Наносистеми, наноматеріали, нанотехнології
Nanosistemi, Nanomateriali, Nanotehnologii
2023, т. 21, № 3, сс. 569–574

PACS numbers: 06.60.Mr, 44.35.+c, 66.70.Lm, 72.80.Tm, 77.22.Ch, 81.05.Qk, 85.30.De

Electrophysical Properties and Thermal Conductivity of Reduced Graphene Oxide–ZnO Composite

B. Turko, V. Vasiliev, and V. Kapustianyk

Ivan Franko National University of Lviv,
50, Drahomanov Str.,
UA-79005 Lviv, Ukraine

The thermal conductivity of the composite materials based on the commercial ZnO micropowder with/without reduced graphene oxide (0.5 vol.%) powder dispersed in the polymethylsiloxane (silicone oil) is measured using the radial heat-flow method. The thermal conductivity of the composite material based on the commercial ZnO micropowder with an average particle size of 50 μm is found to be of 1.2 W/(m·K). The thermal conductivity of the composite material on the base of ZnO and reduced graphene oxide is found to be of 7.5 W/(m·K). At room temperature, the values of the dielectric permittivity at the measuring electric-field frequencies of 50 Hz and 1 MHz as well as the specific bulk electrical resistance for the composites are obtained. The large values of the thermal conductivity and the dielectric permittivity as well as lower specific bulk electrical resistance of the reduced graphene oxide–ZnO composite are associated with the contribution of reduced graphene oxide, the Maxwell–Wagner–Sillars interfacial polarization, and formation of the microcapacitor structures. It is also necessary to take into account that water could be adsorbed onto the powders' surface in the process of composites' fabrication. The high performance of reduced graphene oxide–ZnO composite synthesized by the simple and facile process in this work shows promising potential in thermal control of the electronic devices.

Теплопровідність композитних матеріялів на основі промислового мікропорошку ZnO з порошком/без порошку відновленого графенового оксиду (0,5 об.%), дисперґованого в поліметилсилоксані (силіконовій олії), вимірювали методом радіяльного теплового потоку. Встановлено, що теплопровідність композитного матеріялу на основі промислового мікропорошку ZnO із середнім розміром частинок у 50 мкм становить 1,2 Вт/(м·К). Теплопровідність композитного матеріялу на основі ZnO та відновленого графенового оксиду склала 7,5 Вт/(м·К). За кімнатної температури одержано значення діелектричної проникности на частотах вимірювального електричного поля у 50 Гц і 1 МГц та питомого об'ємного електричного опору для композитів. Великі значення теплопровідности та діелектричної проникности, а також менший питомий об'ємний електричний опір композиту відновленого графенового оксиду–ZnO пов'язані із внеском відновленого графенового оксиду, міжфазною поляризацією Максвелла–Ваґнера–Сілларса та формуванням мікроконденсаторних структур. Необхідно також враховувати, що в процесі виготовлення композитів на поверхні порошків може адсорбуватися вода. Висока продуктивність відновленого композиту графенів оксид–ZnO, синтезованого простим і легким процесом у цій роботі, демонструє перспективність у тепловому контролі електронних пристроїв.

Key words: reduced graphene oxide, zinc oxide, composites, thermal conductivity, dielectric constant, specific bulk electrical resistance.

Ключові слова: відновлений графенів оксид, оксид Цинку, композити, теплопровідність, діелектрична проникність, питомий об'ємний електричний опір.

(Received 14 December, 2022; in revised form, 15 December, 2022)

1. INTRODUCTION

As it is known, the thermal greases are used to remove heat from the heat-generating working elements of electronic devices, in particular, processors, chipsets, computer video accelerators, lasers, high-power LEDs, *etc*. Mostly, all thermal greases contain a polymer (for example, silicone oil) and various fillers–thickeners (for example, aluminium nitride, boron nitride, silver, aluminium oxide, zinc oxide, graphite) [1]. Graphene-based thermal conductive composites have come into notice in recent years [1–4]. A considerable number of works were devoted to enhancement of the thermal conductivity by increasing of the graphene content. However, it is impractical for the fabrication process when the grapheme content is too high [5]. The coefficient of thermal conductivity of graphene is varied within the range between 1500 W/(m·K) and 5800 W/(m·K) that is a record value for all the known materials [4, 6].

