PREPARATION OF COPPER DOPED DLC FILMS BY DC PE-CVD METHOD

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1. Introduction

Diamond-like carbon, the amorphous network of mostly sp^2 and sp^3 bonded carbon atoms has attracted the attention of researchers for his extraordinary properties such as high hardness and wear resistance, low friction coefficient, biocompatibility, transparency in IR, wide potential window and chemical stability. These make them suitable for many various applications in the field of cutting tools, automotive industry, artificial human body parts, optics, electronics and sensors [1]. The main disadvantage for the use of DLC in the field of electronics is the low conductivity caused by high concentration of sp^3 C-C and C-H bonds in the films. Therefore, there are many attempts to increase the conductivity by effective film doping. The most often used doping elements to be incorporated into the amorphous carbon network are nitrogen, boron and different metals [2-6].

The electrical conductivity of amorphous carbon films may be influenced by up to 12 orders of magnitude – from an insulator to a metallic conductor – by adding Au and Ta metal atoms into the growing films. The metal atoms are not homogeneously distributed in the carbon or hydrogenated carbon material, instead metal clusters or metal carbide clusters are formed due to the aggregation processes during the film formation.

This heterogeneous material consists of crystalline conducting metal clusters embedded in a more or less insulating matrix of amorphous carbon which may be hydrogenated as well (Me:a-C:H). Tunneling or hopping of the carriers between the metallic islands was suggested as the dominant conduction mechanism [7]. In this work, the preparation of copper doped DLC (Cu-DLC) films by the DC PE-CVD method is studied.

2. Experimental

DLC thin films were deposited by DC PE-CVD process in a vacuum reactor type UVNIPA-1-001 described previously [8] using a DC power supply. Mirror polished Si and Corning glass substrates were used for deposition of the coatings. Prior to deposition, substrates were cleaned for 20 min with Ar ions within the deposition cycle. Background pressure was 10^{-1} Pa and working pressure was maintained from 3 to 8 Pa according to gas flow. Methane was used as precursor gas for DLC growth while the admixture of argon was responsible for simultaneous sputtering of copper target. The deposition voltage was changed from -1 to -4 kV and the temperature was below 200 ºC. The Cu-DLC composite layers were also annealed at 300 and 500 °C under 10^{-2} Pa vacuum using rapid thermal annealing (RTA) for one hour. Resistivity of the films was measured before and after annealing process employing the Van der Pauw method. The structural properties of DLC films were evaluated by SEM (JEOL 7500F) using SEI and LABE detectors and Raman spectroscopy with 632.8 nm radiation from a He–Ne laser. The acquired Raman spectra were fitted with a Gaussian line to illustrate the D and G peak positions, G peak full width at half maximum (FWHM).

3. Results and discussion

SEM images of annealed DLC layers at various temperatures are shown in Fig.1. We can see (bright dots and areas) the increasing amount of graphitic content in the films with increasing temperature of annealing. Raman spectra (Fig.2 left) show the typical D and G band at 1 350 and 1 580 cm^{-1} associated with disordered (D) and graphite (G) sp^2 C-C bonds. The data from fitted Raman spectra of the annealed films are depicted in Fig.2 right.

