Наносистеми, наноматеріали, нанотехнології
Nanosystems, Nanomaterials, Nanotechnologies
2009, т. 7, № 1, сс. 137–145

PACS numbers: 61.48.De, 77.70.+a, 78.20.Ci, 78.67.Ch, 81.05.ub, 81.07.De

Carbon Nanotubes Based Black Absorbing Coatings for Pyroelectric and Other Thermal Detector Application

S. L. Bravina, N. V. Morozovsky, G. I. Dovbeshko, O. M. Fesenko, and E. D. Obraztsova*

Institute of Physics, N.A.S.U.,
Nauky Prosp., 46,
03028 Kyyiv, Ukraine
**Natural Science Centre of A. M. Prokhorov Institute of General Physics, R.A.S.,*
Vavilov Str., 38,
119991 Moscow, Russia

The study of optical and thermophysical characteristics of the absorbing coatings (AC) for sensitive elements of pyroelectric detectors of radiation based on carbon nanotubes paste (CNTP-black) is performed in comparison with those AC formed from gold disperse layer (Au-black) and dielectric lacquer paint (DLP-black). The spectral dependences of reflectance and absorbance of CNTP-black, Au-black and DLP-black in IR-spectrum range 2.5–25 μm are presented. By photothermomodulation method, the frequency spectra of pyroelectric response amplitude and phase are obtained. The estimation of thermal diffusivity values of the investigated blacks as AC for sensitive elements of pyroelectric detectors is performed *in situ*. Prospects of using CNTP-black based AC for pyroelectric and other thermal detector applications are shown.

Виконано порівняльні дослідження оптичних і теплофізичних характеристик вбирних покриттів (ВП) для чутливих елементів піроелектричних приймачів випромінення на основі пасти з вуглецевих нанорурок (ВНР-пасти), золотої черні (Au-черні) і діелектричної лакофарбової черні (ДЛФ-черні). Представлено спектральні залежності ІЧ-відбивання і вбирання ВНР-черні, Au-черні і ДЛФ-черні в інтервалі довжин хвиль 2,5–25 мкм. За допомогою фототермомодуляційної методи одержано частотні спектри амплітуди і фази піроелектричного відгуку. Визначено «у місці знаходження» величини температуропровідности досліджуваних типів черні як ВП для чутливих елементів піроелектричних приймачів випромінення. Показано перспективність використання ВП на основі черні з ВНР-пасти для піроелектричних й інших теплових приймачів випромінення.

Проведены сравнительные исследования оптических и теплофизических характеристик поглощающих покрытий (ПП) для чувствительных элементов пироэлектрических приемников излучения на основе пасты из углеродных нанотрубок (УНТ-пасты), золотой черни (Au-черни) и диэлектрической лакокрасочной черни (ДЛК-черни). Представлены спектральные зависимости ИК-отражения и поглощения УНТ-черни, Au-черни и ДЛК-черни в интервале длин волн 2,5–25 мкм. С помощью фототермомодуляционного метода получены частотные спектры амплитуды и фазы пироэлектрического отклика. Проведено определение «в месте нахождения» величины температуропроводности исследуемых типов черни как ПП для чувствительных элементов пироэлектрических приемников излучения. Показана перспективность использования ПП на основе черни из УНТ-пасты для пироэлектрических и других тепловых приемников излучения.

Key words: thermal detectors, absorbing coatings, metal black, paint black, carbon nanotubes black.

(Received November 28, 2007)

1. INTRODUCTION

Application field of one of the most important class of thermal detectors, pyroelectric detectors of radiation (PDR), includes all modern engineering branches from space and paramilitary equipment to household appliances, public and individual security and fire alarm systems [1–9].

The principle of operation of PDR is based on the temperature dependence of polarization of sensitive element (SE) material and registration of electrical charge connected with polarization change induced by temperature variation [2, 3, 5–9]. Radiation absorption by the surface or volume of SE is the first and very important stage of radiation conversion into the electrical response of thermal detectors [2, 3, 5]. That is why sensitive and frequency characteristics of commonly used PDR with surface absorption are largely determined by thermophysical parameters of absorbing coating (AC) of SE [10–14].

