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Piezoresistive, optical and electrical properties of diamond like carbon and carbon nitride films

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ABSTRACT

In the present study diamond like carbon (DLC) and carbon nitride (a-CN_x:H) films were deposited by closed drift ion source from the acetylene and nitrogen gas mixture. The piezoresistive, electrical and optical properties of ion beam synthesized DLC films were investigated. Piezoresistive properties of the diamond like carbon and carbon nitride films were evaluated by four point bending test. The piezoresistors were fabricated on crystalline alumina substrates using Al-based interdigitated finger type electrodes. Effects of the nitrogen concentration on the piezoresistive gauge factor were investigated. The dependence of the resistance of the metal/a-CN_x:H/metal structures on temperature has been studied. Current–voltage (*I–V*) and capacitance–voltage characteristics were measured for a-CN_x:H/Si heterostructures. The main current transport mechanisms were analyzed. Optical parameters of the synthesized films such as optical bandgap and *B* parameter (slope of the linear part of the Tauc plot) were investigated to study possible correlation with the piezoresistive properties.

1. Introduction

Diamond like carbon and related films received considerable interest due to their outstanding mechanical, optical and electrical properties as well as chemical inertness and biocompatibility [1]. Recently significant piezoresistive effect was reported for diamond like carbon films enabling fabrication of the novel DLC based sensors [2]. However, there are only a few studies on piezoresistive properties of the diamond like carbon films [2–8]. Particularly doping effects on piezoresistivity of the diamond like carbon films were investigated only for some cases of the metal containing DLC [7,8]. Meanwhile diamond like carbon film doping by different chemical elements is widely used for reduction of the large intrinsic stress of DLC films as well as improvement of the adhesion with different substrates and control of the electrical properties [9–13]. Particularly amorphous carbon nitride (a-CN_x:H) films are widely investigated.

In the present study piezoresistive as well as optical and charge transport properties of a-CN_x:H films were investigated. Optical characteristics and charge transport issues in synthesized films were studied.

2. Experimental

In this research hydrogenated diamond like carbon (DLC) and a-CN_x:H films have been synthesized by direct ion beam deposition using closed drift ion source, on monocrystalline Si and polycrystalline alumina substrates. Detailed description of the deposition system used is presented in [14]. More information on design and operation principles of the closed drift ion sources can be found in [15,16]. High purity acetylene and nitrogen gas have been used as a source of the hydrocarbon and nitrogen respectively. The base pressure was $2 \cdot 10^{-4}$ Pa, work pressure — $(1–2) \cdot 10^{-2}$ Pa, ion beam energy 800 eV and ion beam current density 100 μA/cm^2. Raman spectra of the a-CN_x:H deposited by close drift ion source in all cases were typical for diamond like carbon [14].

Optical transmittance spectra of the samples have been measured by a Fiber optic UV/VIS/NIR Spectrometer AvaSpec-2048. Absorption coefficient α was calculated from the UV–VIS transmittance spectra using a Lambert–Beer law. Optical bandgap of the synthesized films has been estimated using Tauc plot based on the equation for interband transitions in amorphous semiconductors $(\alpha \cdot E)^{1/2} = const \cdot (E - E_{opt})$ [17]. Slope of the Tauc plot (*B* parameter) of the a-CN_x:H films has been calculated as a measure of the disorder in investigated films [18].

Charge transport mechanisms were evaluated by measuring current–voltage (*I–V*) characteristics of the a-CN_x:H/nSi and a-CN_x:H/pSi heterostructures. The dielectric constant (ε) was calculated from the a-CN_x:H/silicon heterostructure capacitance–voltage (*C–V*) measurement data. In all cases Al has been used as a material both for the bottom (common) and top electrode fabrication. The top electrode diameter for fabricated heterostructures was the 500 μm.

In the present study both contact limited (Schottky emission, Fowler–Nordheim tunnelling) and bulk limited (space charge limited

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currents, Poole–Frenkel emission) charge transport mechanisms were considered [19].

Schottky emission (charge flow over the potential barrier) can be described by equation [19]:

$$J = A^{*}T^{2}\exp\left(\frac{\beta_S E^{1/2} - q\varphi_B}{kT}\right), \tag{1}$$

where $\beta_S = (q^3/4\pi\varepsilon_0\varepsilon)^{1/2}$, A^* is the effective Richardson constant, q — electron charge, ε_0 — vacuum dielectric permittivity, k — Boltzmann constant, T — temperature, φ_B — height of the potential barrier, ε — dielectric permittivity of the DLC. Presence of the Schottky emission can be identified from the linear dependence of $ln(J) \sim E^{1/2}$ plot. Possible presence of the Schottky emission can be additionally verified by comparing dielectric permittivity calculated from the capacitance–voltage characteristics of the DLC/Si heterostructure using parallel plate capacitor equation (ε_{CV}), and dielectric permittivity, calculated using Schottky emission model (ε_S) [20,21]. In such a case ε_S can be found from the slope of the linear part of the Schottky plot $S_S = \frac{\beta_S E^{1/2}}{kT}$.

Fowler–Nordheim tunneling is described by the following equation [19]:

$$J = \frac{m}{m^*}\frac{q^3}{8\pi h\phi}E^2\exp\left(\frac{-B}{E}\right) \tag{2}$$

where m^* is an electron effective mass, h — Plank constant, ϕ — cathode potential barrier height. Presence of the Fowler–Nordheim charge transfer mechanism can be identified from the linear dependence of $ln(J/E^2) \sim E^{1/2}$.

Space charge limited currents are related with limiting of the charge transfer by accumulated uncompensated charge in insulator [19]. This mechanism can be revealed by the presence of the linear dependence of $log(J) \sim logV$ ($log(J) \sim log(E)$). In such a case current density will depend on interelectrode distance — it will decrease with the increase of the distance.

