

Research Article

CVD-Graphene-Based Flexible, Thermoelectrochromic Sensor

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The main idea behind this work was demonstrated in a form of a new thermoelectrochromic sensor on a flexible substrate using graphene as an electrically reconfigurable thermal medium (TEChrom™). Our approach relies on electromodulation of thermal properties of graphene on poly(ethylene terephthalate) (PET) via mechanical destruction of a graphene layer. Graphene applied in this work was obtained by chemical vapor deposition (CVD) technique on copper substrate and characterized by Raman and scanning tunneling spectroscopy. Electrical parameters of graphene were evaluated by the van der Pauw method on the transferred graphene layers onto SiO₂ substrates by electrochemical delamination method. Two configurations of architecture of sensors, without and with the thermochromic layer, were investigated, taking into account the increase of voltage from 0 to 50 V and were observed by thermographic camera to define heat energy. Current-voltage characteristics obtained for the sensor with damaged graphene layer are linear, and the resistivity is independent from the current applied. The device investigated under 1000 W/m² exhibited rise of resistivity along with increased temperature. Flexible thermoelectrochromic device with graphene presented here can be widely used as a sensor for both the military and civil monitoring.

1. Introduction

Graphene as a very attractive material has been widely tested in several optoelectronic devices, such as solar cells, supercapacitors, light-emitting diodes, displays, touch screens, smart windows, or sensors [1–3]. However, taking into consideration the parameters of the devices constructed with graphene, the methods of graphene preparation strongly impact the performances of these devices [e.g., [3–7]]. Two main methods of graphene synthesis are known: (1) the top-down method (mechanical exfoliation, chemical oxidation, and exfoliation) and (2) the bottom-up method (epitaxial growth on different substrates, chemical vapor deposition (CVD), and arc discharging methods) [6–8]. CVD method of graphene film preparation is much more attractive for the optoelectronic devices due to its superior electrical and surface properties compared to the reduced graphene oxide (rGO) one. CVD graphene is transferable to varied substrates, making the technique multipurpose for many applications.

One such application is as an electrode in an organic and inorganic (silicon) solar cell. CVD-graphene is quasi-two-dimensional, since electrons can only move between carbon atoms in the 2D lattice. The lack of a third dimension in CVD-graphene influences various novel properties of this material. For example, one such single mobile charge carrier system is created as an effect of electrons interacting with the carbon atoms in the lattice. The ballistic moves of the carrier over the graphene surface are known, and they allow graphene sheets to conduct electricity very well [9]. Additionally, other various interactions among electrons and the hexagonal lattice make CVD-graphene transparent, flexible, and quite strong [10]. Taking into account the specific properties of graphene and its derivatives, photoluminescence (PL) [11], liquid crystalline (LC) [12], and electrochromic (EC) properties [2, 13] are investigated.

However, it is a long way for graphene devices to be used. For this reason, the main goal of this work was the creation of a new thermoelectrochromic sensor on a flexible

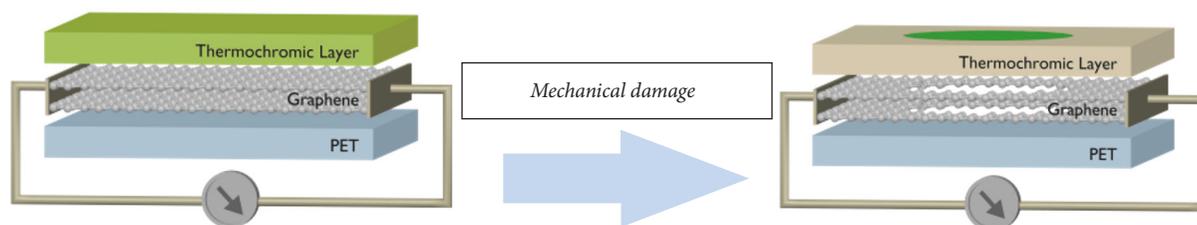


FIGURE 1: CVD-graphene-based thermoelectrochromic sensor on a poly(ethylene terephthalate) (PET) substrate.

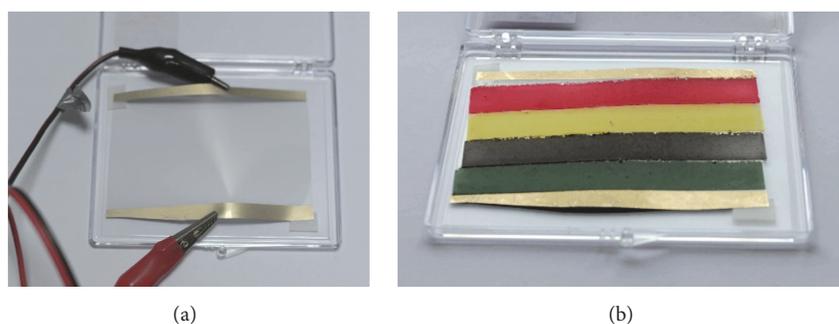


FIGURE 2: Photos of (a) CVD-graphene device on the PET substrate and (b) CVD-graphene device on the PET substrate with thermochromic strips.

poly(ethylene terephthalate) (PET) substrate using CVD-graphene as an electrically reconfigurable thermal medium. Schematically, our idea is presented in Figure 1.

