

Electrical and photoelectric properties of polycrystalline diamond films deposited from an abnormal glow discharge

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Abstract. Electrical and photovoltaic properties of polycrystalline diamond films (PDF), deposited from the abnormal glow discharge were analysed. Features of charge carrier transfer in PDF are determined by continuous energy distribution in the band gap of defect states of different nature. Dominated n-type conductivity activation component of electrical conduction and photoconductivity is complemented by a hopping mechanism with the participation of states near the Fermi level with a density $5.6 \cdot 10^{17} - 2.1 \cdot 10^{21} \text{ eV}^{-1} \text{ cm}^{-3}$. Activation transfer is realized in the exchange of charge carriers between the allowed bands and donor levels with the activation energy 0.007–0.21 eV, which are sparsely populated and have wide variation in their parameters. Trapping centers and carriers recombination are heterogeneously distributed in grain boundaries. Under lighting, the state density increases 3-5 times and probable jump length decreases by 1-3 nm. Spectral distribution centers of photosensitivity are correlated with the distribution of deep-level defects, determining the absorption spectra.

1. Introduction

Unique chemical, mechanical, electrical, thermal, optical and photoelectrical properties of a diamond contribute to its wide application in high-frequency, high-temperature electronics and semiconductor manufacturing of a special purpose [1–5]. Due to the limited possibility of using diamond single crystals and epitaxial diamond films, because of their high cost in the most appropriate instruments are the polycrystalline diamond films (PDF), which are obtained by well-studied methods of the vapor deposition [1-8]. PDF are successfully used for the production of the stable radiation-resistant UV detectors and ionizing radiation, as well as for laser and photodiode structures [1,4]. Dielectric PDF are used for these purposes (electrical conduction ($\sigma=10^{-15}-10^{-11} \text{ S}\cdot\text{cm}^{-1}$). Depending on the characteristics of PDF polycrystalline structure, the content of alloying impurity atoms and defects in the PDF crystal structure, the electrical characteristics, as well as the mechanism of transport and type of charge carriers vary widely ($\sigma=10^{-6}-10^3 \text{ S}\cdot\text{cm}^{-1}$) [1,4–15]. It stimulates the study of the peculiarities of polycrystalline films electric and photoelectric properties, and the investigation of the mechanisms determining these properties and the influence of deposition conditions on the change in the characteristics of the film material.

The aim of the work is to determine the electrical and photovoltaic characteristics of the dominant transfer mechanism, charge carriers and the energy spectrum of the defect levels in PDF, deposited from plasma abnormal glow discharge.



2. Experimental

Methods of film deposition from abnormal glow discharge and the study of their structural features are described in detail in [2]. Dark surface conductivity σ and photoconductivity $\Delta\sigma_{\text{ph}}=\sigma_{\text{ph}}-\sigma$ (σ_{ph} conductivity at lighting), photosensitive $K(h\nu)=\Delta\sigma_{\text{ph}}/\sigma$ were measured at a constant voltage across the electrodes $U=0.01\text{--}300$ V, at temperature $T=300\text{--}700$ K and photon energy $h\nu=1.5\text{--}4.0$ eV. The electrodes were deposited on the surface by rubbing the soft graphite. Temperature dependences of σ , $\Delta\sigma_{\text{ph}}(T)$ are approximated by the equation for the activation mechanism

$$\sigma_a(T) = \sigma_0 \times e^{(-\varepsilon_\sigma/kT)}, \quad (1)$$

where σ_0 – pre-exponential factor, ε_σ – activation energy, k – Boltzmann constant and equation for the hopping mechanism of transport between localized states (LS) near the Fermi level E_F in the model of Mott

$$\sigma_p(T) = \sigma'_0 \times e^{-(T_0/T)^{0.25}}, \quad (2)$$

where σ'_0 – pre-exponential factor, T_0 –activation energy [16–18]. The density of states $N(E_F)$ was calculated from T_0 according to [16–18]. The sign of the dominant charge carriers was determined by the method [16].

