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Synthesis of nanostructured amorphous carbon-copper composite films by plasma-enhanced chemical vapour deposition

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ABSTRACT

Nanostructured amorphous carbon-copper composite films were formed by plasma-enhanced chemical vapour deposition. The formation was done on copper-silicon substrates at 25 °C, 300 °C, 520 °C, and 700 °C temperatures using an acetylene gas at 40–70 Pa pressure. The heating of the Cu—Si substrate induced formation of Cu nanospheres with 50–500 nm size depending on the substrate temperature. The microstructure and composition of nanostructured carbon-copper composite films were investigated. The SEM views showed formation of amorphous carbon films with the randomly distributed nanostructures. The oxygen concentration in the composite films decreased with the increased heating temperature. The surface roughness measurements indicated that the surface roughness values increased with the increase of the temperature. The increase of the substrate temperature stimulated to the graphitization, enhanced the fraction of sp^2 C═C sites and lead to the formation of the nanocrystaline graphite clusters in composite films. The nanohardness values of the formed nanostructured amorphous carbon-Cu films varied in the range of 0.2–3 GPa.

1. Introduction

Recently, considerable attention is given to research of carbon films with metal impurities and various carbon nanostructures, obtained using metal catalyst [1–4]. Amorphous carbon films containing nanostructures (graphite, fullerene, nanocrystalline graphite, or diamond nanoclusters) exhibit unique mechanical, electrical, optical, or tribological properties [5–8]. The fraction of carbon nanostructures in the films is controlled by changing the process parameters (deposition temperature, particle energy, source of the carbon material and etc.) or by using of various metals (incorporation during the film growth or formation of various metal nano- and micro-particles on the surface). Such metal islands could serve as nanostructures nucleation centers or change bonding type of carbon sites [2,5]. A number of metals that form carbides (Ti, V, Cr, Fe, Ni), as well as those that do not form carbides (Cu, Au, Pd, Pt) are used as doping elements for amorphous carbon composites and films or as catalyst for carbon nanostructures [2,4,9]. The copper is one of the most popular metals used in the formation of carbon composites or nanostructures due to low solubility of carbon in Cu, low cost, and availability. The formation of carbon nanotubes using a copper catalyst was investigated by several authors [2,4,10–13]. D. Lifeng et al. [14] investigated the interactions between Cu catalysts and carbon nanomaterials and proposed the effective method for eliminating Cu impurities from the fibres. A.S. Chaus et al. [15] demonstrated that the incorporation of copper in to DLC film caused reduction in microhardness and 2.5 times decreased the internal stress values. B. Ren et al. [16] demonstrated that the graphite-like carbon thin films are promising for non-volatile memory applications. P. Guo et al. [17] found that the increase of the Cu content in DLC films increases the contact angle values and changed the surface energy. The addition of Cu in DLC films minimizes stress and improves the electrical and optical properties. It is also very interesting that copper films can be used as a substrate during the CVD process causing a growth of graphene [18]. The formation of graphene layer on Ni—Cu layer was demonstrated by J. Prekodravac et al. [19]. A. Akbari-Sharbaf et al. [13] obtained that the doping of graphene films with copper nanoparticles increases the conductivity up to 400%. The copper could initiate formation of graphene films [2]. X. Zheng and C.W. Park [20] formed carbon nanotube/Cu composite powders with improved thermo-physical properties. The carbon nanodots modified with Cu(II) due to fluorescence could be used for the detection of guanine [21].

The information regarding formation, characterization, and potential application of the copper containing DLC films is sufficient in the literature

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[3,9,17,22–24]. Meanwhile, there is a lack of literature on the nanostructured carbon-copper composites formation, structure characterization, and application prepared by plasma-enhanced chemical vapour deposition at higher temperatures. However, such micro or nano-structure composite films could be useful to improve an electrical and optical properties or used as Cu-carbon locally dots in amorphous carbon films.

The main purpose of the research was to obtain nanostructured carbon-copper films and to investigate the influence of the substrate temperature on the surface morphology and structure of the synthesized nanostructured composite films.

2. Experimental setup

Pure copper nanolayer film of 20 ± 5 nm thickness was deposited on Si(100) substrates by magnetron sputtering. The deposition was performed using direct current magnetron sputtering from a copper metal target at 345 V voltage using argon gas. Vacuum chamber pressure was 0.4 Pa, argon plasma pressure - 0.005 Pa. The obtained copper films were placed on the heated holder in the plasma-enhanced chemical vapour deposition system. The Cu—Si substrates were cleaned by the argon ions (for 180 s, self-bias was −300 V) at 25 °C temperature, before starting the deposition of carbon films. The argon gas flow rate was ~35 sccm for all samples. The vacuum chamber was equipped with paralleled electrodes. The positive electrode, which was grounded, was connected to a gas source by a pipe through which a gas of acetylene or argon was introduced into the reactor. The deposition was performed on the 25 °C and heated Cu—Si substrates at 300 °C, 520 °C and 700 °C temperatures. The acetylene gas flow rate varied from 32.4 sccm to 53.4 sccm and deposition time was 90 s and 600 s (for sample formed at 700 °C) in order to obtain similar concentration of carbon in the composite films. The substrate self-bias was −300 V, the pressure in vacuum chamber was kept in the range of 40–70 Pa.