In our work, two types of investigations were done and analyzed:

- (i) Synthesis and characterization of graphene obtained via CVD method
- (ii) Construction of thermoelectrochromic sensors with CVD-graphene and their electrical characterization [14]

Finally, we demonstrated how our simple idea could be effectively exploited in a practical application such as a thermoelectrochromic device on flexible substrate with CVD-graphene layer for monitoring.

2. Materials and Methods

2.1. Materials. Multicolor strips with leuco dyes were used as received from the printing office (ETC, Poland).

2.2. Synthesis of CVD-Graphene. Graphene films have been synthesized on copper foils via CVD method using commercially available systems enabling the growth on Cu substrates, the size of which ranged from 6" diam. (Aixtron BM Pro) up to 50 cm × 50 cm (CVD Equipment Corporation, Easy Graphene and GraphMaster Seco/Warwick models). During the thermal process, carbon is liberated from the hydrocarbons and it attaches to the surface of the copper, thus creating graphene rather than precipitating, and segregates from the bulk upon cooling down. Growth on Cu is also limited largely to one monolayer. Copper acts as a catalyst in the reaction, which suggests that the growth is self-limited.

Carbon adsorbates exhibit high mobility on Cu surfaces at elevated temperatures, facilitating diffusion across the surface to join the edge of nucleating crystallites. The CVD process starts with the Cu substrate pretreatment at ~1000°C under an Ar gas flow and then H₂ gas flow at a pressure of less than 100 mbar. The purpose of this step is to improve the quality and enlarge the grain size of the copper. Afterwards, both the hydrocarbon (e.g., CH₄ or C₃H₈) and the H₂ gas are introduced into the reactor for a couple of minutes to grow the graphene layer. Finally, the copper substrate covered with graphene films is cooled down to room temperature in an Ar atmosphere [15–18].

2.3. Preparation of Thermoelectrochromic Devices. At a first attempt, graphene was transferred from copper foil onto flexible substrate by high-speed electrochemical delamination method [17]. Then flexible CVD-graphene substrate (see Figure 2(a)) was covered with four strips of different colors (see Figure 2(b)). Thermally deposited gold (Au) was used as both electrodes in created CVD-graphene devices.

2.4. Characterization. Graphene grown on Copper foil was investigated using a complementary characterization technique. Raman spectroscopy confirmed the formation of graphitic structures. Moreover, it provided information on the domain size, strain, and stacking order of the graphene films. The morphology of graphene on metal grains was analyzed by scanning electron microscopy (SEM) using Hitachi SU8230 Cold Field Emission system, which was also used to show the topography of the graphene substrate's interface and confirm the uniformity of the graphene layer. Electrical parameters were evaluated by van der Pauw method (using Ecopia HMS-3000 unit) on transferred graphene layers to

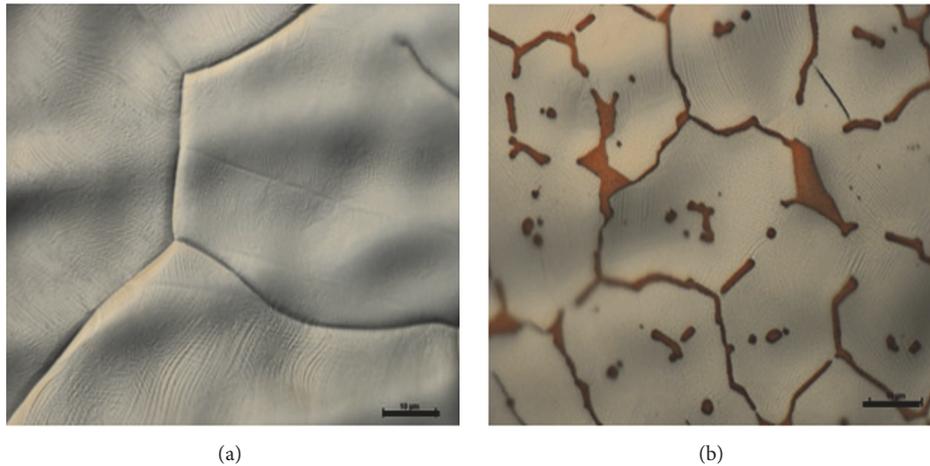


FIGURE 3: Optical images of (a) continuous and (b) discontinuous graphene films on Cu substrates.

