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Piezoresistive properties of diamond like carbon films containing copper

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ABSTRACT

In the present study diamond like carbon films containing copper (DLC:Cu) were deposited by reactive magnetron sputtering. Direct current (DC) sputtering and high power pulsed magnetron sputtering (HIPIMS) were used. The influence of the composition and structure on piezoresistive properties of DLC:Cu films was investigated. Structure of DLC:Cu films was investigated by Raman scattering spectroscopy and transmission electron microscopy (TEM). Chemical composition of the films was studied by using energy-dispersive X-ray spectrometry (EDS) and X-ray photoelectron spectroscopy (XPS). Particularly analysis of XPS O1s spectra revealed oxidation of Cu nanoparticles. Piezoresistive gauge factor of DLC:Cu films was in 3–6 range and decreased with the increase of copper atomic concentration. Tendency of the decrease of the gauge factor of DLC:Cu films with the increased D/G peak area ratio (decreased sp^3/sp^2 carbon bond ratio) was observed. It was found that resistance (R) of DLC:Cu films decreased with the increase of Cu atomic concentration by logarithmic law. It is shown that a quasilinear increase of piezoresistive gauge factor with log(R) is in good accordance with percolation theory. Temperature coefficient of resistance (TCR) of DLC:Cu films was negative and decreased with copper amount in Cu atomic concentrations ranging up to ~40%. Very low TCR values (zero TCR) were observed only for DLC:Cu films with low gauge factor that was close to the gauge factor of the metallic strain gauges. Role of some possible mechanisms: copper amount as well as Cu cluster size on the value of gauge factor is discussed.

1. Introduction

Diamond like carbon (DLC) is a metastable form of amorphous carbon consisting of the sp^2 bonded (graphite-like) carbon nanoclusters embedded into the sp^3 bonded (diamond-like) carbon matrix [1–3]. Besides that, DLC can contain up to several tens of atomic percent of hydrogen [1–3]. The DLC films received considerable interest due to the ultra-smoothness, high hardness, high Young's modulus, low friction coefficient, high wear and corrosion resistance, biocompatibility as well as possibility of deposition at room temperature [1,2]. Recently piezoresistive effect in diamond like carbon films was found [4–32]. Piezoresistive gauge factor comparable with the gauge factor of the main material of the semiconducting strain gauges silicon was reported [4–10]. Thus, in combination with the beneficial properties mentioned above, diamond like carbon films became an attractive material for fabrication of the advanced sensors capable of working in different harsh environments [14,26–32].

Usually resistivity of the materials used for fabrication of the piezoresistive sensors depends on temperature. Therefore special electronic circuits are used to compensate the temperature effects. In the case of the diamond like carbon films, this effect may be eliminated by depositing DLC film nanocomposite containing different metals–DLC nanocomposites. Till now piezoresistive properties of DLC films containing W [15–17], Ag [17,19,20], Ti [17], Cr [18], Sn [21], Ni [6,17,22–25] were investigated and reported. However combination of the relatively high piezoresistive gauge factor (up to 14–16 and even 20–30) and zero temperature coefficient of resistance (TCR) was reported only for DLC films containing nickel [6,17,22–25]. These results were explained by encapsulation of the Ni nanoclusters embedded into the DLC matrix by several layers of graphene [6]. On the other hand, it should be mentioned that along with nickel, the main catalyst used for graphene deposition is copper [33–35]. DLC films containing Cu usually grow in the form of copper nanoparticles embedded into the DLC matrix due to the inability of copper to form bonds with carbon at room temperature [36–38]. It was shown that DLC:Cu films demonstrate plasmonic properties [38,39], so combination of these two effects (piezoresistive and plasmonic) could be of interest for different sensing applications. In the present study DLC films with embedded Cu nanoclusters were deposited and their piezoresistive properties as well as TCR were studied. Dependence of the piezoresistive gauge factor on composition and structure of DLC:Cu films was researched in a wide range content of the copper nanoparticles.