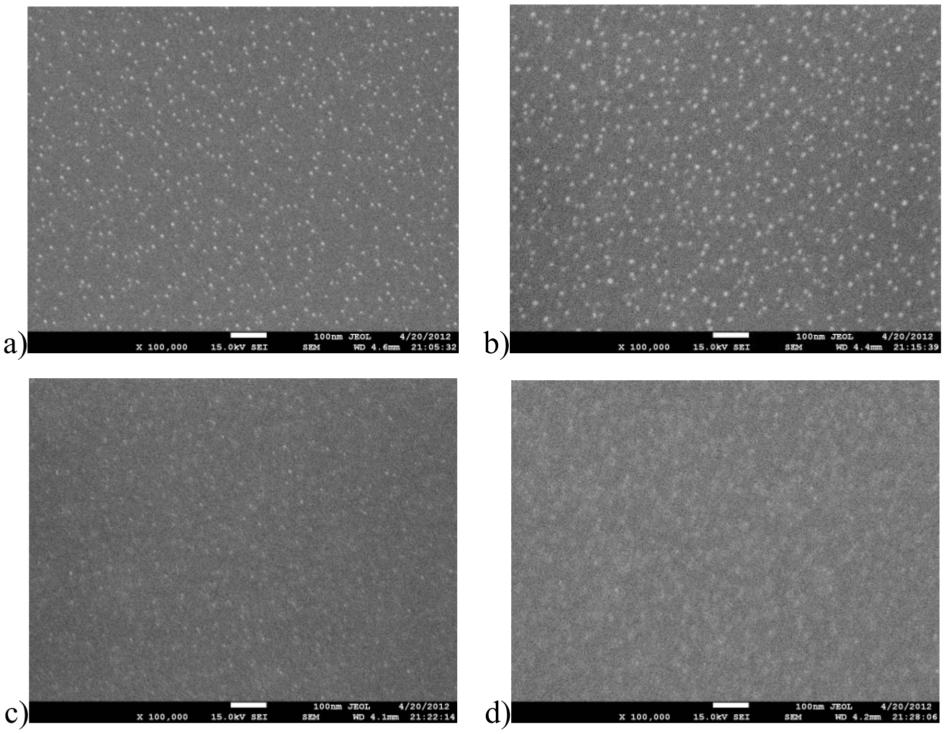

Fig.1: *SEM images of annealed DLC layers at a) 200°C, b) 300°C, c) 400°C, d) 500°C, marker shows 100 nm*

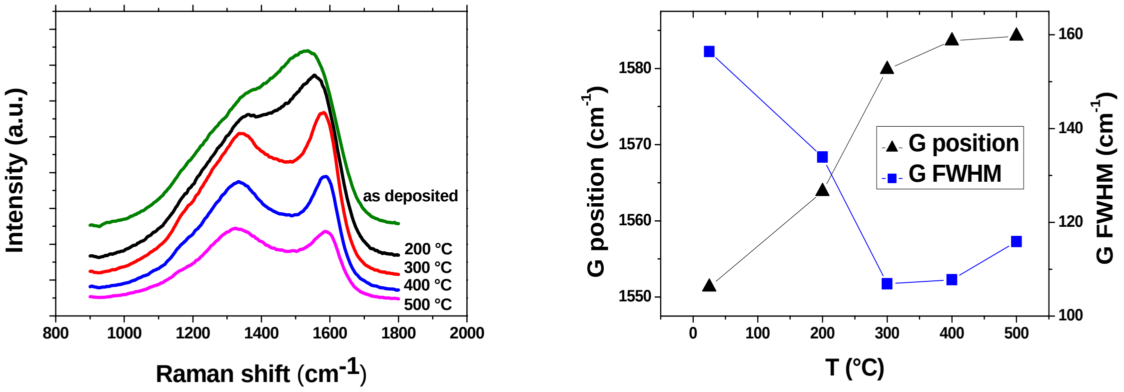

Fig.2: Left: *Raman spectra of as deposited and annealed DLC layers, Right: Dependence of G peak position and its FWHM on annealing temperature*

