

Nanostructure Formation during Amorphous Carbon Films Deposition

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Influence of Cu particles for the carbon nanostructures formation during a-C:H films deposition by plasma enhanced chemical vapor deposition method from pure acetylene gas plasma were analyzed in this work. Silicon wafer and Cu target were simultaneously bombarded by Ar^+ ions for the Cu particles deposition on the silicon before a-C:H films formation. It was obtained that hydrogenated silicon carbide forms on this defected Si/Cu surface during the first stage of carbon film deposition. Structure of a-C:H films and conditions of nanostructures formation depended on substrate temperature and Cu concentration in the film, then deposition time was 300 s.

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1. Introduction

Variety of carbon nanostructures and their unique properties allows discovering the new possibilities of applications. For example, differences of carbon nanotubes (CNT) structure induce changes of electrical properties and this phenomenon allows CNT to be usable for micro and nanoelectronics [1]. High temperature and specific conditions are required for nanostructures and nanotubes formation, so technological process becomes difficult and expensive. The possibilities to form carbon nanostructures vertically aligned or directly spinable CNT by plasma enhanced chemical vapor deposition (PECVD) method at low temperature become perspective and interesting for scientists and technologists [2]. In other case, semiconducting structures with useful electrical and optical properties formed in the nanocomposite a-C:H films with metal impurities also have high possibilities for application. It is well accepted that almost any metal nanoparticles can be used as catalyst for the growth of carbon nanotubes [3]. The possibility to localize the different concentration of metal impurities and grow nanostructures in one technological process during a-C:H film deposition would form applicable zones with different electrical, optical, and mechanical properties.

Formation of nanostructures in the a-C:H films using copper as their catalyst when silicon substrate temperature varied from 25 °C till 250 °C are presented in this work. Deposition of Cu and a-C:H films were going in succession during one technological process.

2. Experimental setup

a-C:H films were formed on silicon surface with metal clusters by PECVD method using C_2H_2 gas plasma. The temperature of silicon substrate was 25 °C, 100 °C, and 250 °C. Duration of deposition was 45 s and 300 s,

bombarding ion energy was 200 eV. The copper was deposited before carbon film formation and the concentration ($\approx 5\%$) was dependent on the copper net bombardment conditions (Ar^+ , $E_i = 500$ eV, 180 s). The films optical properties were determined by null-ellipsometry (Gaertner L117 with a He-Ne laser (632.8 nm)), Raman spectroscopy (RS) (Yvon Jobin spectrometer with a Spectra Physics YAG:Nd laser (532.3 nm, 50 mW, spot size 0.32 mm)). The experimental RS curves were fitted by few Gaussian-shape lines in the spectral range from 500 cm^{-1} to 1100 cm^{-1} , from 1100 cm^{-1} to 2000 cm^{-1} and from 2000 cm^{-1} to 3000 cm^{-1} . The surface morphology was analyzed by scanning electron microscopy JEOL JSM-5600, relative element concentrations were measured by Bruker AXS Microanalysis GmbH.

3. Results and discussions

a-C:H films were deposited during 45 s for the understanding of the first stage of carbon nanoclusters formation. The Raman spectra of films formatted when the substrate temperature was 25 °C shows that few peaks at 518, 560, 616, 813, and at 1057 cm^{-1} were obtained in the 500–1100 cm^{-1} range (Fig. 1). First of them is characteristic for silicon, other two associate with Cu_2O because this compound has related sub-peaks, such as 570, 618, or 624 cm^{-1} [4]. Wide peaks at 813 cm^{-1} and at 1057 cm^{-1} are related with silicon carboxyl bounds. Peak at 1057 cm^{-1} can be divided into two peaks — near 945 cm^{-1} and 1036 cm^{-1} . Peaks at 813 cm^{-1} and at 950 cm^{-1} show that Si–C bound forms there. Peak at 950 cm^{-1} also can be due to the second order Raman spectrum from the Si substrate when films has high sp^3 fraction [5].

Low intensity of the peaks at the typical spectra range of a-C:H (1100–2000 cm^{-1}) shows that formation of this film is burdened. Four weak peaks were obtained there: the *D* peak at 1389 cm^{-1} , *G* peak at 1561 cm^{-1} , and two additional peaks at 1252 cm^{-1} and 1778 cm^{-1} . Shift of the *D* and *G* peaks into the higher means shows that more graphite like (GLC) film forms on the silicon surface.