2. Experimental techniques

In the present study hydrogenated DLC:Cu films were deposited by reactive magnetron sputtering of the copper target. Argon was used as

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a sputtering gas and acetylene was used as reactive gas. High power pulsed magnetron sputtering (HIPIMS) and direct current (DC) magnetron sputtering modes of operation were used in two configurations of the magnetron magnetic field (balanced and unbalanced). In this case HIPIMS provides higher ion/neutral ratio in comparison with DC magnetron sputtering. Use of the unbalanced magnetron results in increased ion current as well as in increased ion bombardment of the growing film in comparison with the balanced magnetron. In both cases it is beneficial for growth of DLC film containing more sp^3 bonded carbon [1,2]. Thus wider versatility of the samples with different structures can be achieved. Argon and acetylene gas flow ratio as well as average power and pulse current were varied, too. In most cases samples were deposited on grounded substrates. However several DLC:Cu films were grown by using additional substrate bias. In such a way DLC:Cu films of different chemical compositions and structures were deposited. Summarized deposition conditions used in the present study are presented in Table 1. More information on the deposition conditions can be found in [38].

DLC:Cu films were deposited on polycrystalline alumina (Al_2O_3) and monocrystalline silicon substrates. DLC:Cu films grown on monocrystalline silicon, which is the most convenient substrate for deposition of DLC films, were used for investigations of the chemical composition and structure. Samples grown on polycrystalline alumina substrates were used for the measurements of the piezoresistive and electrical properties. Usually in the same technological process samples for study of the piezoresistive as well electrical properties and samples for investigations of the structure and composition were deposited. The thickness of the deposited films in all cases was in the range of 50–100 nm.

Strip-shaped DLC:Cu piezoresistors were fabricated on crystalline alumina substrates using vacuum evaporated Al-based top electrodes.

Resistance of the samples was measured by a picoammeter Keithley 5487. Gauge factor of the DLC:Cu films was evaluated by the four-point bending test [40] by using custom-made bending equipment combined with a picoammeter Keithley 5487. The used strain $\varepsilon = \Delta L/L$ in the four point bending test was in the $0 \div 0.25 \times 10^{-3}$ range. The gauge factor was calculated by using equation.

$$GF = \frac{\Delta R}{R} \cdot \frac{1}{\varepsilon}, \quad (1)$$

where R is the nominal electrical resistance, ΔR is the change of resistance due to applied strain, and ε is the strain.

Chemical composition of the films was studied by using an energy-dispersive X-ray spectrometer Bruker Quantax system with an XFlash 4030 detector attached on the field emission scanning electron microscope (FEI-SEM). Selected samples were studied by a KRATOS ANALYTICAL XSAM800 X-ray photoelectron spectroscopy (XPS) analyzer with Al Kα radiation ($h\nu = 1486.6$ eV). As both methods cannot detect hydrogen, in all cases chemical composition of the samples was measured and calculated neglecting presence of hydrogen in the films.

Raman scattering measurements were performed using a Raman microscope inVia (Renishaw) with 532 nm excitation. Integration time was 100 s, power was 0.3 mW, and grating groove density was 2400 grooves/mm. Parameters of the Raman scattering spectra related with sp^3/sp^2 bond ratio such as position of G peak, full width at half maximum of G peak (FWHM), and D/G peak area ratio were determined by fitting the experimental curves by Gaussian form components using XPS peak 3.1 software. It should be mentioned that usually D and G peak intensity (area) ratio decreases with the increase of the sp^3/sp^2 ratio. Position of G peak usually downshifts with the decrease of the sp^3/sp^2 ratio and saturation at higher ratios (>0.6) takes place [1,3]. Full width at half maximum of G peak usually increases with sp^3 content for low sp^3 hydrogenated DLC and decreases with sp^3 content for high sp^3 hydrogenated DLC [41].

