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Piezoresistive properties of amorphous carbon based nanocomposite thin films deposited by plasma assisted methods

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ABSTRACT

The survey of recently completed research concerning relation between the used technology of deposition (plasma enhanced chemical vapor deposition, magnetron sputtering), reagents, structure and piezoresistive properties of diamond like carbon (DLC) films containing different nanoparticles is presented. The effects of systematically varied deposition conditions during plasma assisted methods, such as bias voltage, gas flow ratio on chemical composition, structure and properties of diamond like carbon nanocomposites are discussed, and attention is paid to the origin of piezoresistive effect and role of matrix on the main parameters, such as gauge factor and temperature coefficient of resistance. The role of the carbon matrix and the size of silver nanoparticles in the DC magnetron deposited diamond like carbon films are analyzed. It is shown that according to the Raman scattering the sp^3/sp^2 ratio in the silver containing diamond like carbon (DLC:Ag) films increases with the acetylene/argon flux ratio. The surface plasmon resonance related peak was observed in the optical absorbance spectra of DLC:Ag films when silver atomic concentration in films reached 3.7%. It was revealed that the gauge factor of silver containing DLC films is dependent on both structure of the diamond like carbon matrix and on size of the silver clusters.

1. Introduction

Diamond like carbon (DLC) films, present an umbrella term that refers to at least 7 forms of amorphous carbon materials [1] (hydrogen-free amorphous carbon film (a-C); tetrahedral hydrogen-free amorphous carbon film (ta-C); metal-containing hydrogen-free amorphous carbon film (a-C:Me); hydrogenated amorphous carbon film (a-C:H); tetrahedral hydrogenated amorphous carbon film (ta-C:H); metal-containing hydrogenated amorphous carbon film (a-C:H:Me (Me = W, Ti, …)); and modified hydrogenated amorphous carbon film (a-C:H:X (X = Si, O, N,F, B,…))). They display some of the unique properties of natural diamond, and received considerable interest due to their outstanding physical properties and low temperature deposition possibility. The DLC coatings already have found many industrial applications covering a wide range of properties (hardness, friction coefficient, surface energy, electrical conductivity, abrasion resistance etc.) and variety of products with different coating architectures are known by commercial names like DYLYN, MAXIT, CAVIDUR etc. and are already available on the market [2]. Recently the piezoresistive effect of a-C and a-C:H films showing changes of resistivity due to exposure of the film by pressure was discovered [3–5]. Piezoresistive gauge factor comparable with the gauge factor of crystalline silicon was reported in some studies [6]. In combination with high hardness, low friction coefficient, high corrosion resistance [7] diamond like carbon became an attractive material for fabrication of the advanced sensors capable to work in corrosive environments under different mechanical influences, such as wear.

It was recognized that the electrical characteristics of the DLC coatings can be tailored by the addition of metal dopants. Mechanical properties of the hard carbon films can also be improved by incorporating a small percentage of metal dopant in the final carbon structure. The resulting films usually have excellent friction and wear properties. Doping of DLC film by metals of group1B such as gold, silver, copper results in an interesting modification of the film's optical properties. In this manner, diamond like nanocomposite films exhibiting a surface plasmon resonance effect can be grown [8]. On the other hand, it was demonstrated in [9] that Ni containing a-C:Ni films demonstrate high strain sensitivity and low value of the temperature coefficient of resistivity (TCR). I.e. such kind of films combine the necessary attributes of the piezosensitive material that can be applied without any additional temperature compensation circuit in a wide range of temperatures. This and other publications have triggered systematic research in the field of piezoresistivity of DLC aiming at the understanding of the phenomenon, and seeking for the optimum conditions of deposition of thin films as well as development of different technologies of sensors and variety of applications [10–26]. Keeping in mind recently reported values of the gauge factor for DLC films exceeding 1000 [23,24] as well as the possibility to tune value of the TCR, one can expect huge potential of applications of DLC as well as DLC containing metal films in the field of sensors working in harsh environment, such as high temperature, ionizing radiation or chemical attack.

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Despite numerous publications in this field, questions concerning the piezoresistivity effect in dependence on technological conditions, ways of deposition, and the role of the embedded nanoparticles still need to be further clarified. The present work aims to survey shortly the situation in the field, to overview the deposition techniques and deposition conditions as well as to contribute to further understanding of piezoresistivity effect in DLC based Ag nanocomposites (DLC:Ag).

2. Piezoresistive effect

The piezoresistive effect describes change in the electrical resistivity of material when mechanical stress is applied. In contrast to the piezoelectric effect, the piezoresistive effect only causes a change in electrical resistance, and not in electric potential [27]. This effect is used in the strain gauges to control stress, force, pressure or torque in different systems. It should be noted that all semiconductor materials exhibit changes in resistance due to strain and probably the most common material in the applications of strain gauges is silicon, because of physical properties of this material as well as because of well developed micromachining techniques. In addition to the semiconductor materials, resistive metallic strain gauges in the form of thin conducting layers deposited on an insulating substrate and etched to form long wire are used. Typical material for these applications is constantan (60% of copper, and 40% of nickel). The piezoresistivity is characterized by a gauge factor that for small deformations is proportional to the fractional change in the resistance [27]:

$$\mathrm{GF} = \frac{\Delta R}{R}\frac{1}{s} \tag{1}$$

where R is the nominal electrical resistance and ε is the strain.