In general, graphene behaves as hydrophobic material. On the other hand, graphene with the functional groups, which is called reduced graphene oxide (*r*GO), possesses better stability due to the hydrogen bonding [7]. The thermal conductivity of the *r*GO can reach 2600 W/(m·K) and depends on the concentration of oxygen atoms in *r*GO [8]. The coefficient of thermal conductivity decreases, when the number of oxygen atoms increases [6].

At the same time, the number of publications concerning the thermal conductivity of the composite materials based on ZnO and *r*GO still is limited [9, 10]. One can note in this respect that we could not find any literature data concerning the thermal properties of composite materials based on ZnO, *r*GO and polymethylsiloxane.

This work is concerned with study of the electrophysical parameters, such as specific bulk electrical resistance and dielectric permittivity as well as with the testing of the thermal conductive properties of the composites based on ZnO, *r*GO and polymethylsiloxane with the prospect of their application in the computer technique.

2. EXPERIMENT

The composite materials were produced by dispersing of ZnO micropowder with an average particle size of 50 μm (99.7%, UKRZINC, Kyiv, Ukraine) with/without *r*GO powder (0.5 vol.%, purchased from Sigma-Aldrich, Saint Louis, USA) in the polymethylsiloxane PMS 1000 (silicone oil, SOFEX, Moscow, Russia). The silicone oil and the fillers were taken in a volume ratio of 3:7. According to the certificate of analysis obtained from Sigma-Aldrich, the *r*GO contained 83% of carbon and 4% of nitrogen by mass.

Determination of the thermal conductivity of the composites was carried out by radial heat-flow method [11].

The values of dielectric permittivity and specific bulk electrical resistance at room temperature and different frequencies of measuring electric field were obtained by LCR Meter IM3536-01 (HIOKI E. E. Corporation, Nagano, Japan).

The free software 'RealTemp' and 'CPU Burn-in v1.0' were used for testing of the thermally conductive composites. 'RealTemp' is a program for monitoring the temperature of computer-processor cores. It was designed for Intel Single Core, Dual Core, Quad Core and Core i7 processors. Each core in these processors has a digital thermal sensor. 'CPU Burn-in v1.0' is a program that 'heats' any processor with 'x86' architecture to the maximum possible operating temperature, accessible using a conventional software.

3. RESULT AND DISCUSSION

Figure presents the time dependences of the processor operating temperature measured starting from the moment of turning off the stable load of the computer, using different layers of composite material between the surfaces of the processor and the copper heatsink used for heat dissipation. It has been found that heat was removed much better when using a composite based on *r*GO powder.

At room temperature, the obtained values of the dielectric permittivity ε at the frequencies of electric measuring field $\nu = 50$ Hz

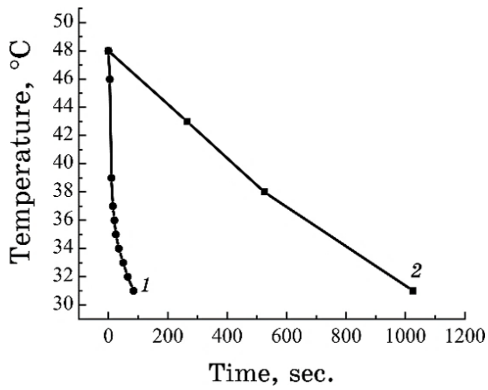

Fig. The time dependences of the processor operating temperature measured starting from the moment of turning off the stable load of the computer, using different layers of composite material between the surfaces of the processor and the copper heatsink used for heat dissipation: *1*—composite based on ZnO and polymethylsiloxane; *2*—composite based on ZnO, *r*GO and polymethylsiloxane.

or $\nu = 1$ MHz and specific bulk electrical resistance ρ ($\nu = 50$ Hz) for the two composites are given in Table.