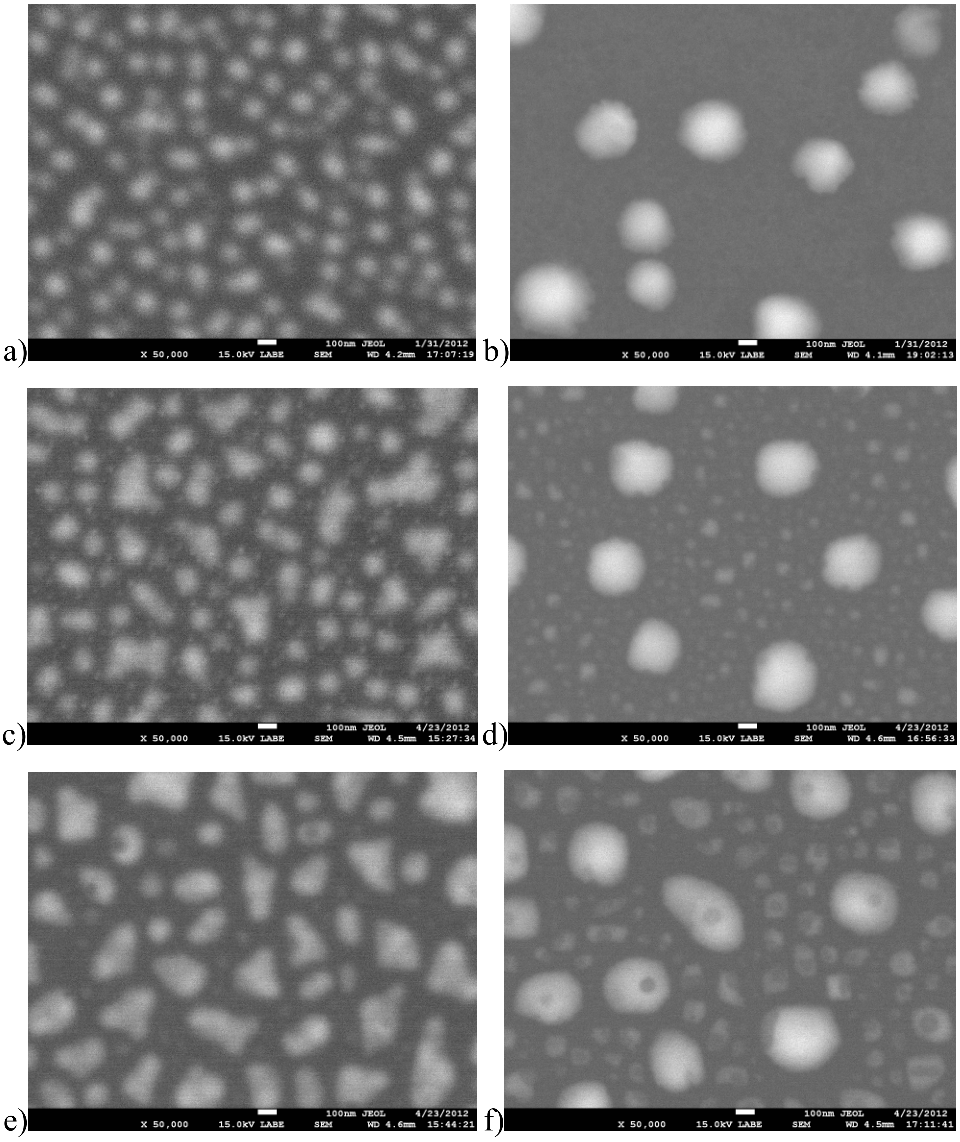

Fig.3: *SEM images of as deposited (a,b) and annealed (c,d – 300°C, e,f – 500°C) Cu-doped DLC films, marker shows 100 nm*

With increased annealing temperature, the G peak position increased towards the value of graphite and the FWHM decreased, which means the film became more crystalline. From SEM images and the Raman spectra we can assume that, with increasing of the annealing temperature, the films became more graphitic.

Fig.3 a), b) shows two differently deposited Cu-DLC films. The bright dots are the copper particles deposited homogenously within the films. We can see that the size of the copper particles and distances between them changed with the different deposition conditions. The average size of copper particles varied from tenths to hundreds of nm. The images c) and d) show the layers annealed at 300 °C and e) and f) are the layers annealed at 500 °C. In the case of first layer, after annealing at 300 °C we can observe small Cu particles appeared in the empty space in between the previously deposited larger particles. After annealing at higher temperature, there are still new small Cu particles and all of the particles seem to join together creating larger clusters. After annealing of the next layer (Fig.3 d) at 300 °C there are the new small particles between the deposited ones again. It is clear from the image taken from layer annealed at 500 °C that the origin of them is in the larger as deposited particles which contain holes and empty spaces. After annealing process, the distribution of Cu over the DLC thin films seems to be much more homogenous and distances between conductive Cu particles are visibly smaller.

While the R_{bulk} of non-doped DLC thin films was with our equipment not measurable (was extremely high), the values of resistivity of as deposited Cu-DLC layers was measured in the range from 10 to $6x10^3$ Ωcm according to deposition properties and the resulting amount, size and distribution of Cu particles in the films. After annealing process at 500 °C, the resistivity drops by several orders of magnitude to values ranged from $4x10^{-2}$ to 3 Ωcm.

4. Conclusions

We used PECVD method for deposition of Cu incorporated DLC thin films from CH_4/Ar gas mixture. The size of nanoparticles varied with changing the deposition conditions in the range of tenth to hundreds of nm. After annealing process, new small Cu particles appeared in the space between the as deposited ones, and all the particles were distributed more homogenous within the films. The resistivity of the DLC films decreased first with adding of copper to 10 to $6x10^3$ Ωcm, and second with the annealing process to $4x10^{-2}$ to 3 Ωcm. Raman spectra show the tendency of DLCs to become more graphitic with increasing annealing temperature, which may be one possible contribution to increased conductivity of the annealed Cu-DLC films.

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