The change in resistance is due to the change in the dimension of the resistor and the change in the resistivity of the material itself. Total resistivity change of the isotropic material can be expressed in terms of longitudinal and transverse stress component [27]:

$$\frac{\Delta\rho}{\rho} = \pi_l\sigma_l + \pi_t\sigma_t \tag{2}$$

where π_l and π_t are piezoresistive coefficients relating change of resistivity ($\Delta\rho/\rho$) due to stress in longitudinal direction (σ_l) and transverse direction (σ_t).

Another important parameter that is essential in the piezoresistive applications is temperature coefficient of resistance (TCR) (or sometimes used temperature coefficient of gauge factor TCGF). The temperature coefficient of resistance (measured in ppm/K) describes the parts per million change in resistance per 1° change in temperature:

$$\mathrm{TCR} = \frac{1}{\Delta T}\frac{\Delta R}{R} = \frac{1}{\Delta T}\frac{R_T - R_0}{R_0} \tag{3}$$

where ΔT is the change in temperature, R_0 is the electrical resistance measured at room temperature (or reference temperature), R_T is the electrical resistance measured at operating temperature.

These two parameters are critical in terms of applications because a sensor with good performance should exhibit high GF and low TCR. Increasing demands for piezoresistive sensors capable to operate at high temperatures, harsh environments like automotive, petrochemical, space and other applications have stimulated research in developing of advanced materials. Analysis of performance of strain sensors based on sputter-deposited different semiconductor thin films such as titanium dioxide (TiO_2), silicon carbide (SiC), indium tin oxide and diamond-like carbon operated at elevated temperatures (up to 250 °C) [17,25,27] has indicated increasing interest of the researchers to different types of DLC films. It should be noted that all reported DLC films as well as DLC films including metallic nanoparticles, indicating piezoresistive properties have been deposited by different types of plasma based methods: reactive rf powered diode sputtering [9,20,24], rf magnetron sputtering [10,11], reactive DC and rf magnetron sputtering [22], plasma assisted chemical vapor deposition (PACVD) [11,12,14–16,22], rf plasma chemical vapor deposition [13], combined PVD (physical vapor deposition)/PACVD [17,18,23], direct ion beam deposition [19], and DC or pulsed DC magnetron sputtering [21,22]. It should be noted that most of these methods are used on industrial scale and choice of the method depends mainly on the type of targeted DLC films (a-C, a-C:H or a-C:H:Me (Me = W, Ti, Ni…)). In many cases deposition was performed at low temperature (sometimes room temperature) and usually did not exceed 200 °C. Post annealing of the films at 180 °C [18] (in some cases up to 300 °C [24]) was applied to stabilize properties of the films. In summary, one can conclude that the reported DLC films demonstrating piezoresistive properties were deposited using low substrate temperature processes. On the other hand, producing highly sensitive sensors with GF reaching up to 1000 needs careful control of many technological parameters, like substrate bias voltage, working pressure, and gas flow [22]. Substrate temperature control appears to be an important technological parameter and increase of the temperature even by 20 °C can result in substantial reduction of the gauge factor [21].

To explain the origin of the piezoresistive effect in DLC films, a qualitative model adopted from a work on thick film resistor was proposed in [11] where DLC films were described as a composite of conductive sp^2 clusters in insulating sp^3 matrix. Depending on the deposition conditions the percentage of sp^2 and sp^3 varies causing changes in the sp^2 cluster size and the distance between two clusters (noted as d). The gauge factor was expressed as:

$$\mathrm{GF} = \left(\frac{2d}{\xi}\right) \tag{4}$$

where ξ is the localization length (the expression is valid for $\mathrm{GF}\varepsilon \ll 1$). This approach was in line with the experimental findings where value of the cluster size defined from the Raman scattering spectra was evaluated. It was shown that DLC films deposited by PACVD at high bias voltage have high sp^2 content leading to a large sp^2 cluster and finally to lower value of the registered gauge factor. Similar results were demonstrated in [21] where correlations of the GF of DC magnetron deposited DLC hydrogen free films with the DLC Raman scattering parameters (I_D/I_G ratio, G peak position as well as full width at half maximum (FWHM) of G peak),were observed. The gauge factor increased with the sp^3/sp^2 bond ratio and decrease of size of sp^2 clusters. The gauge factor increased as well with the resistivity of the film and this dependence could be presented as a logarithmic law:

$$\mathrm{GF} \sim log(R). \tag{5}$$

Electrical properties of such compound depend on the conductive volume fraction (sp^2 bonded carbon) and tunneling is supposed to be the main charge transfer mechanism. The experimental results are in accordance with the tunneling–percolation model of conductor and insulator where linear decrease of the gauge factor with logarithm of electrical conductivity (decrease of electrical resistivity) is predicted [28]. It should be noted as well that the gauge factor correlated with the refractive index of DLC that converged to the value typical for diamond with the increase of sp^3/sp^2 ratio.

On the hand, the stabilized atomic scale composites 'diamond-like carbon-metal' are virtually ideal metal-dielectric percolating systems [28]. The metals may be introduced in the diamond-like dielectric during its growth in a combined plasma or PVD deposition process. In this way, combination of a semiconducting material with high gauge factor (negative TCR) and a metal (positive TCR) enables the production of sensor material with a TCR close to zero. Different metals (Ni, W, Ti, Cr, Ag) have been tested in a-C or in a-C:H matrix [9,16–18,20,22]. In this type of nanocomposites the maximum metal concentration and temperature limiting the composite stability depend on the atom radius and metal-matrix interaction. The most promising results in terms of