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The influence of metal impurities to a-C:H films

Abstract. *The carbon coatings on the silicon substrate by chemical vapour phase precipitation as the insertion of platinum and copper impurities were observed in this paper. It was obtained that growing films are more polymeric like. The refractive index of all films are similar and varies from 1,6 to 1,75 and does not depend on nature of metal. Analysis of Raman spectra showed that typical for amorphous carbon G peaks become dominant and move to the lower means (from 1682 cm^{-1} to approximately 1553 cm^{-1}) and then metal impurities were introduced to the film. Also a new peak at about 1800 cm^{-1} was obtained there. Typical D peak in films with platinum impurities is less intensive and disappears when Cu impurities are involved in film.*

Streszczenie. *Analizowano powłokę węglową na podłożu krzemowym poprzez chemiczne rozpuszczanie domieszek platyny i miedzi. Stwierdzono że współczynnik odbicia warstw był podobny dla wszystkich warstw i wynosił 1,6 do 1,75 niezależnie od domieszek. Spektralna analiza Ramanowska wykazała dominujące i zmniejszała się do ok 1553 cm-1 przy wprowadzaniu domieszek (**Wpływ metalowych zanieczyszczeń do filmów a-C:H**).*

Keywords: amorphous carbon films, metal impurities, Raman spectroscopy, ellipsometry, IR spectroscopy.
Słowa kluczowe: amorphous carbon films, metal impurities, Raman spectroscopy, ellipsometry, IR spectroscopy.

Introduction

Amorphous carbon films can be used in various spheres because of unique (high hardness [1, 2], optical transparence [2], chemical inertness, high electrical resistance [1]) similar to diamond properties. High stresses in the films and film – substrate interface are the reason for using DLC films.

Hydrogenous carbon films with metallic impurities distinguish by reduced stresses, low friction coefficient, extremely low abrasive wear rates, improved adhesion, lowed sensibilities humidity, etc. [3-8]. The conductivity of films can be enhanced from pure insulator to metallic conductivity depending on amount of metal impurities. These properties increase the possibilities of such coating use (e.g. a-C:H/Cr thin films obtained by method of DC deposition on oxygen-free copper substrate has higher than 90% absorption in 0.3-2.5 μm wave range with a very low thermal (0,004) radiation. It enable use these films as solar absorbers [9].

The reactive magnetron sputtering of a metal target in an argon-hydrocarbon gas mixture [5, 8-9] and dual-source magnetron sputter deposition with metal and graphite targets are the most popular methods for metallic carbon films formation. The combining sputter-deposition of metal and microwave plasma-assisted chemical vapor deposition of carbon [3, 6], pulsed laser deposition [10], and other are used there also.

The research of cupper and platinum influences to surface morphology, bonds structure, optical properties of carbon thin films obtained for C_2H_2 gases are the main purpose of this work.

Experimental setup

a-C:H films were formed in pure acetylene gas by PEVCD method. Ion energy was 100 eV, ion current densities vere 0.02 mA/cm^2, pressure was below 2.3 Pa, and the deposition duration was 3 min. Si wafers temperature varied from 25 °C to 200°C. Before deposition silicon substrate and metallic net fixed between plasma source were bombarded by Ar$^+$ with 500 eV ion energy. The quantity of metal on the silicon surface was not controlled. Concentration of deposited metal particles (~1.5%) was measured by Bruker AXS Microanalysis GmbH. The optical properties of a-C:H films were studied by the Raman scattering (RS) using an Ivon 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 two or three Gaussian-shape lines in the spectral range from 1000 cm^{-1} to 1900 cm^{-1}. Infrared (IR) absorption and reflection spectra (Perkin Elmer spectrometer Spectrum GX) were measured in the ranges of 100 cm^{-1} - 4000 cm^{-1} and 670 cm^{-1} - 4000 cm^{-1}, respectively. The thickness, refractive and extinction indices of surface layers were determined using a null-ellipsometer Gaertner L117 operating with a He–Ne laser (632.8 nm). The surface morphology was analyzed by scanning electron microscopy (SEM) model JEOL JSM–5600.

Results and discussions

Hydrogenous carbon films with and without metal impurities were formed in 25°C temperature with 100 eV ion energy in order to determine the influence of metallic impurities introducing the change of coatings structure.

The data of Raman spectroscopy and null-ellipsometry of films with and without metal impurities are given in Table 1. Characteristic Raman spectra in 1100 cm^{-1} – 2000 cm^{-1} range of these films are shown in Fig. 1.