Well-known technologies for making up the AC of PDR use thin disperse layers of noble (Pt, Au and Ag) and other (Ni, Cr and Ni–Cr) metals evaporated in the conditions of 'imperfect' vacuum and deposited in certain atmosphere and temperature conditions [10–13]. Thin layers of different lacquer and paints [10, 14] formed by smearing or pulverization are also used as AC. These so-called metal and dielectric blacks possess sufficient spectral characteristics in the near- and middle-IR range [11, 14]. However, these blacks have relatively low thermal conductivity and restrict the speed of response of PDR by the time of thermal diffusion through the layer of AC [10, 12, 13] that demands the further development of AC technologies.

Progress in modern technology allows enriching AC stock with blacks based on carbon nanotubes (CNT), which are mainly characterized by the combination of high values of thermal and electrical conductivity [15–17] and resulted in the development of effective absorbing CNT-coating for pyroelectric detectors [17].

Recently, we reported about the development of AC based on thin (~ 1 μm) layers of SiO<Cu> metal–oxide composite [18] and AC based on CNT-paint [19].

In a given paper, we present the results of the comparative study of AC thin layers based on metal disperse layer and dielectric paint blacks and also carbon nanotubes paint black as AC for sensitive elements of pyroelectric detectors and other types of thermal detectors of radiation.

2. EXPERIMENTAL

2.1. Sample preparation

Metal-black AC were manufactured by evaporation of corresponding metal (gold in this experiment) and deposition of its vapours on the SE electrode surface under imperfect vacuum condition of 0.1–10 Torr in nitrogen atmosphere with a low content of oxygen at the substrate temperature of about 200 K [18].

For the manufacture of dielectric lacquer paint (DLP) black AC, the solution of industrial multi-pigment black lacquer paint was used.

For the manufacture of CNT-based black AC, the carbon single wall nanotubes (SWNT) prepared by the method of arc discharge in He-atmosphere [20] were used. The characterization of these SWNT by Raman scattering and electron microscopy was performed. The length and diameter of the SWNT were of 1–2 μm and 14–15 Å, respectively. Then, suspension on the base of SWNT crumbled preliminary, organic binder and dissolvent were prepared.

The DLP-black AC and CNTP-black AC were prepared by depositing a thin layer of solution of low viscosity on the SE electrode surface and subsequent evaporating solvent at heightened temperature. After drying on the electrode surface were obtained the layers of 5–20 μm thickness close to that of Au-black AC. For manufactured CNTP-black, AC has the value of 20–50 kΩ/ surface resistance and a high degree of blackness close to that of DLP-black and Au-black AC.

For the pyroelectric investigations, the SE with AC deposed directly on the main surfaces of 100–200 μm $LiNbO_3$ plates of polar Z-cut with evaporated Cu/Cr-electrodes of 20–50 mm^2 of area were formed. Such SE with various types of AC were connected by means of a ring-shape holder to the input of the FET matching stage [21] with variable from high (~ 10 GΩ at the frequency of 20 Hz) to relatively low (~ 100 kΩ) input impedance value.

2.2. Measurements

For the optical investigations, Au-black, DLP-black and CNTP-black AC were put on the electroded $LiNbO_3$ thin plates. The measurements of reflectance of the samples were performed in the middle infrared range 2.5–25 μm with IFS 66 Bruker Instrument.

The pyroelectric response measurements were performed by the modulation photopyroelectric thermowave method [22] in the frequency range 10 Hz $\le f_m \le$ 100 kHz of modulation of IR-radiation flux. The measuring system for thermowave probing allowed us to obtain the amplitude-to-frequency $U_\pi(f_m)$ and phase-to-frequency $\phi_\pi(f_m)$ dependences of pyroelectric response in two operation modes of pyroelectric current and pyroelectric voltage characteristic for PDR operation. Due to the fact that, in the pyroelectric current mode, $U_\pi = U_{\pi 1} \propto \gamma / c_1$, and, in the pyroelectric voltage mode, $U_\pi = U_{\pi 2} \propto \gamma / c_1 \varepsilon f_m$, where γ is the pyroelectric coefficient, c_1 is the volume heat capacity, there is possibility to evaluate the dielectric permittivity ε from pyroelectric measurements [2, 21, 22] by introducing the dielectric ratio $D_\pi = U_{\pi 1} / U_{\pi 2} f_m \propto \varepsilon_\pi$.