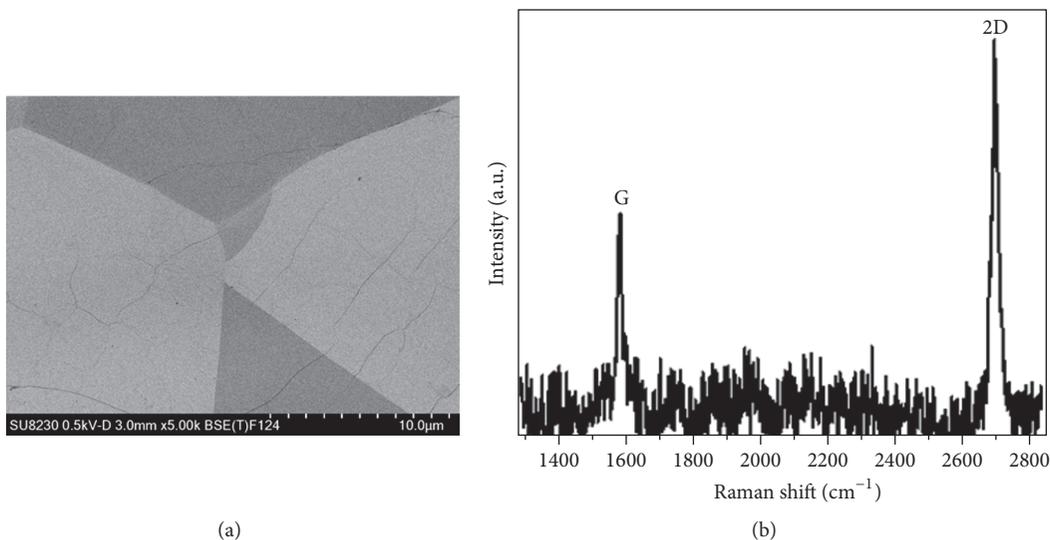


FIGURE 4: SEM images of graphene layers (a) of high-quality graphene grown on Cu substrate and the typical Raman spectra (b) of graphene layer grown on Cu substrate.

SiO₂ substrates by electrochemical delamination method. The charge carriers' concentration was typically in the range of $1 \times 10^{12} - 1 \times 10^{13}/\text{cm}^2$, while the Hall mobility at RT was in the level of 2000–4000 cm²/Vs with *p*-type of conductivity.

Raman spectroscopy (Renishaw's inVia Raman microscope system with a 532 nm Nd:YAG laser as an excitation source) is normally used to confirm the presence of graphene on the Cu substrates (see Figure 4(b)). However, optical microscopy with Nomarski contrast is also very useful (Figure 3). This fast and easy measurement exposes cracks and microholes in the graphene layer and allows an analysis of the substrate deformation process, which can affect graphene film's quality.

Measurements done by SEM (see Figure 4(a)) can identify dark spots interpreted as adlayers of graphene (nonexistent in the sample presented). In addition, wrinkles characteristic of graphene grown on a copper substrate are visible.

Electrical properties of both devices with the size of 70 mm × 100 mm were investigated by laboratory power supply (PWR400L, Kikusui Electronics Corporation, Japan) and universal electric meter (UNI-T UT70A, AXIOMET, Poland). Starting temperature, $T_0 = 25^\circ\text{C}$, was the temperature before current application, while $T_k = 27^\circ\text{C}$ was the temperature after current had been applied to the graphene layer, as demonstrated with TESTO 435 (Testo AG, Germany).

A hand-made SOLARBOX (Military Institute of Engineer Technology, Wroclaw, Poland) was used to investigate the electrical behavior of CVD-graphene-based device under 1000 W/m² solar irradiation along with increase of temperature from 13 to 30°C.

Mechanical damage of graphene layer was done via technical calipers, drawing circular patterns at the middle of graphene layer with increasing diameter (from 0 to 60 mm), and observed using thermographic camera (VIGOCam v50, VIGO System S.A., Poland).