3. Result and discussion

Current voltage characteristic (CVC) $I(U)$, field dependence of $K(U)$ and carrier transfer characteristics ε_σ , σ_0 , T_0 , σ'_0 , $N(E_F)$ vary in thickness and deposition plane, due to the inhomogeneity of PDF properties (figures 1, 2). Quantitative differences in the parameters σ and $\Delta\sigma_{\text{ph}}$ are recorded from the growth smooth and the opposite rough sides (figures 1, 3). Conductivity from the growth side is higher than from the side of the substrate and the ratio between K is opposite (figure 1). In vacuum σ in 1.1–1.3 times lower than in the air, due to the weak influence of the absorption currents. Only physical adsorption of molecules of atmospheric gases on the surface of PDF affects the change of $\sigma(T)$, so stable chemical bindings are not formed. CVC coincidence at $U>0$ and $U<0$ indicates a weak influence of space charge cloud on σ and $\Delta\sigma_{\text{ph}}$. The annealing of the films before $T_{\text{ann}}<600$ K stabilizes the properties. CVC PDF with $\sigma=10^{-10}\text{--}10^{-4}$ S is ohmic (figure 1). These films have a low, but stable photosensitivity to heat and change U ($K=0.005\text{--}0.1$), as compared with dielectric PDF ($K=0.1\text{--}1.0$). In PDF with $\sigma=10^{-14}\text{--}10^{-11}$ S deviation from the linear law is fixed, CVC obeys the equation $I \propto \exp(\beta U)$, where $\beta=0.02\text{--}0.05$ (figure 1, curves 4 and 5)), which indicates the current effect, limited by the space charge, as in [8]. In CVC nonlinearity makes the spatial distribution of the energy barrier that exists on the border with electrodes and grain boundaries [6–8]. Variation in PDF electrical parameters may be caused by inhomogeneity in the distribution of crystallites on size and growth defects in their entirety and on the boundaries or by the influence of hydrogen impurity in the surface layers [4, 11–14].

Dependencies σ , $\Delta\sigma_{\text{ph}}(T)$ in the interval $\Delta T=300\text{--}600$ K are determined by thermally stimulated electron exchange between the shallow donor levels with energy $\varepsilon_\sigma=0.007\text{--}0.21$ eV and the conduction band (CB). For $\Delta\sigma_{\text{ph}}$ value ε_σ at 0.03–0.05 eV is lower than for σ by reducing the population of LS upon excitation by 5–10 times. There is usual quenching $\Delta\sigma_{\text{ph}}(T)$ at $T \geq 340$ K. N-type σ and $\Delta\sigma_{\text{ph}}$ are dominated in PDF layers. It cannot be excluded the influence on CVC, σ , $\Delta\sigma_{\text{ph}}(T)$ and $K(U, h\nu)$ the exchange of holes between LS defects and the valence band (VB) [13]. The parameters ε_σ , σ_0 indicate the effect on the transfer of hopping conductivity, which is confirmed by approximation $\sigma(T)$ in the interval $\Delta T=300\text{--}600$ K (figure 2). LS density calculated from σ , $\Delta\sigma_{\text{ph}}(T)$ is large $N(E_F)=5.6 \cdot 10^{17}\text{--}1.5 \cdot 10^{21}$ eV⁻¹cm⁻³ in PDF with $\varepsilon_\sigma=0.007\text{--}0.15$ eV. In PDF LS density, exponentially distributed near E_F consist $N(E_F)=(4\text{--}8) \cdot 10^{19}$ [17, 18] and $10^{15}\text{--}10^{18}$ eV⁻¹cm⁻³ [19]. The magnitude of the most probable jump length is calculated according to [16–18] for the values of $N(E_F)$, is $R=1.1\text{--}8.1$ nm and under

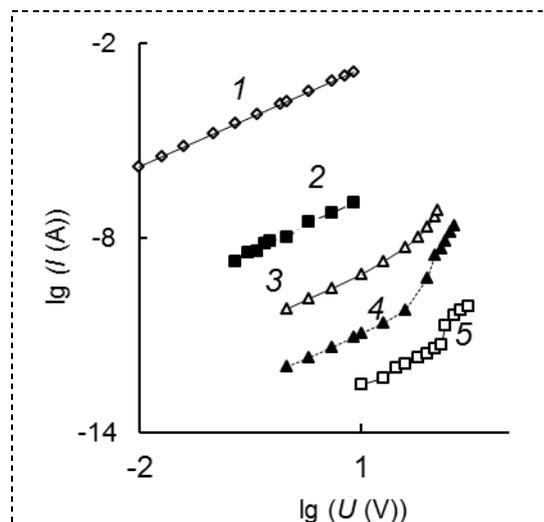


Figure 1. CVC of PDF from the growth side (curves 1 and 2) and from the substrate side (curve 3–5) in the center (curves 1,3) and on edge deposition (curves 2, 4 and 5).