The surface morphology was analysed by the scanning electron microscope (SEM) Hitachi S-3400N. The elemental composition of the films was investigated by the energy dispersive X-ray spectroscopy (EDX) (Bruker Quad 5040 spectrometer, AXS Microanalysis GmbH). It should be noted that the EDX was measured in the depth exceeding carbon-copper composite thickness. Atomic force microscopy (AFM) experiments were carried out in air at room temperature using an atomic force microscope NT-206 (Microtestmachines Co.) and SPM-data processing software SurfaceXplorer. V-shaped silicon cantilever (spring constant of 3 N/m, tip curvature radius 10.0 nm, cone angle 20°) operating in a contact image mode was used. Surface morphology was determined in terms of AFM surface topography images, roughness parameters: root mean square roughness (R_q), average roughness (R_a), skewness (R_{sk}) and kurtosis (R_{ku}). The optical properties were determined by null-ellipsometry (Gaertner L117 with a He—Ne laser (632.8 nm)). The structure of samples was analysed by μRaman spectroscopy (Renishaw inVia spectrometer, using 1 mW excitation at the wavelength of 532 nm, focused to 2 μm spot, the accumulation time was 100 s) in the spectral range of 100–4000 cm^{-1}. The Raman spectra were fitted by Lorenzian-shape lines in the spectral range of (1200–1850) cm^{-1}. Fourier transform infrared (FTIR) reflection spectra were measured in the range of 650–4000 cm^{-1}. Spectra were recorded on Bruker Vertex 70 (Bruker Optik GmbH, Ettlingen, Germany) spectrometer with 0.5 cm^{-1} spectral resolution, MCT detector and globar source. Nanoindentation tests were performed by MTS-Agilent G200 nanoindenter with a Berkovich diamond tip using the continuous stiffness measurement technique. The measurements were conducted at the strain rate of 0.05 s^{-1}. The nanoindenter was calibrated using a reference sample of fused silica. The hardness and elastic modulus of films were calculated using Oliver and Pharr method [25] and determined continuously as a function of the indentation depth. Results were averaged from 10 individual measurements.

3. Results and discussions

The elemental composition of the deposited carbon - copper composite films are given in the Table 1. It should be noted that the EDX measurements were measured in the depth exceeding the film thickness. The EDX measurements indicated that the oxygen concentration of the Cu/Si substrates heated at various temperatures were ~1 at.%. The film produce at the lowest temperature has the highest fraction of the oxygen and carbon (Table 1). The carbon concentration varied in the range of 29–30 at.%, while the oxygen changed from 1.1 to 3.7 at.% for films deposited at higher temperatures. The fraction of the Cu was ~3.5 at.%, when deposition was done on the heated substrates. The concentrations of the elements were normalized taking into account that the nanostructure films consisted of carbon, oxygen and copper nanoparticles for the composites deposited on heated substrates. In order to investigate influence of the temperature to the oxygen fraction in the composite films, the C/O ratio was calculated. As the substrate temperature increased from 25 °C to 700 °C, the C/O ratio increased from ~4.0 to the maximal value of 27.3. These results indicated that the concentration of the oxygen was reduced at higher temperature and the fraction of the sp^2 carbon sites increased with the increase of the temperature.

Observed SEM micrograph shows the spreading of microparticles on the surface of the film formed at 25 °C (Fig. 1a). The diameter of such microparticles is ~1 μm, also a randomly distributed clusters of agglomerated microparticles of 5–10 μm size was found. The heating of the Cu—Si substrate up to 300 °C induced formation of carbon-copper nanoparticles with 50–200 nm size (Fig. 1b). The formation of similar size copper nanoparticles with the increase of the substrate temperature up to 520 °C was observed. However, these nanoparticles were covered by the carbon layers or embedded in to the composite during deposition (Fig. 1c). The deposition at the highest temperature resulted in the formation of the 200–500 nm size structures and appearance of high fraction of ~50 nm size nanostructures (Fig. 1d).

Fig. 2 shows the EDX maps of C, Cu, and O, collected from the composite film deposited at 300 °C. The distribution of the various elements on the surface indicates that the oxygen is equally spread on the surface (Fig. 2c). The growth of the larger 100–200 nm size structures is directly related to the carbon nanostructures (Fig. 2a). Elementary analysis of the scanned area of composite deposited at 700 °C (Fig. 3), confirmed that the most abundant elements on the surface are carbon, oxygen and copper. Figs. 3a–c presents distribution of different elements. The blue colour originate from the copper, red colour determine distribution of carbon, and green colour indicate the oxygen. The formed ~300 nm size particle originate consist of copper and is covered by the carbon. Meanwhile, the oxygen is eventually spread on the surface (Fig. 3c). It was demonstrated that the increased annealing temperatures from 300 °C to 550 °C increased the average Cu particles diameter from 12 nm to 24 nm [13]. The SEM and EDX measurements demonstrated formation of the nano and microparticles on the heated substrates. Moreover, the formation of larger diameter structures was observed with the increase of heating temperature.

In order to investigate the surface roughness variation, the AFM measurements of the prepared nanostructured films was performed. Table 2 presents the main roughness parameters (root mean square roughness, mean roughness, skewness, kurtosis, and mean height) of films deposited at different temperatures. It can be seen that the film

Table 1
Elemental composition and thickness values of films.

Temperature, °C	C, at.%	O, at.%	C, at.%	O, at.%	C/O ratio	d, nm
25	61.7	15.3	80.1	19.9	4.0	250
300	28.6	3.7	79	10.7	7.3	95
520	30.4	1.4	86.1	3.9	21.7	70
700	30.0	1.1	86.7	3.2	27.3	140