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Optical properties of diamond like carbon films containing copper, grown by high power pulsed magnetron sputtering and direct current magnetron sputtering: Structure and composition effects

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ABSTRACT

In the present study chemical composition, structure and optical properties of hydrogenated diamond like carbon films containing copper (DLC:Cu films) deposited by reactive magnetron sputtering were studied. Different modes of deposition — direct current (DC) sputtering and high power pulsed magnetron sputtering (HIPIMS) as well as two configurations of the magnetron magnetic field (balanced and unbalanced) were applied. X-ray diffractometry, Raman scattering spectroscopy, energy-dispersive X-ray spectroscopy and atomic force microscopy were used to study the structure and composition of the films. It was shown that by using HIPIMS mode contamination of the cathode during the deposition of DLC:Cu films can be suppressed. In all cases oxygen atomic concentration in the films was in 5–10 at.% range and it increased with the copper atomic concentration. The highest oxygen content was observed in the films deposited employing low ion/neutral ratio balanced DC magnetron sputtering process. According to the analysis of the parameters of Raman scattering spectra, sp^3/sp^2 bond ratio decreased with the increase of Cu atomic concentration in the DLC films. Clear dependence of the extinction, absorbance and reflectance spectra on copper atomic concentration in the films was observed independently of the method of deposition. Surface plasmon resonance effect was observed only when Cu atomic concentration in DLC:Cu film was at least 15 at.%. The maximum of the surface plasmon resonance peak of the absorbance spectra of DLC:Cu films was in 600–700 nm range and redshifted with the increase of Cu amount. The ratio between the intensities of the plasmonic peak and hydrogenated amorphous carbon related peak at ~220 nm both in the extinction and absorbance spectra as well as peak to background ratio of DLC:Cu films increased linearly with Cu amount in the investigated 0–40 at.% range. Reflectance of the plasmonic DLC:Cu films was in 30–50% range that could be important in practical optical applications of DLC:Cu films.

1. Introduction

Nanoparticles of the group IB metals such as copper, silver and gold received a significant interest as plasmonic nanomaterials. In the case of Cu and Au, surface plasmon resonance effect can be observed in very similar range of electromagnetic waves [1]. In this case Cu has some advantages over gold. Copper is a substantially cheaper material. It is compatible with semiconductor device technology [2]. However problem of the copper surface oxidation arises [3]. Nanocomposites where nanoparticles are embedded in a matrix can be used to solve this problem. Particularly, copper containing diamond like carbon (DLC:Cu) films are deposited in the form of the metal (metal oxide) nanoparticles inserted into the diamond like carbon matrix [4–12]. Similar tendencies were reported for the silver containing and gold containing DLC films, too [12–15]. Despite the growing interest to copper as a plasmonic nanomaterial, along with most often used silver and gold, there are very few studies on optical properties of the copper containing DLC films [6,9,11]. In the absorbance spectra of DLC:Cu films deposited by reactive diode sputtering only traces of the plasmonic peaks were observed [11]. In [6,9] optical properties of DLC:Cu films synthesized by electrochemical deposition were studied and plasmonic peaks were observed in the absorbance spectra of some samples. However, in these studies no data on the chemical composition of the films as well as on the structure of the carbon matrix were provided. In addition, it should be mentioned that electrochemical deposition is rarely used for the synthesis of DLC films and it is only suitable for conductive substrates.

It should be mentioned that diamond like carbon (DLC) is an amorphous allotrope of carbon consisting of the sp^2 bonded (graphite-like) carbon nanoclusters embedded into the sp^3 bonded (diamond-like) carbon matrix [16–18]. It may contain from zero up to several tens of atomic percents of hydrogen [16–18]. Usually optical transmittance of DLC in a visible light range as well as hardness and Young's modulus increase with sp^3/sp^2 bond ratio. In such a way, the hardness of DLC can reach up to 80% of the diamond hardness, while optical transmittance

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may be comparable with transmittance of the nanocrystalline diamond films [19].

In the present study the influence of composition and structure on optical properties of DLC:Cu films deposited by reactive magnetron sputtering were investigated. Along with direct current (DC) magnetron sputtering, innovative deposition method – high power pulsed magnetron sputtering (HIPIMS) – was applied to deposit the diamond like carbon films. HIPIMS deposition method provides high ion/neutral ratio [20] preferable for the formation of DLC films containing a high amount of sp^3 bonded carbon [16]. Plasma density in HIPIMS is similar to the case of the cathodic arc deposition and pulsed laser ablation — synthesis methods that are most often used to deposit high sp^3/sp^2 bond ratio films [20]. Yet main drawbacks of the cathodic arc deposition and pulsed laser ablation (contamination of the film by droplets of target and problems with large area deposition) are avoided [20].

2. Experimental techniques

In the present study reactive magnetron sputtering was used for the deposition of DLC:Cu films. Two modes of operation (direct current (DC) and HIPIMS) were used. Two configurations of the magnetron magnetic field (balanced and unbalanced) were applied. In all cases mixture of the hydrocarbons (acetylene) and argon gas was used. The diameter of magnetron was 3″ and the copper target was used.