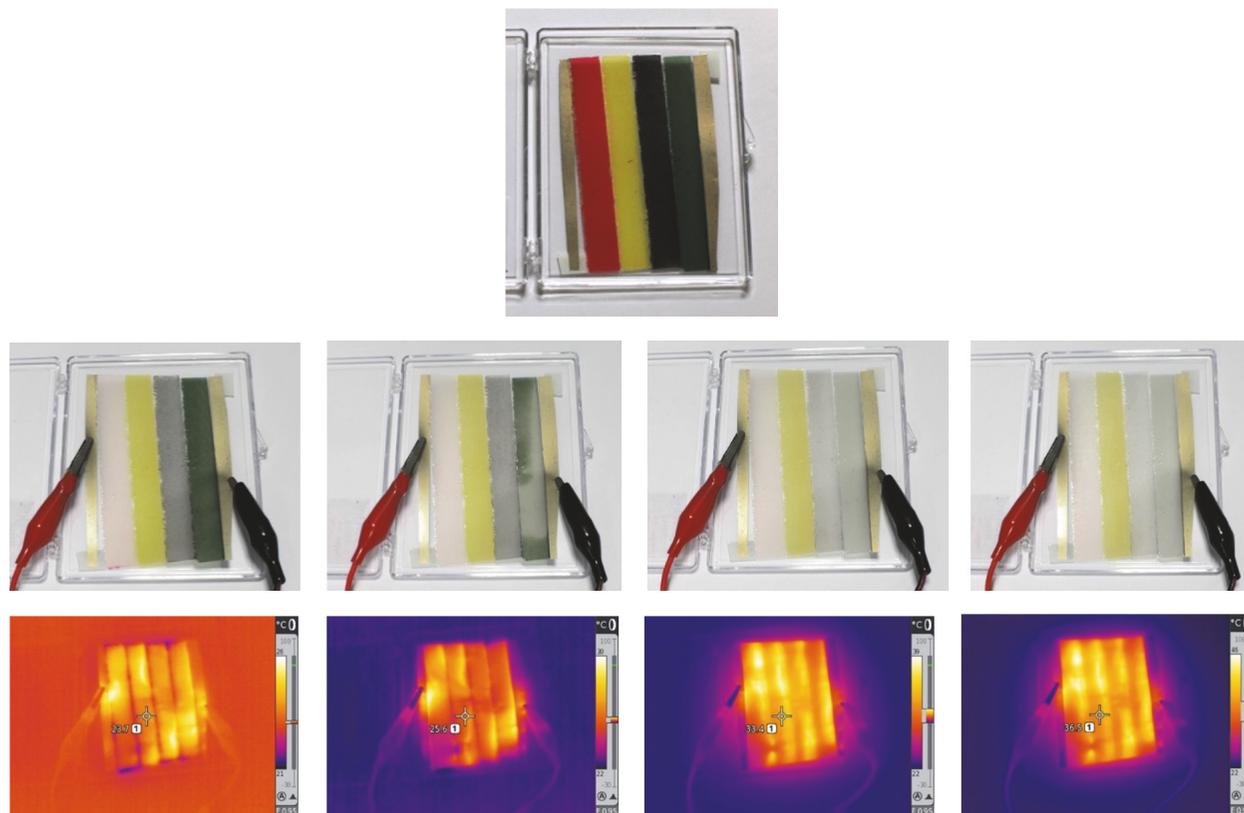


FIGURE 5: Photos of CVD-graphene devices with thermochromic strips at 0 V (20°C), 10 V (23.5°C), 17.5 V (26°C), 25 V (33.5°C), and 30.1 V (37°C), respectively, from left to right together with thermal images.

3. Results and Discussions

3.1. CVD-Graphene Preparation. Graphene synthesis using CVD method performed on the surface of transition metals is one of the most promising techniques for producing graphene for low-cost applications on a large scale. The precipitation of graphene on bulk transition metals occurs as a result of the temperature-dependent solubility of carbon. The bonding of a single graphene layer to a metal surface is determined by the metal surface itself, the quality of substrate, and the grain size.

3.2. Thermoelectrochromic Behavior of CVD-Graphene Device with Thermochromic Strips. At the first stage of our work, we tested the possibility of changing the color of the thermochromic strips as a result of electromodulation of thermal properties of graphene. For this reason, the device was investigated taking into account increase of voltage from 0 to 30 V. As is presented in Figure 5, along with increase of voltage and consequently temperature applied, the multicolor layer changed its color. This behavior clearly confirmed that our idea had worked and thermal properties of electromodulation of CVD-graphene could be used in sensors.

As is presented in Figure 5 along with increase of voltage, change in the color of selected strips was found as a result of increased temperature of graphene layer as is clearly indicated by thermographic camera.

Our CVD-graphene device exhibited reversible effect and is stable in air atmosphere. In our work, used strips are air- and time-stable and exhibited reversible change of color along with variation of the temperature. To explain this effect, we used commercially available Peltier device to change the temperature of the strips as is shown in Figure 6 as an example for the red strip and in Supplementary Material available online at <https://doi.org/10.1155/2017/2757590>.

The idea behind the study is a practical and efficient use of a 2D graphene structure in a flexible thermoelectrochromic sensor. The advantage lies in electric properties of graphene which, in this particular solution, are quite favorable: applying voltage to the graphene layer via electrodes results in the increase of this layer's temperature. The application of thermochromic materials in the sensor affects changes of its transparency and/or color.