The connection of amplitude and phase of pyroelectric response with the thermal parameters of both SE of PDR and AC material in consequence of the fundamental frequency dependence of the length of temperature wave $\lambda_T = (a_T / \pi f_m)^{1/2}$, where a_T is the thermal diffusivity [18, 19, 22], allows one to estimate the value of a_T for material of AC by analysing $U_\pi(f_m)$ and $\phi_\pi(f_m)$ dependences.

3. RESULTS AND DISCUSSION

3.1. Optical IR Characterization

In Figure 1, the spectral dependences of reflectance $R(\nu)$ (Fig. 1, *a*) and absorbance (Fig. 1, *b*) of Au-black, DLP-black and CNTP-black in IR-spectrum range of wavenumbers $400 \le \nu \le 4000$ cm^{-1} corresponding to that of wavelengths $5 \le \lambda \le 25$ μm are presented.

For Au-black, $R(\nu)$ value changes in the limits 1.5–6% and corresponding $A(\lambda)$ value changes in the limits 94–98%. For both types of the paints, $R(\nu)$ change is no more than 3%. Due to opacity of prepared paint layers, the $A(\lambda)$ value is no less than 97%.

It should be pointed out the different shapes of obtained spectra for Au-black, DLP-black and CNTP-black in all spectral range and particularly in the range of 8–20 μm.

The regularity of $R(\nu)$ and $A(\lambda)$ spectrum for CNTP-black is better than for DLP-black, which results in a better level of spectral non-selectivity and in a higher value of integral absorbance of CNTP-black in the investigated spectral range. The absorbance value for CNTP-

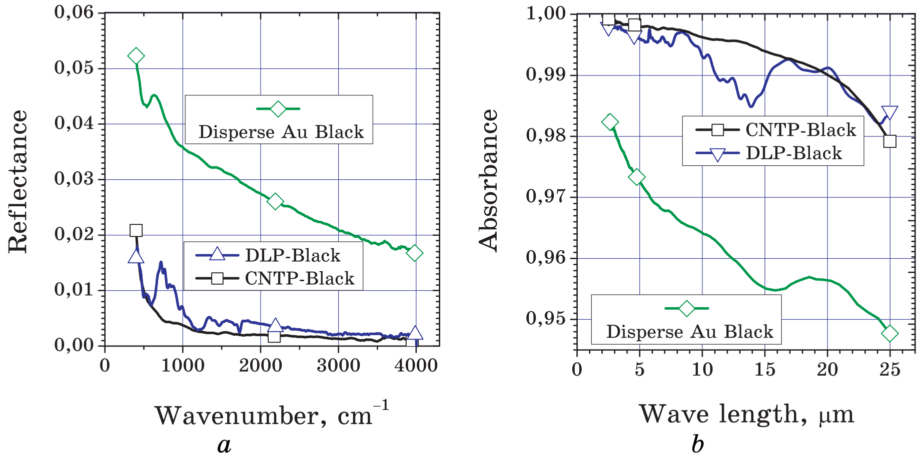

Fig. 1. Spectral dependences of reflectance (*a*) and absorbance (*b*) of Au-black, dielectric lacquer-paint black and CNT-paint black.

black AC is higher and its spectral uniformity is better than the same for DLP-black AC.

3.2. Photopyroelectric Characterization

In Figure 2, the dependences of $U_{\pi1,2}(f_m)$ and $\phi_{\pi1,2}(f_m)$ are shown for SE of PDR obtained under irradiation of the Cu-electrode without AC and the other one with AC from Au-black.

Significant difference in $U_{\pi1,2}$ levels for the electrodes with AC and without it at low frequencies corresponds to a good quality of Au-black.

The existence of 180°-difference for $\phi_{\pi1,2}(f_m)$ dependences obtained for Cu-electrode side and Au-black side corresponds to different signs of pyroelectric reaction at the different polar Z^+ and Z^- surfaces.

Flat frequency dependences of $U_{\pi1}$, $U_{\pi2}f_m$, D_π and $\phi_{\pi1,2}$ under irradiation of the side of Cu-electrode (Fig. 2, left side) correspond to thermal, polar and dielectric uniformity.