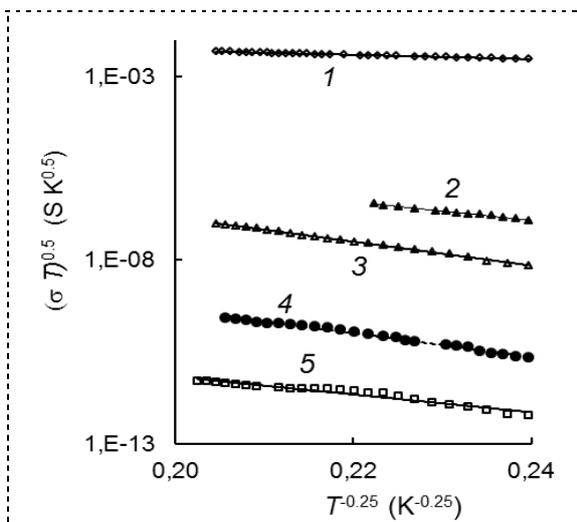


Figure 2. Temperature dependences of conductivity of PDF from the growth side (curves 1 and 2) and from the substrate side (curves 3–5) and in the center (curves 1 and 3) and on edge deposition (curves 2, 4 and 5).

lighting was reduced to 1.0–6.0 nm in line with the increase in the LS density of 3–5 times for PDF with $\sigma < 10^{-10}$ S.

Dependencies between parameters σ_h , σ_a and K allow establishing the predominance of one of the transfer mechanisms. Decrease σ_0 with the increasing ϵ_σ indicates the predominance of σ_a (figure 3, curve 1). This interrelationship is confirmed by $N(E_F)(\epsilon_\sigma)$ is typical for the uncrystalline semiconductors with a high content of defects [16–19]. By analogy with [6–13, 16–19], we can conclude that PDF hopping conductivity on LS near the Fermi level dominates over the activation in the range of $T=300$ – 400 K. At $T=400$ – 600 K is determined by the electrical conductivity activation $\sigma_a(T)$ with LS defects interference on grain boundaries and distributed in band gap (BG) in the area of "tails" of the allowed bands. Charge carriers are excited through mobility gap in the area of delocalized states. At $T > 600$ K, the influence of the barrier between the crystallites is increases [6, 8]. The largest contribution to $\Delta\sigma_{ph}(T)$ gives the activation component σ_a , as confirmed by $K(T, U, \epsilon_\sigma)$ (figure 3, curve 2).

Shape of the spectrum $K(h\nu)$ is similar to the shape of PDF absorption spectra (figure 4) [1, 4]. There is a constant value of photosensitivity in the interval $h\nu=1.2$ – 2.0 eV. In the interval $h\nu=2.0$ – 3.2 eV there is an increase of photosensitivity with further decrease in $h\nu \geq 3.2$ eV. A similar change of $K(h\nu)$ is recorded in PDF at $h\nu=1.8$ – 2.9 eV [4]. In [12], the threshold at 2.6 eV is determined by electronic transitions between the VB and LS defects in diamond thin oxidized layer after hydrogenization. Such a spectrum $K(h\nu)$ in UNCD films is induced with transitions in LS tails zones and LS of inclusions of graphite-like phase [1]. Growth in K at $h\nu > 3.4$ eV is typical for most structures based on PDF in detectors of ultraviolet irradiation [4]. The oxygen from the air adsorbed on growth defects may have a passivating effect on the increase in photosensitivity of surface of deposited PDF in ultraviolet band.

Accumulation of optical concentration levels is associated with decreasing of LS density near the Fermi level which are involved in hopping transfer, as it is shown by its reduction from $N(E_F)=10^{19}$ to $5 \cdot 10^{17}$ $eV^{-1} \cdot cm^{-3}$ an increase of the absorption coefficient from $\alpha=2 \cdot 10^4$ to $5 \cdot 10^4$ cm^{-1} . Reduction of density responsible for $\sigma_h(T)$ states $N(E_F)$ is also correlated with an increase in the Urbach energy E_U levels which determine the characteristics of the optical absorption in the intervals $h\nu=1.15$ – 1.3 eV