The electrochromic layer, which had been applied as a cover for the graphene structure and previously had a color, is now colorless (transparent). Layering these layers onto a flexible substrate (base layer) made of PET, for example, enables the sensor to adapt to the surface of the object which is to be monitored.

The resultant changes (damage) can be observed either using a voltage/current meter for current-voltage characteristics, employing a thermal imaging camera, or even with an unaided eye, as the change in color of the thermochromic material is visible.



FIGURE 6: Photos of red strip along with increase in temperature from 20 and 22 to 24°C, respectively.

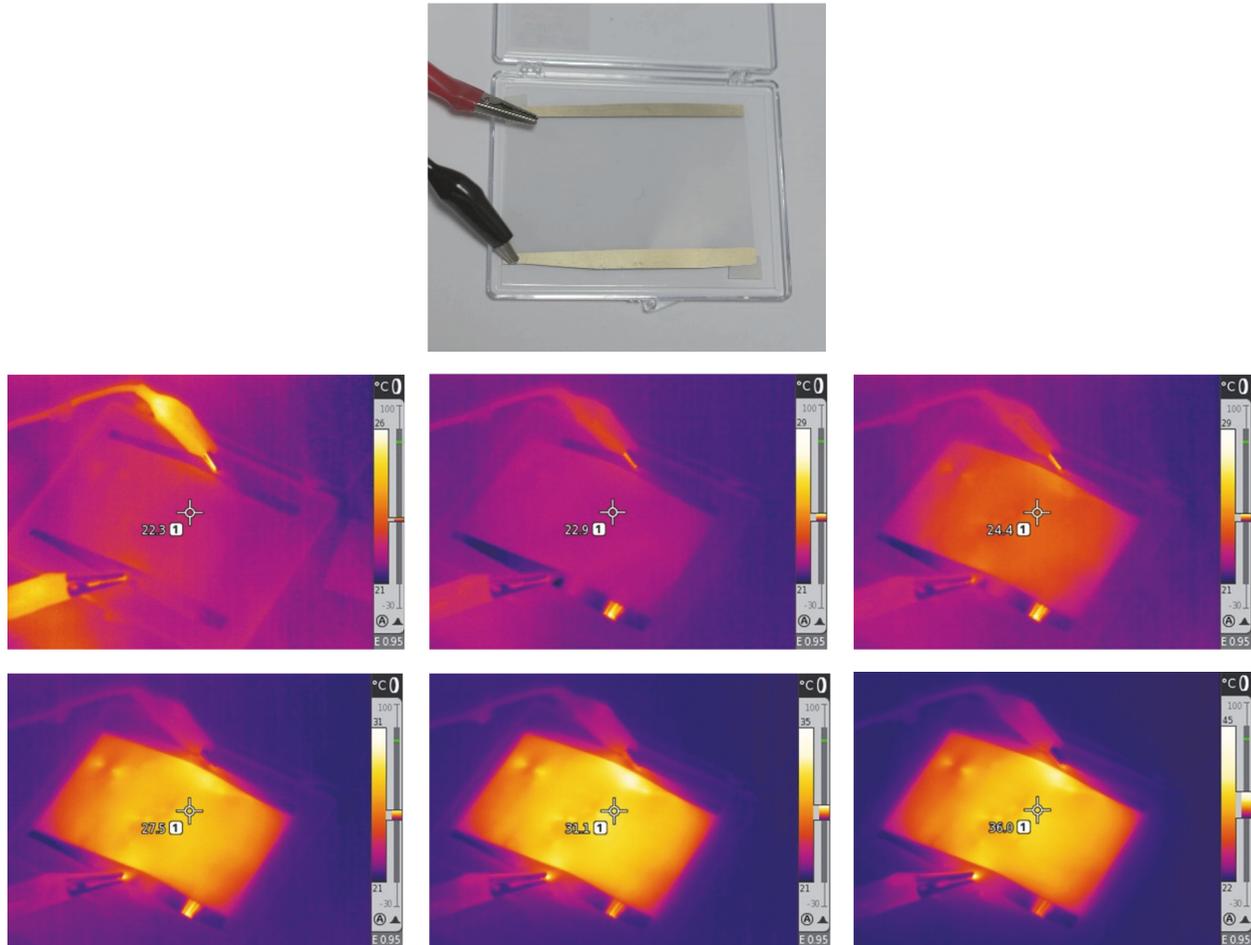


FIGURE 7: Photographs of CVD-graphene device before mechanical damage, together with thermal images at various voltages applied (22.3, 22.9, 24.4, 27.5, 31.1, and 36 V from left to right, resp.).