Then, the following types of $U_{\pi1}(f_m)$, $\phi_{\pi1}(f_m)$ and $U_{\pi2}(f_m)$, $\phi_{\pi2}(f_m)$ dependences are characteristic [3, 5, 18, 19, 22]: $U_{\pi1}(f_m) = \text{const}(f_m)$ and $\phi_{\pi1}(f_m) = \text{const}(f_m)$ in the pyroelectric current mode, $U_{\pi2}(f_m) \propto 1/f_m$ and $\phi_{\pi2}(f_m) = \text{const}(f_m)$ in the pyroelectric voltage mode. In this case, $U_{\pi2}(f_m)f_m = \text{const}(f_m)$ and $D_\pi(f_m) = U_{\pi1}(f_m)/U_{\pi2}(f_m)f_m \propto \varepsilon_\pi = \text{const}(f_m)$, and also $\varphi_{\pi2} - \varphi_{\pi1} = 90°$ due to capacitive character of current and voltage in the circuit of pyroelectric SE.

The noticeable approaching the values of $U_{\pi1}(f_m)$ to $U_{\pi2}(f_m)$ and $\phi_{\pi1}(f_m)$ to $\phi_{\pi2}(f_m)$ under f_m increasing is connected with deviation from

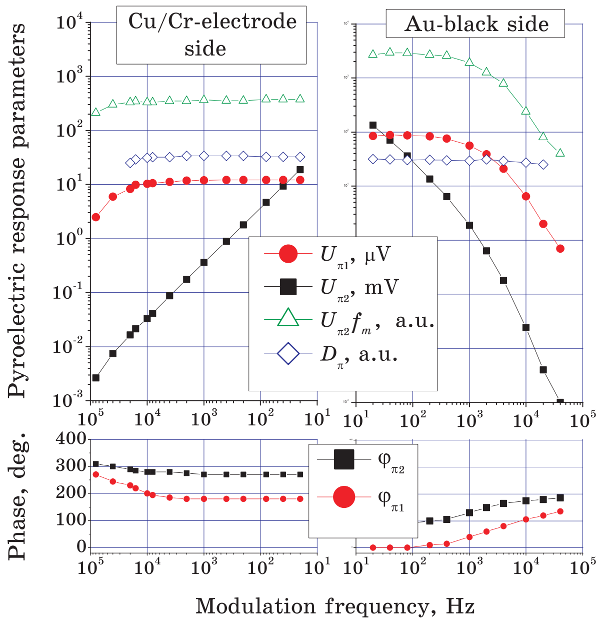

Fig. 2. Modulation frequency dependences, $U_{\pi 2}(f_m)$, $U_{\pi 2}(f_m) f_m$ and $D_\pi(f_m)$ and also $\phi_{\pi 1}(f_m)$ and $\phi_{\pi 2}(f_m)$ for SE of PDR with AC from Au-black on one side.

the conditions of pyroelectric current mode. Under that with f_m increasing, the SE impedance $1/2\pi f_m C$ (C is the total capacity of SE and load circuit) becomes less than the load resistance R_L and the inequality $2\pi f_m R_L C << 1$ necessary for performing pyroelectric current mode changes for the opposite $2\pi f_m R_L C >> 1$, characteristic for the pyroelectric voltage mode, which leads to the coincidence of the dependences.

The weak high-frequency drop of $U_{\pi 2}(f_m) f_m$, $U_{\pi 1}(f_m)$ and increase of $\phi_{\pi 2}(f_m)$ noticeable at the high-frequency interval corresponds to the existence of under-electrode non-homogeneity. Taking into consideration the value of $a_T = 1.5 \cdot 10^{-6}$ m^2/s known for $LiNbO_3$ [5], with regard to the value of λ_T for $f_m = 40$ kHz, it is possible to evaluate the thickness of this non-homogeneity as about 3 μm.

Under irradiation from the side of Au-black (Fig. 2, right side), flat frequency dependences of $U_{\pi 1}$, $U_{\pi 2} f_m$ and $\phi_{\pi 1,2}$ are characteristic at low frequencies which corresponds to inequality $\lambda_T / L >> 1$ between the length of temperature wave and the thickness L of the AC layer. At frequencies higher than 1 kHz, we observed a significant decrease of response amplitude and additional positive phase shift. Such peculiarities are connected with damping action of AC, which is manifested under approaching λ_T to L with increasing f_m value. Under further increase of f_m, the inequality $\lambda_T / L < 1$ is getting valid. Enhancement of this inequality leads to decrease of exponential in respect to $f_m^{1/2}$ multiplier for