The coefficients of thermal conductivity α of the investigated composites were calculated based on the following relation [11]:

$$\alpha = K \frac{\ln(r_1/r_2)}{2\pi l (T_1 - T_2)} UI , \quad (1)$$

where K is the factor of the axial heat loss through the plugs of the measuring cell (it depends on the plug material and is calculated by reference to a sample with known thermal conductivity); r_1 and r_2 are the inner and outer radii of the cylindrical composite layer; T_1 and T_2 are the temperatures of the internal and external surfaces of the composite layers; l is the length of the cylindrical composite layer; U is the voltage on the heater; I is the current in a heater.

The values of the thermal conductivity of the composite materials based on ZnO powders with a grain size of 50 μm without/with *r*GO calculated according to Eq. (1) were found to be equal to 1.2 W/(m·K) and 7.5 W/(m·K), respectively. The relative measurement error did not exceed 10%.

The thermal conductivity of the polymethylsiloxane is known to be equal $\alpha = 0.15$ W/(m·K) at room temperature [12]. Besides, it is known [13–15] that the coefficient of thermal conductivity of ZnO single crystals is in the range from 100 W/(m·K) up to 120 W/(m·K) and depends on the manufacturing technology and processing of the samples.

TABLE. Room-temperature electrophysical parameters of the studied materials.

Parameter	Composite based on ZnO powder	Composite based on the ZnO and *r*GO powders
Specific bulk electrical resistance at frequency of 50 Hz, Ohm·cm	$4\cdot10^{10}$	$8\cdot10^{9}$
Dielectric constant at frequency of:		
50 Hz	8	60
1 MHz	6	43

Large values of thermal conductivity and dielectric constant as well as lower specific bulk electrical resistance of the *r*GO–ZnO composite are associated with the physical properties of *r*GO ($\alpha = 2600$ W/(m·K), $\varepsilon = 1130$ ($\nu = 50$ Hz), $\rho = 1.4\cdot10^{-2}$ Ohm·cm) [8, 16, 17], Maxwell–Wagner–Sillars interfacial polarization [16, 18, 19] and formation of the microcapacitor structures [16, 18, 19]. The dielectric permittivity of water at room temperature is of about 80 [20]. It is much higher than the dielectric constants of silicone oil ($\varepsilon = 2.5$) [21] or zinc oxide ($\varepsilon = 8.5$) [22]; so, even a small amount of water in the composite can significantly affect its characteristics. Therefore, it is also necessary to take into account that water could be adsorbed onto the powders surface in the process of composites' manufacturing.

4. CONCLUSIONS

In summary, the coefficients of thermal conductivity of the composite materials based on the ZnO or ZnO with *r*GO (0.5 vol.%) powders dispersed in the polymethylsiloxane were determined by radial heat-flow method. They were found to be equal to 1.2 W/(m·K) and 7.5 W/(m·K), respectively. The difference in electrophysical properties of ZnO/polymethylsiloxane and *r*GO–ZnO/polymethylsiloxane composites is explained by the Maxwell–Wagner–Sillars interfacial polarization, microcapacitor structures and by the impact of reduced graphene oxide. The high performance of *r*GO–ZnO composite synthesized by a simple and facile process in this work shows promising potential in thermal control of the electronic devices.

