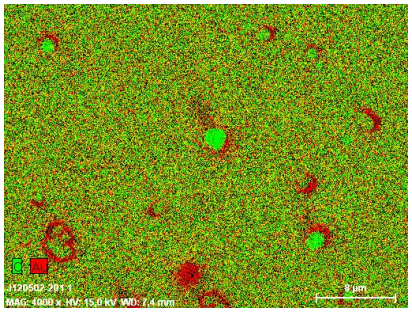


(b) Spatially resolved EDX.

Figure 3: Carbon layer on gold created during low pressure microwave PECVD (sample 2).



(a) SEM picture.



(b) Spatially resolved EDX.

Figure 4: Carbon spheres generated on gold during atmospheric pressure radiofrequency PECVD (sample 3).

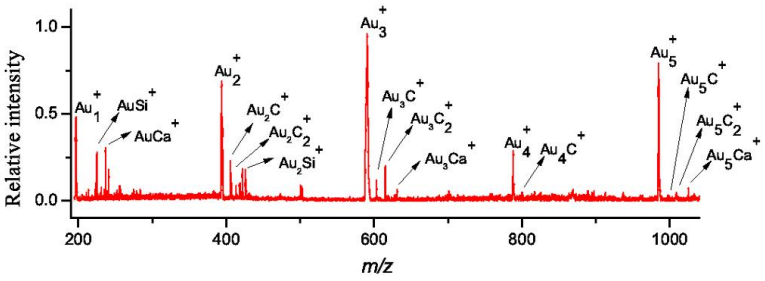


Figure 5: LDI-TOF MS of sample 3, positive ion mode, 5 laser shots used at laser energy 140 a.u.

4 Conclusions

Three different CVD deposition techniques of the carbon deposition on gold have been investigated. Gold mesoflowers were prepared by low pressure thermal CVD in CH_4/H_2 atmosphere. To the best of our knowledge we are not aware that someone has used the thermal CVD for growth of these structures before. We propose a growth mechanism which consists of local melting, renucleation and aggregation of gold in the form of islands, self-assembling of gold and further growth of mesoflower. Homogenous a-C:H film has been deposited using ntAPPJ and various $Au_mC_n^+$ clusters were detected after the laser ablation of corresponding sample using mass spectrometry.

References

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