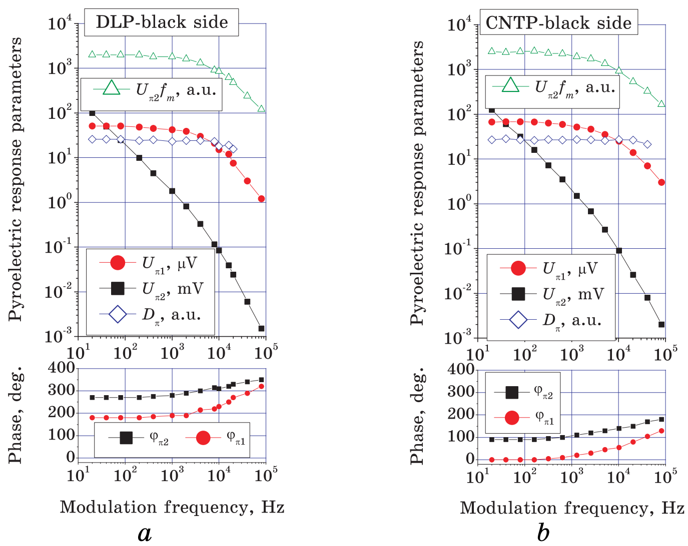

Fig. 3. Modulation frequency dependences $U_{\pi 1}(f_m)$, $U_{\pi 2}(f_m)$, $U_{\pi 2}(f_m)f_m$ and $D_\pi(f_m)$ and also $\phi_{\pi 1}(f_m)$ and $\phi_{\pi 2}(f_m)$ for similar SE of PDR with AC from dielectric lacquer-paint black (*a*) and AC from CNT-paint black (*b*).

the response amplitude $\Delta U_\pi(f_m) \propto \exp(-L/\lambda_T) = \exp(-L(\pi f_m/a_T)^{1/2})$ and increase of a linear in respect to $f_m^{1/2}$ contribution to the phase $\Delta\phi_\pi(f_m) = L/\lambda_T = L(\pi f_m/a_T)^{1/2}$. As a result, with increasing f_m, the level of pyroelectric response under irradiation from the Au-black side becomes even lower than under irradiation from the side of the Cu-electrode (see Fig. 2, left and right sides).

In Figure 3, $U_{\pi 1,2}(f_m)$, $U_{\pi 2}(f_m)f_m$, $D_\pi(f_m)$ and $\phi_{\pi 1,2}(f_m)$ dependences for SE of PDR with AC from DLP-black and AC from CNTP-black are shown.

Under irradiation of the side with DLP-black AC (Fig. 3, *a*), the behaviour of $U_{\pi 1,2}(f_m)$ and $\phi_{\pi 1,2}(f_m)$ dependences similar to that observed for Au-black AC (Fig. 2) is shifted to higher frequencies and the region of high-frequency drop of amplitude–frequency dependence is observed for $f_m > 5$ kHz.

Under irradiation of the side with CNTP-black (Fig. 3, *b*), the dependences of $U_{\pi 1,2}(f_m)$ as for DLP-black are less sharp than observed in the case of irradiation as Au-black AC (see Fig. 2 and Fig. 3, *b*). Near the same levels of $U_{\pi 1,2}$ for Au-black AC, DLP-black AC and CNTP-black AC at low frequencies correspond to good absorption of CNTP-black AC.

The high-frequency drop of $U_{\pi 2}(f_m)f_m$ and increase of $\phi_{\pi 2}(f_m)$ for CNTP-black AC connected with thermal damping are not so sharp and are observed at the frequencies of 1 order higher than those ones for AC from Au-black (compare Fig. 2 and Fig. 3, *b*).

TABLE. Thermal diffusivities of black absorption coatings for pyroelectric detectors, dielectric and resistive bolometres.

Type of the coating	Thickness interval, μm	Thermal diffusivity, m^2/s
Au-black Dispersion Layer	2–10	$(1–3)\cdot10^{-7}$
Dielectric Lacquer Paint Black	3–10	$(2–4)\cdot10^{-7}$
Carbon Nanotube Paint Black	5–20	$(5–25)\cdot10^{-6}$
Graphite (extruded)	200–500	$(2–7)\cdot10^{-5}$

The obtained $U_{\pi1,2}(f_m)$ and $\phi_{\pi1,2}(f_m)$ dependences for SE with different AC allow one to estimate the value of thermal diffusivity of each AC material. It can be done by analyzing the characteristic dependences of $U_{\pi}(f_m)$ and $\phi_{\pi}(f_m)$ in the frequency range where the thermal damping is significant. The estimated a_T values for Au-black AC, DLP-black AC and for CNTP-black AC are presented in Table.