Table 1. The data of Raman spectroscopy and null-ellipsometry of films with and without metal impurities

Sample	Metal free	With Pt	With Cu
D peak position [cm^{-1}]	1335	1299	-
G peak position [cm^{-1}]	1628	1553	1578
I_D/I_G	0,6	0,6	
ΔD [cm^{-1}]	278	234	-
ΔG [cm^{-1}]	273	210	352
Other peaks [cm^{-1}]		1757	1209; 1812
Refractive index	2,15	1,75	1,69
Extinction coefficient	0,054	0,033	0,014
Thickness of the films [nm]	439	200	232

Films without impurities can be distinguished to diamond like (DLC) because of high refractive index and low extinction coefficient. Films refractive index and extinction coefficient reduce by adding platinum and cuprum impurities. Thickness of films decreased twice, so lower velocity of the film formation when metal fragment are on silicon surface predominant there. Such changes are usually related with sp^3 and sp^2 phase transformations. Raman spectra for the synthesis of films without metal impurities in typical for amorphous carbon range (1100 cm^{-1} - 1800 cm^{-1}) showed that film is amorphous, typical D and

G bands (1335 cm^{-1} and 1628 cm^{-1}) exist there. Broad (half width about 273 cm^{-1}) and shifted to higher mean (from 1560 to 1628 cm^{-1}) G peak means that angle and length of sp^2 bonds distributed chaotically and typical graphite net does not form in the film. High stresses there also can be the reason of higher G peak mean. D peak existence is conditioned by sp^2 vibration in the grain of clusters or crystallites. Low I_D/I_G rate showed that the film is DLC with dominating sp^3 bonds. IR spectra showed that carbon hydrogenous bonds are more responsible for sp^3 and sp^2 bonds because characteristic for C-C bonds peaks are very weak in the 1600 cm^{-1} - 1690 cm^{-1}. Rising of Raman spectra in the 400 cm^{-1} - 2000 cm^{-1} range also confirm the high concentration of hydrogen in the films.

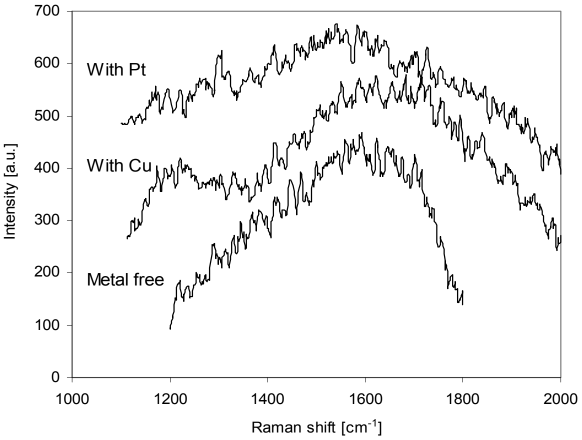

Fig.1. RS spectra of a-C:H films deposited at 25°C temperature

Concentration of hydrogen decreased when cuprum or platinum impurities were incorporated in carbon film; the intensity of hydrogenous bonds in the IR spectra is considerable lower (Fig. 2). Not so sharp increasing of Raman spectra intensity in the 400 - 1000 cm^{-1} range also confirm the lower component of polymerization. From the other side, null-ellipsometry measurements showed vice versa – the lower refraction index and the lower extinction coefficient. These changes can be associated with strong polymerization or formation of nanoclusters when metal impurities exist in the film.