REFERENCES

1. W. Xing, Y. Xu, C. Song, and T. Deng, *Nanomaterials*, **12**: 3365 (2022);

https://doi.org/10.3390/nano12193365
2. M. T. Phuong, P. V. Trinh, N. V. Tuyen, N. N. Dinh, P. N. Minh, N. D. Dung, and B. H. Thang, *J. Nano- Electron Phys.*, **11**: 05039 (2019); https://doi.org/10.21272/jnep.11(5).05039
3. C.-N. Hsu, K.-W. Lee, and C.-C. Chen, *Processes*, **9**: 847 (2021); https://doi.org/10.3390/pr9050847
4. M. Sang, J. Shin, K. Kim, and K. J. Yu, *Nanomaterials*, **9**: 374 (2019); https://doi.org/10.3390/nano9030374
5. D. Han, Y.-H. Zhao, Y.-F. Zhang, and S.-L. Bai, *RSC Adv.*, **5**: 94426 (2015); https://doi.org/10.1039/C5RA16780A
6. X. Mu, X. Wu, T. Zhang, D. B. Go, and T. Luo, *Scientific Reports*, **4**: 3909 (2014); https://doi.org/10.1038/srep03909
7. R. Kamatchi and K. G. Kannan, *International Journal of Renewable Energy Research*, **8**: 313 (2018); https://doi.org/10.20508/ijrer.v8i1.6766.g7305
8. Y. Zeng, T. Li, Y. Yao, T. Li, L. Hu, and A. Marconnet, *Adv. Funct. Mater.*, **29**: 1901388 (2019); https://doi.org/10.1016/j.jallcom.2010.03.076
9. H. Mandhare, D. P. Barai, B. A. Bhanvase, and V. K. Saharan, *Materials Research Innovations*, **24**: 433 (2020); https://doi.org/10.1080/14328917.2020.1721809
10. S. Biswas, S. Singh, S. Singh, S. Chattopadhyay, K. K. H. De Silva, M. Yoshimura, J. Mitra, and V. B. Kamble, *ACS Appl. Mater. Interfaces*, **13**: 23771 (2021); https://doi.org/10.1021/acsami.1c04125
11. B. I. Turko, V. B. Kapustianyk, V. P. Rudyk, and Y. V. Rudyk, *J. Nano-Electron. Phys.*, **8**: 02004 (2016); https://doi.org/10.21272/jnep.8(2).02004
12. B. Kolade, K. E. Goodson, and J. K. Eaton, *J. Heat Transf.*, **131**: 052402 (2009); https://doi.org/10.1115/1.3013831
13. U. Ozgur, X. Gu, S. Chevtchenko, J. Spradlin, S. Cho, H. Morkoc, F. H. Pollak, H. O. Everitt, B. Nemeth, and J. E. Nause, *J. Electron. Mater.*, **35**: 550 (2006); https://doi.org/10.1007/s11664-006-0098-9
14. D. I. Florescu, L. G. Mourikh, F. H. Pollak, D. C. Look, G. Cantwell, and X. Li, *J. Appl. Phys.*, **91**: 890 (2002); https://doi.org/10.1063/1.1426234
15. C. F. Klingshirn, B. K. Meyer, A. Waag, A. Hoffmann, and J. Geurts, *Zinc Oxide. From Fundamental Properties to Wards Novel Applications* (New York: Springer: 2010), p. 359 (in German).
16. Z. Chen, Y. Liu, L. Fang, P. Jiang, and X. Huang, *Appl. Surf. Sci.*, **470**: 348 (2019); https://doi.org/10.1016/j.apsusc.2018.11.150
17. A. Bhaumik and J. Narayan, *J. Appl. Phys.*, **120**: 105304 (2016); https://doi.org/10.1063/1.4962210
18. W. Tuichai, A. Karaphun, and C. Ruttanapun, *Materials Research Bulletin*, **145**: 111552 (2022); https://doi.org/10.1016/j.materresbull.2021.111552
19. D. Wang, X. Zhang, J.-W. Zha, J. Zhao, Z.-M. Dang, and G.-H. Hu, *Polymer*, **54**: 1916 (2013); http://dx.doi.org/10.1016/j.polymer.2013.02.012
20. S.-Y. Lo, A. Lo, L. W. Chong, L. Tianzhang, L. H. Hua, and X. Geng, *Modern Physics Letters B*, **10**: 921 (1996); https://doi.org/10.1142/S0217984996001048
21. Y. Otsubo, *KONA Powder and Particle Journal*, **15**: 43–43 (1997); https://doi.org/10.14356/kona.1997009
22. U. Ozgur, Y. Alivov, C. Liu, A. Teke, M. Reshchikov, S. Dogan, V. Avrutin, S. Cho, and H. Morkoc, *J. Appl. Phys.*, **98**: 041301 (2005); https://doi.org/10.1063/1.1992666