The obtained a_T values for CNTP-paint black are at least of an order of value higher than a_T values for other black AC under investigation and are comparative with a_T values for massive graphite. It can be connected with a high contribution of relatively large regions of high contacted CNT-bundles interconnected through developed surrounding of small CNT-bunches.

4. CONCLUSION

Combination of enhanced spectral characteristics and thermal parameters of CNT paint black in comparison with those inherent to Au-black and dielectric lacquer paint black with foresight of further progress in CNT-based technologies allows us to consider the CNT-based paint black as promising for absorbing coatings of thermal detectors of radiation.

REFERENCES

1. B. J. Mates and T. A. Perls, *Rev. Sci. Instr.*, **32**, No. 3: 332 (1961).
2. L. S. Kremenchugsky, *Ferroelectric Detectors of Radiation* (Kiev: Naukova Dumka: 1971) (in Russian).
3. S. B. Lang, *Sourcebook of Pyroelectricity* (London–NewYork–Paris: Gordon&Breach Sci. Publ.: 1974).
4. F. G. Brown, *Soc. Photoopt. Instrum. Engrs,* **62**: 201 (1975).
5. L. S. Kremenchugsky and O. V. Roitsina, *Pyroelectric Detectors of Radiation* (Kiev: Naukova Dumka: 1979) (in Russian).
6. L. S. Kremenchugsky and O. V. Roitsina, *Pyroelectric Detecting Devices* (Kiev: Naukova Dumka: 1982) (in Russian).
7. R .Watton, *Ferroelectrics,* **91**, No. 1–4: 87 (1989)

8. R. W. Whatmore, *Ferroelectrics*, **118**, No. 1–4: 241 (1991).
9. R. W. Whatmore and R. Watton, *Ferroelectrics*, **236**, No. 1–4: 259 (2000).
10. W. R. Blevin and W. J. Brown, *Metrologia*, **2**: 139 (1966).
11. V. S. Lysenko and A. F. Malnev, *Thermal Detectors of Radiation* (Kiev: Naukova Dumka: 1967), p. 146 (in Russian).
12. N. Sintsov, *Thermal Detectors of Radiation* (Kiev: Naukova Dumka: 1967), p. 164 (in Russian).
13. W. R .Blevin and J. Geist, *Appl. Opt.*, **13**, No. 24: 1171 (1974).
14. A. A. Kmito, V. A. Parfinsky, and M. M. Seredenko, *Thermal Detectors of Radiation* (Leningrad: GOI: 1978), p. 112 (in Russian).
15. S. Xie, W. Li, Z. Pan, B. Chang, and L. Sun, *J. of Phys. and Chem. of Solids*, **61**: 1153 (2000).
16. S. Berber, Y.-K. Kwon, and D. Tomanek, *Phys. Rev. Lett.*, **84**: 4613 (2000).
17. J. H. Lehman, C. Engtracul, T. Gennett, and A. C. Dillon, *Appl. Opt.*, **44**: 483 (2005).
18. S. L. Bravina, N. V. Morozovsky, A. A. Strokach, K. V. Mikhailovskaya, P. E. Shepeliavyi, and I. Z. Indutnyi, *Material Science and Material Properties for Infrared Optoelectronics* (Ed. F. F. Sizov) (Bellingham: SPIE: 2001), No. 4355, p. 96.
19. S. L. Bravina, N. V. Morozovsky, G. I. Dovbeshko, and E. D. Obraztsova, http://arxiv.org/abs/cond.-mat/0603529 (2006).
20. E. D. Obraztsova, J. Bonard, V. Kuznetsov, V. Zaikovskii, S. Pimenov, S. Terekhov, V. Konov, A. Obraztsov, and Volkov, *Nanostruct. Mater.*, **12**: 567 (1999).
21. S. L. Bravina, L. S. Kremenchugsky, N. V. Morozovsky, V. B. Samoilov, and I. A. Stoianov (Preprint Inst. of Phys., Acad. Sci. of Ukraine) (Kiev: 1982) (in Russian).
22. S. L. Bravina, N. V. Morozovsky, and A. A. Strokach, *Material Science and Material Properties for Infrared Optoelectronics* (Ed. F. F. Sizov) (Bellingham: SPIE: 1998), No. 3182, p. 85.