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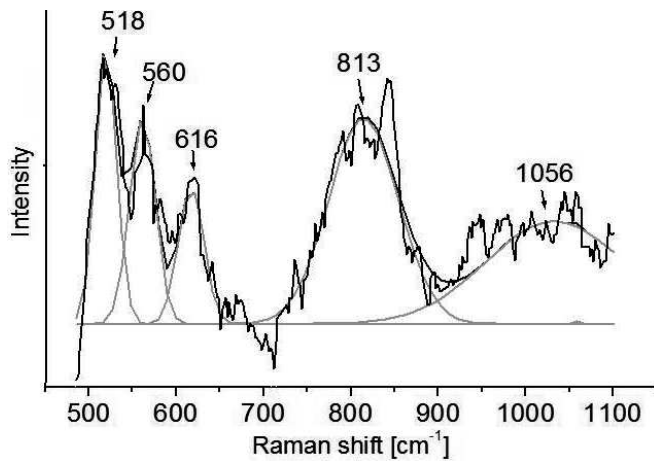


Fig. 1. Raman spectra of a-C:H film with copper impurities formed with 200 eV ion energy at 25 °C substrate temperature. Deposition duration 45 s.

The peak at 1252 cm^{-1} is related to CH_3 symmetric bending. Peak at 1778 cm^{-1} is the most interesting because it associates with three layer graphene (3LG) rhombohedral (ABC) structure. Cong et al. [6] obtained that peak at 1774 cm^{-1} is assigned to the overtone mode of the out-of-plane tangential optic (2oTO) mode. Low intensive $G'(2D)$ peak at 2690 cm^{-1} related with graphene also was obtained in the spectra. Peak for graphene is at 2680 cm^{-1} , but Ferrari et al. [7] explain that the shifts of it into the higher mean depend on the number of graphene layers.

The low refractive index (≈ 1.4), the high intensity of peaks associated with hydrogenated silicon carbide and weak peaks related with a-C:H suggest that SiCOH formation on the defected silicon surface is dominant in the first stage of the films deposition when the substrate temperature was 25 °C.

Thin GLC films with high concentration of stresses between graphite monolayers form on the top of SiCOH. Stresses conditioning the breaking of weak bonds between graphite layers and multi-layer graphene can form. The films cracking during 45 s after quickly removing sample from vacuum to the environment confirm existence of the stress. For this reason all samples are always left about 120 min in the vacuum for stress relaxing.

The same peaks (expected Cu_2O peaks) were obtained in the RS range from 500 cm^{-1} to 1100 cm^{-1} when the substrate temperature increases to 100 °C. Peaks in the 1100–2000 cm^{-1} range become more intensive. The D and G peaks shift to the lower means (1295 cm^{-1} and 1515 cm^{-1} , respectively) and it confirms that concentration of sp^3 phase in the films is lower. The Raman peak at 1712 cm^{-1} is associated with $\text{C}=\text{O}$ stretching peak. Peak near 1250 cm^{-1} was not obtained, so it can be concluded that hydrogen is partially removed from films because of the heating. Relative concentration of carbon becomes lower in comparison with 25 °C (61% and 57%, respec-

tively), so film is thinner but having stronger expressed amorphous carbon phase. Refractive index (≈ 1.6) is more characteristic for a-C:H than SiCOH.

Differences in the Raman spectra were obtained only in the range from 1000 cm^{-1} to 2000 cm^{-1} when the sample temperature increases to 250 °C. The four peaks were found there: D at 1314 cm^{-1} , G at 1503 cm^{-1} , peak associated C–H in plane bending mode near 1169 cm^{-1} and peak at 1757 cm^{-1} . The last of them is the result of the second-order Raman process involving the combination of the RBM and tangential mode (G -line), which strongly supports the growth of single wall nanotubes (SWNTs) [8]. Scanning electron microscopy (SEM) pictures show the first stage of nanoclusters formation (Fig. 2). So, high temperature, Cu clusters, and graphite-like carbon film are the conditions for the nanostructures formation in the first stage of process.

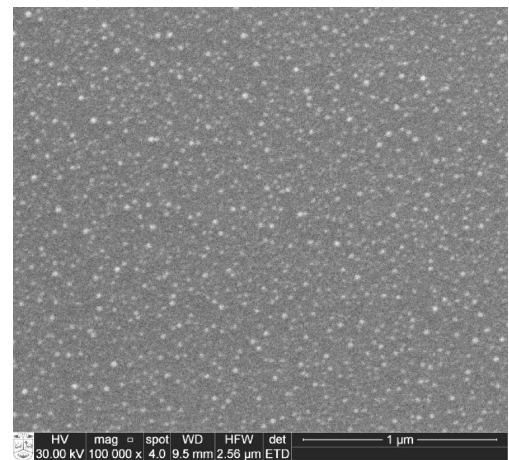


Fig. 2. SEM images of a-C:H film with copper impurities formed with 200 eV ion energy at 25 °C substrate temperature. Deposition duration 45 s.