Poole–Frenkel emission is related with field-enhanced thermal excitation of trapped charge carriers. It can be described by the following equation [19]:

$$J = J_0\exp\left(\frac{\beta_{PF}E^{1/2} - q\varphi_{PF}}{kT}\right) \tag{3}$$

where J_0 is the low-field current density, $\beta_{PF} = (q^3/4\pi\varepsilon_0\varepsilon)^{1/2}$. q — electron charge, ε_0 — vacuum dielectric permittivity, ε — dielectric permittivity of the DLC, k — Boltzmann constant, and T — temperature. Poole–Frenkel emission can be identified from the linear dependence of $ln(J/E) \sim E^{1/2}$. Possible presence of the Poole–Frenkel emission can be additionally verified by comparing dielectric permittivity calculated from the capacitance–voltage characteristics of the DLC/Si heterostructure using parallel plate capacitor equation (ε_{CV}) and dielectric permittivity calculated using Poole–Frenkel emission model (ε_{PF}) [20,21]. In such a case ε_{PF} can be found from the slope of the linear part of the Schottky plot $S_{PF} = \frac{\beta_{PF}E^{1/2}}{kT}$.

Samples for the study of piezoresistive properties and resistance dependence on temperature were fabricated on polycrystalline alumina substrates. Interdigitted aluminum electrodes were deposited on top of the DLC a-CN_x:H films. For more information on the fabrication of the samples please see [6]. The resistance dependence on temperature in 253–343 K range was studied. Piezoresistive properties of the diamond like carbon films were evaluated by four point bending test [22]. Gauge factor was calculated as a measure of the piezoresistive properties of the DLC a-CN_x:H films:

$$k = \frac{R - R0}{R}\cdot\frac{1}{\varepsilon} \tag{4}$$

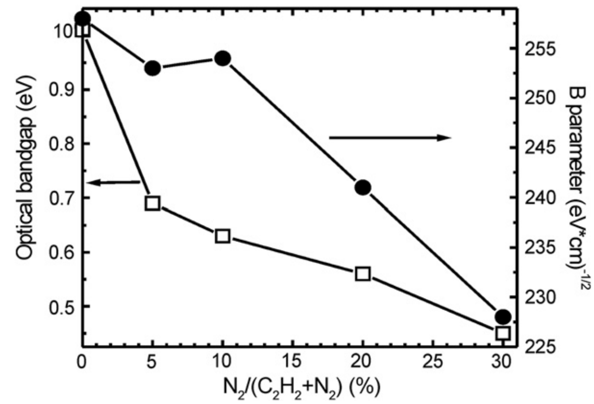

Fig. 1. Effects of the N_2 concentration on optical properties of the diamond like carbon films.

where ε is applied strain, R_0 — resistance at zero strain, and R — resistance at applied strain ε.

Thickness of the films was controlled by a laser ellipsometer Gaertner L115 ($\lambda = 633$ nm). In most cases thickness of the a-CN_x:H films was 200 nm. However, several samples of 60 nm thickness were fabricated on n-type and p-type monocrystalline silicon substrates to study charge transport mechanisms.

3. Experimental results and discussion

The optical bandgap of the synthesized films has been investigated as an indirect measure of the sp^2 bonded carbon cluster size, because optical bandgap decreases with the increase of the sp^2 cluster size [23] and increase of the amount of sp^2 fraction [24]. It can be seen, that in our case N_2 doping resulted in a steady decrease of the optical bandgap (Fig. 1). It is in good accordance with the behavior reported in [25,26]. Slope of the Tauc plot decreased as well with the increase of the N_2 concentration in gas mixture (Fig. 1); nitrogen doping resulted in formation of the more disordered films.

In all cases (nitrogen concentration range 5–30%) both for a-CN_x:H/nSi and a-CN_x:H/pSi heterojunctions diode-like *I–V* characteristics were observed, despite n-type conductivity was reported for amorphous carbon nitride films in numerous studies [11–13] (Fig. 2). It should be mentioned, that similar to the present study diode-like characteristics were reported both for hydrogenated DLC/nSi and hydrogenated DLC/pSi heterojunctions in [6,27], although conductivity of the hydrogenated undoped DLC is of the p-type [28–30]. Such a behavior possibly can be explained by DLC/Si heterojunction offset as well as by high irradiation defects related states density at DLC/Si interface and by the presence of the ultra-thin native SiO_2 layer at the surface of the silicon.

Transport properties of the a-CN_x:H/nSi and a-CN_x:H/pSi heterojunctions were investigated. Some linear parts in Poole–Frenkel, Schottky and double logarithmic plots were observed indicating

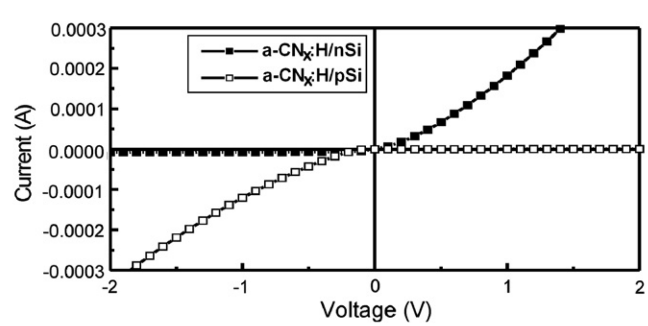

Fig. 2. Typical *I–V* characteristics of the a-CN_x:H/nSi and a-CN_x:H/pSi heterojunctions ($N_2/(N_2 + C_2H_2)$ flow rate 5%).