In the case of HIPIMS deposition various pulse currents in 2.4–30 A range were used. Pulse on time in all cases was set at 100 μs, duty cycle of 1%, and frequency of 100 Hz. Base pressure was 5×10^{-4} Pa and work pressure $(4 \pm 1) \times 10^{-1}$ Pa was maintained throughout the deposition process. In the case of DC sputtering, magnetron target current was 0.1 A, base pressure was 5×10^{-4} Pa and work pressure was $(4 \pm 1) \times 10^{-1}$ Pa. Thin films were deposited on monocrystalline silicon and quartz substrates. In all experiments substrate–target gap was set at 0.1 m and the substrates were grounded. The thickness of the deposited films in all cases was in the range of 50–100 nm.

Optical properties of the films were investigated using an optical spectrometer Avantes that is composed of a deuterium halogen light source (AvaLight DHc) and spectrometer (Avaspec-2048). Extinction (complete optical losses due to the reflection and absorption of light), absorbance and reflectance of the films were analyzed in the wavelength region from 180 nm to 1100 nm.

The microstructure of DLC:Cu films was studied and linear dimensions of the copper nanoparticles/clusters in DLC matrix were estimated by employing a field emission scanning electron microscope (FE-SEM) FEI Quanta 200 FEG in a high vacuum mode. Theoretical resolution of the FE-SEM at 30 kV accelerating voltage is 1.2 nm in a high vacuum mode. 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).

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.

The structure of the crystalline copper nanoclusters was studied by an X-ray diffractometer D8 Advance (Bruker AXS, Germany). Grazing incidence angle arrangement combined with parallel beam X-ray diffraction geometry was used. Multilayer Ni/graphite parabolic monochromator was placed in front of the sample. X-ray diffraction patterns were recorded using Cu cathode at 40 kV, anode current of 40 mA, and scanning step D2Q = 0.04° and average time of integration was 15 s.

The morphology of the surface was analyzed with an atomic force microscope NanoWizard®3 (JPK, Germany) working in an AC Mode. Silicon probes with a reflective backside Al coating (ACTA-10, APPNano, USA) with a resonance frequency of 200–400 kHz and force constant of 13–77 N/m were used. Nominal tip radius was less than 10 nm. The scanning rate of 0.8 Hz was selected.

3. Experimental results

3.1. Deposition conditions effects on target contamination

Target contamination by the products of reactions with reactive gas components is one of the main problems related to the reactive magnetron sputtering [21]. In the present study during the deposition of DLC:Cu films containing copper (up to 30 at.%) by DC magnetron sputtering resulted in contamination of the sputtering target by carbon film and resultant subsequent drop of the deposition rate during growth of the film. According to our findings this problem can be avoided by using HIPIMS. For DLC:Cu films deposited by reactive HIPIMS such a problem was observed only for the films containing small amounts of copper (up to several atomic percents).

3.2. Structure and composition

Raman scattering spectra of the DLC:Cu films deposited by unbalanced HIPIMS are presented in Fig. 1. In all cases the spectra were typical for diamond like carbon [16–18]. There were no clear differences between the Raman scattering spectra of DLC:Cu films deposited by both balanced and unbalanced HIPIMS as well as balanced DC magnetron sputtering. In all spectra G peak (stretching vibration mode of sp^2 bonded carbon) at ~1500–1600 cm^{-1} and shoulder at ~200–1400 cm^{-1} related to disorder-induced D peak (breathing modes of sp^2 bonded carbon rings) [16–18] were observed.

SEM study revealed the nanocomposite microstructure of DLC:Cu films: copper nanoclusters embedded into the diamond like carbon matrix. From the FE-SEM micrographs of DLC:Cu nanocomposite film (Fig. 2) one can see 10–20 nm sized bright features that could be attributed to the copper nanoparticles as the metal gives a higher electron contrast than dielectric matrix i.e. DLC.

X-ray diffraction (XRD) diffractograms of DLC:Cu films are presented in Fig. 3. In the case of DLC:Cu film deposited by balanced HIPIMS and

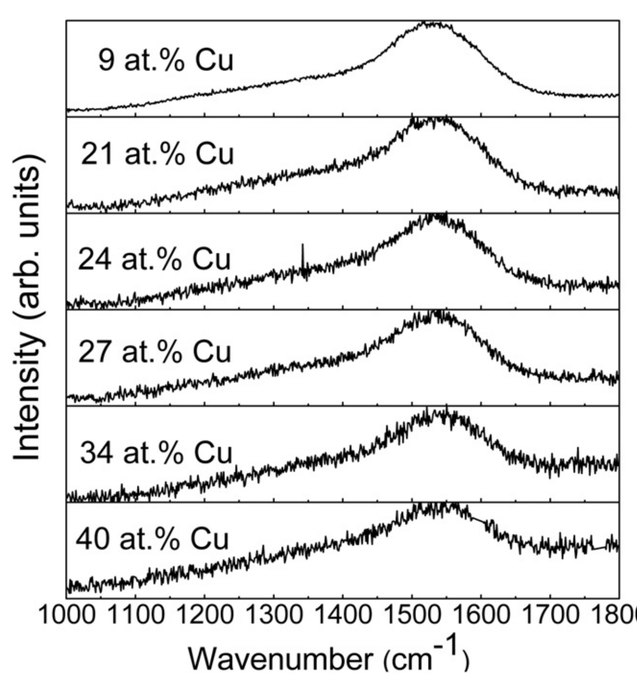

Fig. 1. Typical Raman scattering spectra of DLC:Cu films (all films presented were deposited by unbalanced HIPIMS).