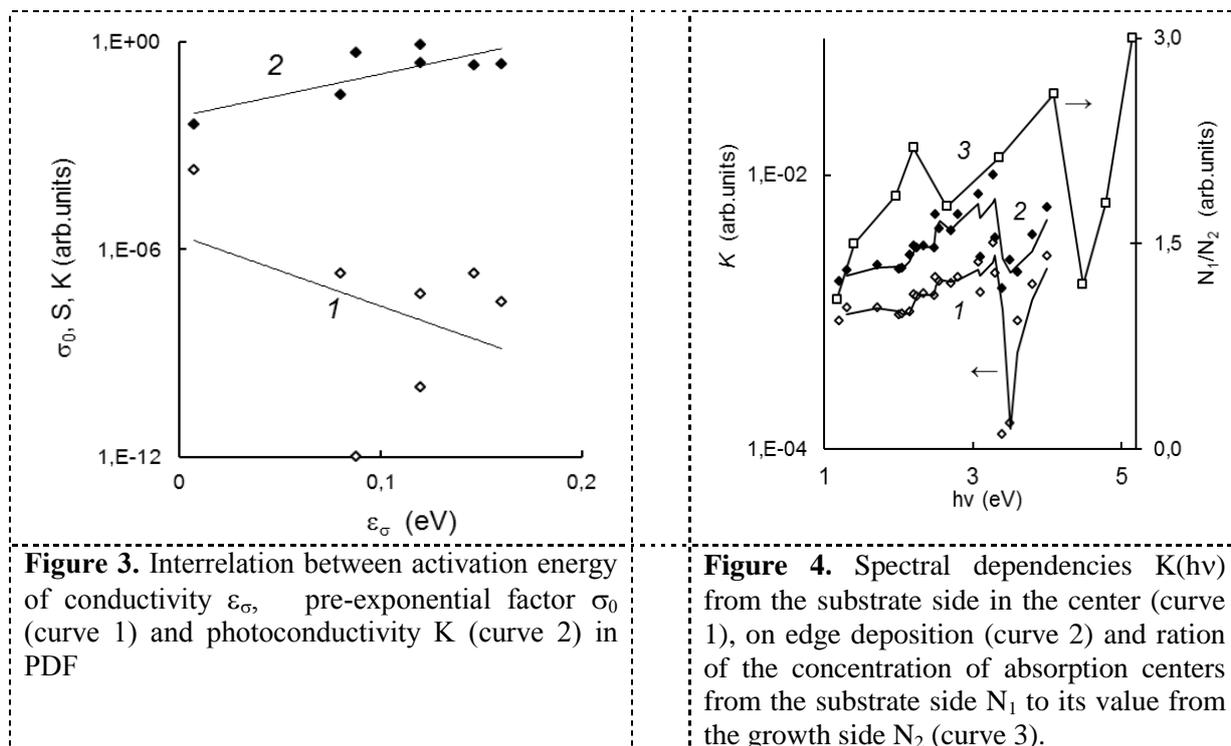


Figure 3. Interrelation between activation energy of conductivity ε_{σ} , pre-exponential factor σ_0 (curve 1) and photoconductivity K (curve 2) in PDF

Figure 4. Spectral dependencies $K(h\nu)$ from the substrate side in the center (curve 1), on edge deposition (curve 2) and ration of the concentration of absorption centers from the substrate side N_1 to its value from the growth side N_2 (curve 3).

and 1.6–3.0 eV. Growth of its value from $E_U=0.07$ to 0.15 eV with the decreasing of conductivity from $\sigma=10^{-4}$ to 10^{-11} S and the increasing of the activation energy from $\varepsilon_{\sigma}=0.007$ to 0.16 eV is determined by influence on the properties of the disorder induced with defects in the crystalline phase material due to the presence of disordered graphite-like phase in the films. As a result, exponential distribution of LS on energy is formed in BG [8, 17, 19].

4. Conclusion

Electrical and photoelectric characteristics, mechanism of charge transfer in the deposited PDF are caused by the defects, the levels of which are continuously distributed across the energy in BG. Activation component of dark and photoconductivity of n-type is realized in the exchange of charge carriers between the conduction band and shallow donor levels with the activation energy $\varepsilon \leq 0.21$ eV. Conductivity of the activation type is complemented by a hopping mechanism, involving localized states in the band gap near the Fermi level. Density of states, where the hopping conduction occurs, is significant $N(E_F)=5.6 \cdot 10^{17} - 2.1 \cdot 10^{21} \text{ eV}^{-1} \text{ cm}^{-3}$, its variation over the surface and the film thickness is determined by the content of growth defects, heterogeneously distributed in grain boundaries. Thermal quenching of photoconductivity is appeared. Under lighting LS density increases 3–5 times, and the probable jump length of photoconductivity decreases on values 1–3 nm. The spectral distribution of photosensitivity levels is correlated with the spectrum of deep levels of the optical absorption defects, which are induced in BG defects.

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