When the voltage is applied, the developed flexible thermoelectrochromic sensor is characterized by two states: 1, operating, or 0, damaged. We can differentiate between the two due to the color change and/or change in the transparency.

1, Operating. The device is transparent and does not exhibit any color resulting from a dye contained in the thermochromic layer.

0, Damaged. The device becomes nontransparent due to physiochemical processes within the thermochromic layer which occur due to drop in the temperature of the graphene layer.

To summarize, the invention can be used as a sensor which confirms the presence and the location of damage to, for example, shop window panes, automotive glazing or ballistic covers of helicopters, bulletproof vests, or flak jackets. Thanks to this sensor, the level of safety can be monitored and the safety of the users, such as police officers, soldiers, and ordinary citizens, can be greatly improved.

This structure can serve as an example of combining two unique properties, the electrical properties of graphene layer and optical properties of thermochromic material, which can be applied as an inner layer of glass panes or ballistic covers.

3.3. Electrical Properties of CVD-Graphene-Based Device before and after Mechanical Damage. The main goal of this

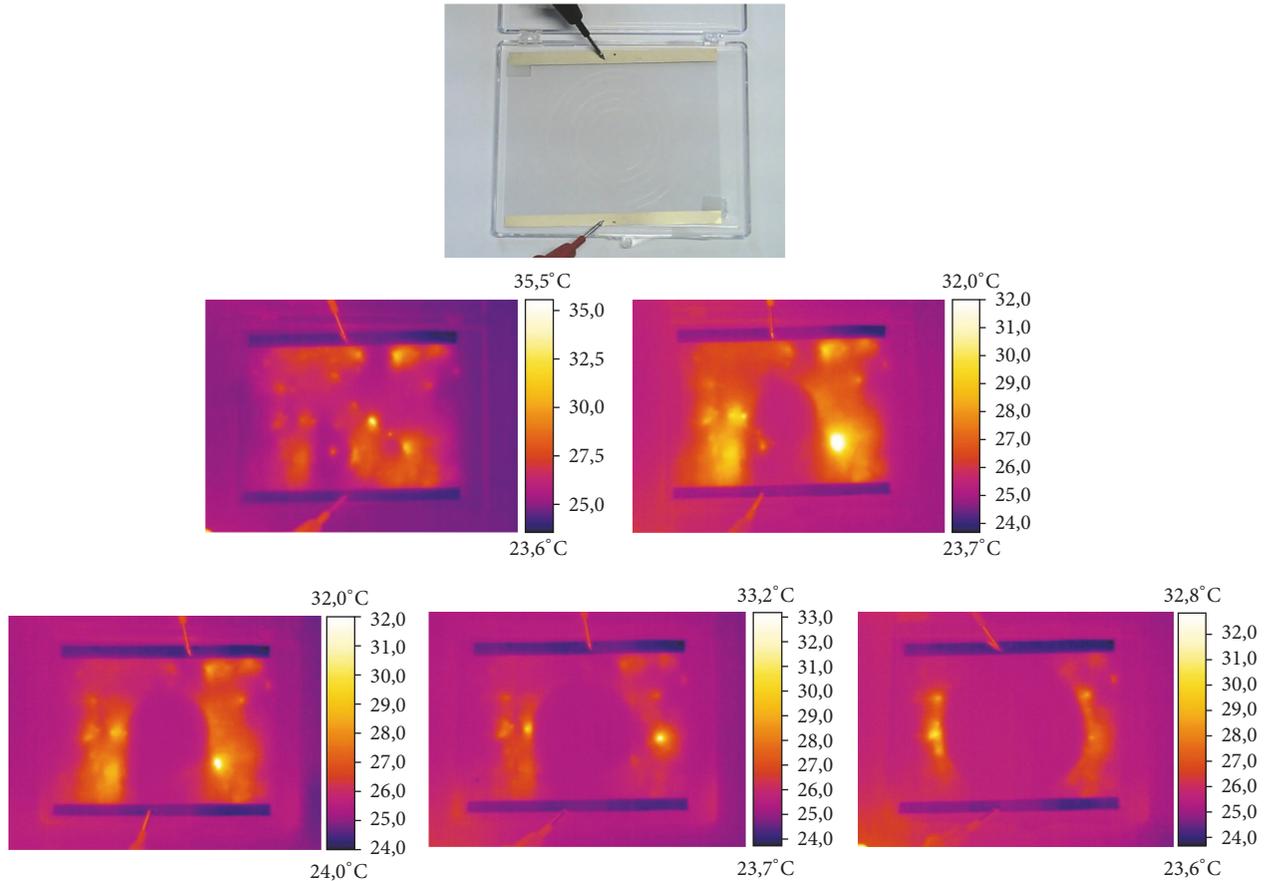


FIGURE 8: Photos of CVD-graphene device after mechanical damage at 30 V, together with thermal images (diameter size: 0, 20, 30, 40, and 60 mm, from left to right, resp.).