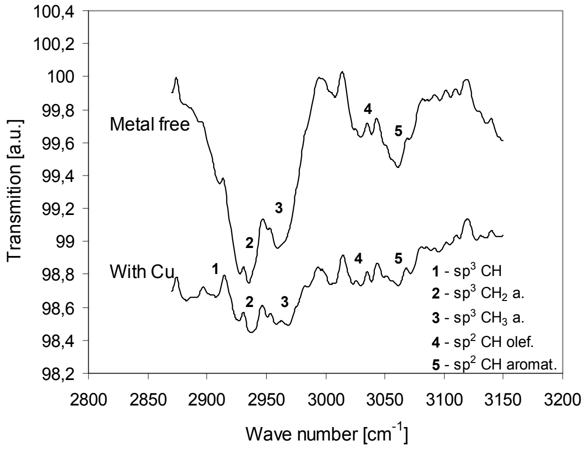

Fig.2. IR spectra of a-C:H films with Cu impurities and metal free samples

Three peaks at 1299 cm^{-1}, 1553 cm^{-1} an 1757 cm^{-1} were obtained in the Raman spectra of the films with platinum impurities in the typical for DLC range (from 1200 cm^{-1} to 1800 cm^{-1}) and it is different in comparison to the case of pure hydrogenated amorphous carbon films where are significant two peaks. The first of them can be attributed as D mode existing in RS spectra of the nanoformation [11]. So, I_D/I_G ration (0,6) was calculated exactly from this peak mean. Slowly shifted G bands mean to the lower position and accompanying peak near 1757 cm^{-1} also are characteristic for metallic nanoformation as the second-order Raman peak of the radial breathing mode (RBM) around 180 cm^{-1} (it cannot be measured with this type of RS equipment) and the tangential modes between 1500 cm^{-1} - 1600 cm^{-1}. The RBM is uniquely observed in the Raman spectra of single wall carbon nanotubes(SWNTS), and therefore the presence of this second-order Raman peak is a signature of SWNTs [12]. It should be noted that obtained Raman spectra are not typical for nanotube or nanoclusters because of platinum or copper atoms are fragmentary distributed on the silicon surface during initial deposition of metals and concentration of them is very low (about 1.5 %). So, it is mistaken hope that strong and intensive peaks typical for carbon nanotubes will be obtained in this case. Fragmentation of nanoformation on the coating surface is showed in Fig. 3.

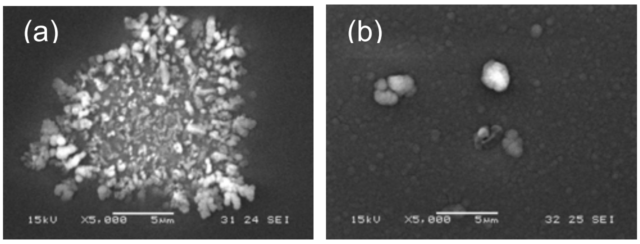

Fig.3. Surface morpholgy of films *(a)* with Pt and *(b)* with Cu impurities

Typical for amorphous hydrogenated carbon films D band fully disappear when copper is included in the film, but a new intensive peak at 1209 cm^{-1} attributed to the formation of $CuCO_3$ [13] is highlighted there. The false assumption to attribute this peak to SWNT [14] or nondiamond phase [15] because of accompanying peak at 1330cm^{-1} isn't obtained in those cases. G band is shifted to higher means (1578 cm^{-1}), and typical for metallic carbides peak at 1812 cm^{-1} also exist there [16].

So, the cuprum stimulate formation of carbides and the platinum is the excellent catalyst for nanoformations in the hydrogenated carbon films and it can be concluded after IR, RS and null-ellipsometr measurements.

Refraction indexes decreased to 1.6 and this decreasing is not depending on temperature or nature of impurities when the temperature of substrate increased to 100°C or 200°C during the formation process, but extinction coefficient is the function from that. Ellipsometry measurement showed that extinction coefficient decreases with the temperature increase at the platinum case (k=0.008 when temperature is 100°C and equal zero for 632.8 nm laser wave length when 200°C). Thickness of films slowly increased (d=254 nm when T=100°C, and d=217 nm when T = 200°C). Analysis of RS spectra showed that intensity of G band at 1542 cm^{-1} dissolved but peaks at 1274 cm^{-1} and 1754 cm^{-1} become more intensive. I_D/I_G ratio increased to 0.73 or to 1.2 when substrate temperature was 100°C or 200°C respectively, if to take into account the view that D peak for nanoformations is 1274 cm^{-1}. So, films become more graphitic like and formation of nanoclusters become more intensive in these cases because the D peak and accompanying peak are more intensive in the RS spectra and it varied with temperature increasing.

Extinction coefficient is equal to about zero and film growth velocity is low at the cuprum case when substrate temperature is 100°C. Film thickness after 3 min. deposition is about 100 nm. Two very intensive peaks at 1629 cm^{-1} and 1843 cm^{-1} were obtained in the Raman spectra of 1100 cm^{-1} - 2000 cm^{-1} range. It can be maintained that metallic carbides intensively forms in the graphitic matric because of D band disappearance, hydrogen and oxygen are removed from the film. Lower increasing intensity of Raman spectra in the range 400 cm^{-1} - 2000cm^{-1} confirms it.

Thickness of film and extinction coefficient slowly increased (d=262 nm, k=0.009) when the temperature of the substrate was 200°C. G peak is weak and strongly shifted to the lower means (1500 cm^{-1}), the peak at 1233 cm^{-1} becomes more intensive and narrow peak at 1352 cm^{-1} was registered in the RS spectra. The two mentioned peaks can be attributed as the characteristics for the nanoformations [14]. So, copper impurities and high temperature reduce cuprum carbide formation in the graphite phase, hydrogen concentration in the film, and activate formation of nanclusters.

Conclusions

Analysis of RS, IR, and ellipsometry data of films showed that cuprum inclusion in the carbon film activate metallic carbide formation; platinum is excellent catalyst for nanoclusters at substrate temperature of 25°C. Copper carbide formation becomes more intensive at the temperature increasing to 100°C. Copper also can be the catalyst for nanoformations only when substrate temperature is high (~200°C). Formation of nanoclusters is activated when platinum is included in the carbon film.

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