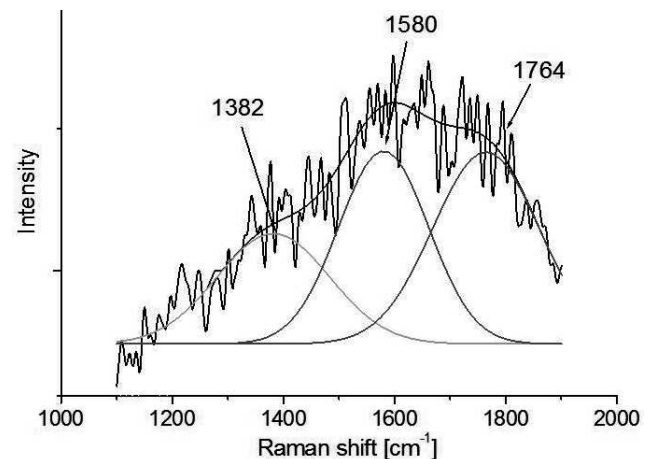


Fig. 3. Raman spectra of a-C:H film with copper impurities formed with 200 eV ion energy at 25 °C substrate temperature. Deposition duration 300 s.

The Raman spectra in the 500–1000 cm^{-1} range were changed when duration of film deposition increases to 300 s. Peaks related with hydrogenated silicon carbide were not obtained in RS spectra, the refractive indexes were about 1.7 for all films in all temperature ranges. Typical *D* (1382 cm^{-1}) and *G* peaks (1580 cm^{-1}) with additional peak at 1764 cm^{-1} become dominant when the substrate temperature was low (25 °C) (Fig. 3). Formation of carbon nanostructures at 25 °C becomes understandable (Fig. 4) because of formation of graphene layers in the first stage (after 45 s) were obtained. Cu relative concentration in the film was $\approx 1.2\%$ (carbon 69.7%).

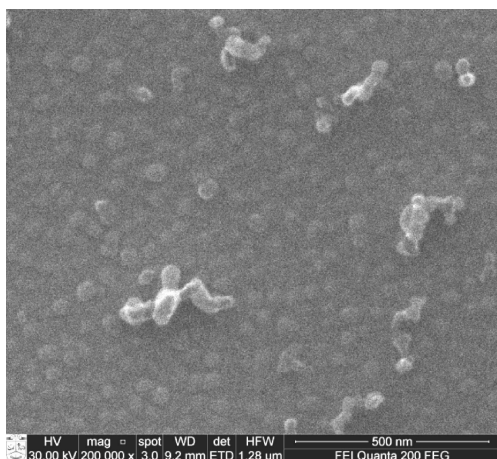


Fig. 4. SEM images of a-C:H film with copper impurities formed with 200 eV ion energy at 25 °C substrate temperature. Deposition duration 300 s.

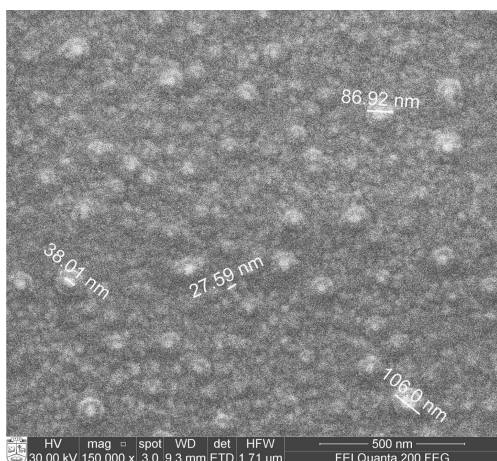


Fig. 5. SEM images of a-C:H film with copper impurities formed with 200 eV ion energy at 250 °C substrate temperature. Deposition duration 300 s.

The *D* and *G* peaks with increasing substrate temperatures to 100 °C are shifted to the lower means as in the short time case, but peak of C=O stretching becomes weak. Formation of nanostructures was not obtained

and related concentration of Cu drastically decreased to 0.27%. Thickness of films is higher (194 nm) than 25 °C (78 nm), but it is not so important in comparison with Cu concentration changes (thickness was changed twice, Cu about four times). Decrease of Cu concentration can be conditioned by the diffusion to the silicon bulk because coefficient of diffusion increases with increasing temperature ($1.1 \times 10^{-9} \text{ cm}^2/\text{s}$ at 25 °C and $2.4 \times 10^{-8} \text{ cm}^2/\text{s}$ at 100 °C).

Rudiments of CNT formation were obtained in the early stage when the substrate temperature was 250 °C (Fig. 1) and they continued growing during long deposition process (Fig. 5). Cu concentration (1.91%) and the temperature are sufficient for nanostructures formation. It is important that diameter of Cu clusters is about 50 nm, so only nano onion-like structures can form on the surface (Fig. 5). Diameter of metal clusters necessary for SWNT or MWNT catalyst is about $\approx 1\text{--}5 \text{ nm}$ and $\approx 20\text{--}50 \text{ nm}$ [9].

4. Conclusions

It was obtained that hydrogenate silicon carbide forms on the defected silicon surface during first stage of a-C:H deposition. Thin GLC film is on the top of this SiCOH layer. Stresses in the thin GLC film can produce multi-layer graphene formation and it conditioned nanostructure growing at the room temperature. Carbons microstructures begin forming also when the temperature of silicon surface with carbon cluster is 250 °C.

Acknowledgments

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