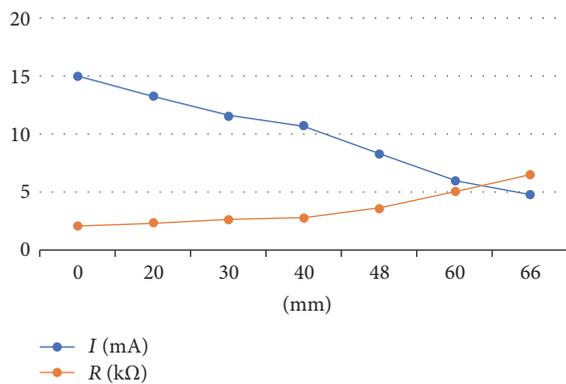


FIGURE 9: Dependence of I and R on the diameter of CVD-graphene-based device.

work was the verification of the proposed CVD-graphene-based device's potential application as sensor to identify mechanical damage. A device with CVD-graphene before and after mechanical damage was investigated by electrical method. In Figures 7 and 8, photographs of CVD-graphene-based devices before and after mechanical scratch are shown together with thermal images.

The device was investigated taking into account increase of voltage from 0 to 50 V. Total degradation of the graphene device was found over 50 V. Electrical properties of the mechanically damaged CVD-graphene layers are presented in Table 1 and in Figure 9.

Our study has shown that, along with increase of the diameter of circle on the graphene layer from 0 to 66 mm and consequently the increase of mechanical damage to the graphene layer, the value of current (I) decreased from 15 mA to about 4.7 mA (see Figure 9). For the CVD-graphene layer before mechanical destruction, we found that, along with the increase of current to 15 mA, the value of voltage increased linearly and resistance (R) was independent from the current applied.

3.4. Electrical Properties of CVD-Graphene-Based Device under 1000 W/m² Solar Irradiation. Finally, preliminary test concerning the impact of 1000 W/m² solar irradiation on the resistivity of CVD-graphene-based device was investigated along with the increase of temperature from 13 to 30°C as an effect of solar irradiation. A hand-made SOLARBOX was used to investigate the electrical behavior of the sensor (see Figure 10).

Our preliminary study shows that, along with increase of temperature from 13 to 30°C as an effect of solar irradiation,

TABLE 1: Electrical properties of CVD-graphene-based device before and after mechanical damage.

Parameters	Diameter [mm]						
	0	20	30	40	48	60	66
S^* [cm ²]	0	3.1	7.1	12.6	18.1	28.3	34.2
I [mA]	15.0	13.2	11.5	10.7	8.2	6.0	4.7
R [k Ω]	2.0	2.3	2.6	2.8	3.6	5.0	6.4

*Surface area.



FIGURE 10: SOLARBOX constructed at Military Institute of Engineer Technology, Wrocław, Poland.

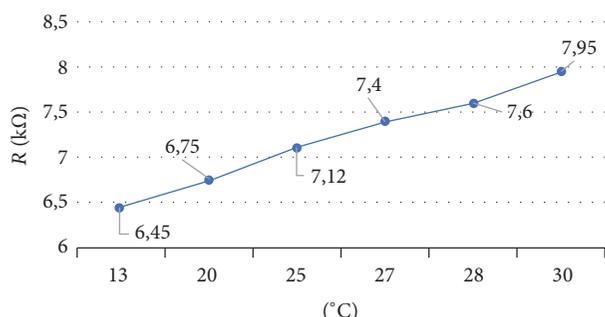


FIGURE 11: Resistance of CVD-graphene-based sensor under 1000 W/m² solar irradiation.

linear increase of resistance (R) for the investigated sensor was found (see Figure 11).

Moreover, we calculated a temperature resistance coefficient (α) of graphene sensor based on the equation $\alpha = (R_T/R_o) - 1/(T-T_o)$. The value obtained equaled $13.6 \times 10^{-3} [K^{-1}]$ and it is few times higher than, for example, that for Cu ($3.9 \times 10^{-3} [K^{-1}]$). Based on the preliminary study, we can conclude that the developed CVD-graphene-based device can be applied as a sensor for temperature and detection of mechanical defects. Moreover, taking into account other practical applications of graphene, our experiment provides first feedback on graphene being applied as electrode or in an encapsulated form as a layer in solar cells.