Structure of the DLC:Cu nanocomposite and size of the Cu nanoclusters embedded into the DLC matrix were acquired by using a transmission electron microscope (TEM) FEI Tecnai G2 F20 X-TWIN (FEI) with a Schottky type field emission electron source operated at 200 kV. Samples were prepared by focused Gallium ion beam sputtering in a scanning electron microscope Helios NanoLab 650 (FEI).

Table 1
Deposition conditions used in present research.

	Unbalanced HIPIMS	Balanced HIPIMS	Balanced DC magnetron sputtering
C_2H_2/Ar gas flow ratio	0.63 ÷ 1.67	0.09 ÷ 0.79	0.024 ÷ 0.24
DC current (A)	–	–	0.1 ÷ 0.15
Peak current (A)	16 ÷ 30	20	–
Target voltage (V)	635 ÷ 750	490 ÷ 660	360 ÷ 400
Substrate bias (V)	0 ÷ 200	0	0
Duty cycle (%)	1 ÷ 4	1	100
Pulse time (μs)	100 ÷ 400	100	–

3. Experimental results

3.1. Structure and composition

TEM study of the selected DLC:Cu films revealed the presence of Cu nanoclusters embedded into the diamond like carbon matrix. Typical TEM micrograph can be seen in Fig. 1.

Typical Raman scattering spectra of DLC films containing Cu are presented in Fig. 2. In all cases Raman scattering spectra of the nanocomposite films were typical for diamond like carbon [1–3]. Broad Raman scattering spectral feature in the 1200–1700 cm^{-1} wavenumber range can be seen. This feature consists of the main peak at ~1500–1600 cm^{-1} and shoulder at ~1200–1400 cm^{-1}. It can be described as G peak related to the stretching vibration mode of sp^2 bonded carbon and disorder-induced D peak (shoulder) related to the breathing mode vibrations of sp^2 bonded carbon rings [1–3].

In the energy-dispersive X-ray spectra (EDS) of the investigated nanocomposite films Cu, O and C related peaks were recorded. According to the EDS measurement data, Cu atomic concentration in DLC:Cu films deposited by using different growth regimes was in the 0–40 at.% range. All films contained from 5 at.% up to 10 at.% of oxygen.

In the XPS spectra of DLC:Cu films, Cu, O and C related peaks were observed. Analysis of O1s XPS peak of DLC:Cu film containing 34 at.% Cu is presented in Fig. 3. In the case of the as deposited DLC:Cu film, the O1s peak binding energy is ~532 eV. Thus it can be supposed that the as deposited DLC:Cu film is coated by adsorbed oxygen due to air exposure [42,43]. In situ ion beam etching of DLC:Cu film results in

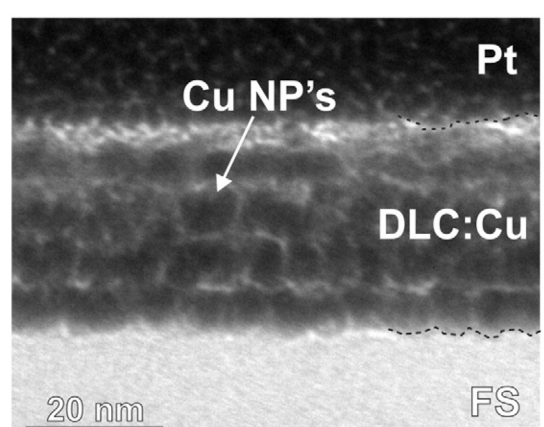

Fig. 1. Typical TEM cross-section micrograph of DLC:Cu film illustrating structure of the DLC:Cu film (Cu nanoparticles embedded into the DLC matrix). FS stands for fused silica substrate, Pt — platinum used for sample preparation. The arrow indicates Cu nanoparticle. Scale bar length is 20 nm. Investigated film contains ~33 at.% Cu.