4. Conclusions

New thermoelectrochromic sensor (TEChrom) on flexible substrate was constructed using CVD-graphene layers. We

showed that the electrical properties of the investigated sensor can be controlled by change in temperature, area of mechanical destruction of sensor, and time of solar irradiation. The main advantage of our flexible sensor is the simplicity of the device architecture. CVD technique applied in order to create graphene layers in the sensor gave us the possibility to obtain high-quality graphene and potentially, on a large scale, use it in flexible solar cells integrated with textiles or buildings. The presented flexible thermoelectrochromic device with graphene can be widely used as a sensor for both the military and civil monitoring.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

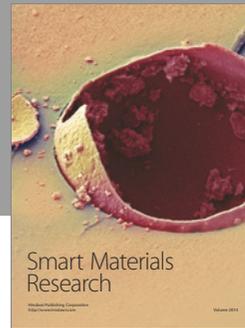
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References

- [1] R. Gupta, K. D. M. Rao, S. Kiruthika, and G. U. Kulkarni, "Visibly transparent heaters," *ACS Applied Materials and Interfaces*, vol. 8, no. 20, pp. 12559–12575, 2016.
- [2] E. O. Polat, O. Balç, and C. Kocabas, "Graphene based flexible electrochromic devices," *Scientific Reports*, vol. 4, article 6484, 2014.
- [3] A. Iwan and A. Chuchmała, "Perspectives of applied graphene: polymer solar cells," *Progress in Polymer Science*, vol. 37, no. 12, pp. 1805–1828, 2012.
- [4] N. G. Sahoo, Y. Pan, L. Li, and S. H. Chan, "Graphene-based materials for energy conversion," *Advanced Materials*, vol. 24, no. 30, pp. 4203–4210, 2012.
- [5] Z. Pan, H. Gu, M-T. Wu, Y. Li, and Y. Chen, "Graphene-based functional materials for organic solar cells," *Optical Materials Express*, vol. 2, pp. 815–824, 2012.
- [6] X. Wan, Y. Huang, and Y. Chen, "Focusing on energy and optoelectronic applications: a journey for graphene and graphene oxide at large scale," *Accounts of Chemical Research*, vol. 45, no. 4, pp. 598–607, 2012.

- [7] Z.-S. Wu, G. Zhou, L.-C. Yin, W. Ren, F. Li, and H.-M. Cheng, "Graphene/metal oxide composite electrode materials for energy storage," *Nano Energy*, vol. 1, no. 1, pp. 107–131, 2012.
- [8] D. R. Dreyer, S. Park, C. W. Bielawski, and R. S. Ruoff, "The chemistry of graphene oxide," *Chemical Society Reviews*, vol. 39, no. 1, pp. 228–240, 2010.
- [9] A. A. K. Geim and K. S. Novoselov, "The rise of graphene," *Nature Materials*, vol. 6, no. 3, pp. 183–191, 2007.
- [10] J. S. Bunch, S. S. Verbridge, J. S. Alden et al., "Impermeable atomic membranes from graphene sheets," *Nano Letters*, vol. 8, no. 8, pp. 2458–2462, 2008.
- [11] D. Pan, J. Zhang, Z. Li, and M. Wu, "Hydrothermal route for cutting graphene sheets into blue-luminescent graphene quantum dots," *Advanced Materials*, vol. 22, no. 6, pp. 734–738, 2010.
- [12] H. K. Bisoyi and S. Kumar, "Carbon-based liquid crystals: art and science," *Liquid Crystals*, vol. 38, no. 11-12, pp. 1427–1449, 2011.
- [13] Z. Ji, S. K. Doorn, and M. Sykora, "Electrochromic graphene molecules," *ACS Nano*, vol. 9, no. 4, pp. 4043–4049, 2015.
- [14] A. Januszko, W. Przybył, A. Krajewska, I. Pasternak, A. Przewłoka, and W. Strupinski, Patent application P.413693, 2015.
- [15] L. Misseeuw, A. Krajewska, I. Pasternak et al., "Optical-quality controllable wet-chemical doping of graphene through a uniform, transparent and low-roughness F4-TCNQ/MEK layer," *RSC Advances*, vol. 6, no. 106, pp. 104491–104501, 2016.
- [16] I. Pasternak, A. Krajewska, K. Grodecki, I. Jozwik-Biala, K. Sobczak, and W. Strupinski, "Graphene films transfer using marker-frame method," *AIP Advances*, vol. 4, no. 9, Article ID 097133, 2014.
- [17] T. Ciuk, I. Pasternak, A. Krajewska et al., "Properties of chemical vapor deposition graphene transferred by high-speed electrochemical delamination," *Journal of Physical Chemistry C*, vol. 117, no. 40, pp. 20833–20837, 2013.
- [18] I. Wlasny, P. Dabrowski, M. Rogala et al., "Role of graphene defects in corrosion of graphene-coated Cu(111) surface," *Applied Physics Letters*, vol. 102, no. 11, Article ID 111601, 2013.



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