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A NEW APPROACH TO INCREASING THE SENSITIVITY OF A GAS SENSOR BASED ON NANOCRYSTALLINE SILICON CARBIDE FILMS

It was shown the possibility of increasing the sensitivity of a gas sensor based on nanocrystalline SiC films by using a scheme of a two-component sensing element, one of which is an n-nc-SiC film with electronic conductivity, and the second is an p-nc-SiC film with hole conductivity. It is shown that due to the opposite polarity of changes in resistance in the films under the simultaneous action of gases, the difference in relative resistance changes Δ in the n-nc-SiC and p-nc-SiC films will always be greater than in each film separately. The expediency of using a two-component sensing element of a gas sensor based on nc-SiC films with electron and hole conduction is shown.

Keywords: nanocrystalline SiC films, gas sensor, gas sensitivity, electronic conductivity, hole conductivity.

Recently, the problem of global monitoring of technogenic and natural gas pollution of the Earth's atmosphere has become more and more urgent. Particular harm and danger to human health are aggressive (hydrogen sulfide, carbon dioxide, hydrogen fluoride, nitrogen oxides, etc.), toxic (sulfur dioxide, carbon monoxide, hydrogen sulfide, etc.), fire-explosive (methanol, ammonia, methanol, etc.) gas emissions into the atmosphere. The analysis of such gas contaminants requires the development of new gas sensors with fast response and recovery, with the possibility of long-term operation in extreme conditions. This line of research is very relevant because gas sensors are the most important components of advanced communication technologies: Internet of Things, cloud computing, etc. [1].

In recent decades, semiconductor gas sensors based on a wide range of materials (metal oxides [2, 3], graphene [4, 5], polymers [6, 7]) have become widespread due to their good manufacturability, excellent design possibilities, and low cost. However, the relatively long response/recovery times and the lack of reliable operation at high temperatures and in corrosive environments severely limits their use in the future. Additional requirements for the stability of sensors under the influence of intense radiation and electromagnetic fields also sharply raise the problem of finding new functional semiconductor materials for the creation of highly sensitive gas sensors that slightly change their properties under severe external influences.

One of the promising materials with chemical inertness, resistance to radiation effects, and temporary stability of properties are materials based on a wide-gap third-generation semiconductor SiC [8]. High rates of charge transfer in SiC ensure the fabrication of gas sensors with short response/recovery times [9]. Studies of the properties of SiC sensors have shown that SiC materials are the best candidates for gas sensors for operation in extreme conditions [9—11]. Recent studies have shown that nanostructured SiC materials, at a lower cost, exhibit high stability of properties and increased gas sensitivity in comparison with bulk materials, due to a significantly larger surface area of interaction with the analyzed gas [12, 13].

Particular attention is attracted by films of nanocrystalline SiC (nc-SiC) obtained by direct ion deposition [14], which contain more than 80% of SiC nanocrystals in volume. This significantly exceeds the volumetric content of SiC nanocrystals in nanostructured materials obtained by the traditional method of grinding SiC polycrystals in a ball mill [12] or by the PECVD method [13]. The authors of this work have studied the electrophysical properties of nc-SiC films [15], the gas-sensitive properties of the films to reducing and oxidizing gases [16], the effect of the structure and type of conductivity of the films on their gas-sensitive properties [17]. As a result of the performed studies, the optimal structure and type of conductivity of the films were determined for the manifestation of the maximum gas sensitivity of nc-SiC to oxidizing and reducing gases. However, the problem of improving the characteristics of gas-sensitive materials is constantly in the center of the attention of all sensor developers, including authors.

The aim of this work is to study the possibility of increasing the sensitivity of sensors based on nc-SiC by simultaneously including films with different types of conductivity in the measuring circuit.

Experiment

Samples of nc-SiC films with different types of conductivity were obtained by direct ion deposition due to the ability of SiC to self-doping. Silicon carbide is a unique semiconductor in terms of the ability to change the type of conductivity with a small mismatch in stoichiometry, that is, to exhibit self-doping. An excess of Si in SiC leads to donor doping, i.e. to electronic conductivity. An excess of C in SiC creates acceptor centers and leads to hole conduction [18, 19]. The processes of controlled stoichiometry for self-doping were implemented under nonequilibrium conditions during the deposition of carbon and silicon ions with an energy of ~ 100 eV by the method of direct ion deposition [14].

An excess of silicon or carbon in the films was provided during deposition by changing the composition of the ion flux [20]. Using the capabilities of this method for self-doping, two series of nc-SiC films of a mixture of cubic and rhombohedral polytypes with different types of conductivity were prepared on sapphire substrates [17]. One series of films, designated *n*-nc-SiC, had electronic conductivity. Another series of films, *p*-nc-SiC, had hole conductivity. The deviation of stoichiometry in the SiC films samples was 5—10% for both silicon and carbon. However, we did not investigate the levels of doping as part of the excess elements was deposited in the intercrystalline space. It is known from the literature that the maximum limit of non-stoichiometry in silicon carbide is 1—2% [21]. The type of conductivity in the films was determined from the sign of the Seebeck thermoelectric coefficient using a thermal probe [22]. In this case, the concentration of charge carriers was not measured.

At the same time, under the conditions of preparation, samples of films with close resistances (~ 100 MΩ) were prepared at the same thicknesses and contact areas in order to provide close concentrations of charge carriers.

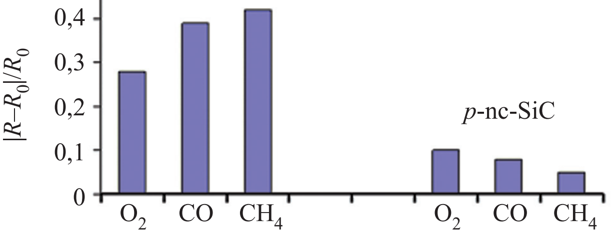

Fig. 1. Gas sensitivity of *n*-nc-SiC and *p*-nc-SiC films to oxidizing (O_2, O_3) and reducing (CH_4, CO) gases [17]

In [17], we measured the gas sensitivity of *n*-nc-SiC and *p*-nc-SiC films to oxidizing (O_2, O_3) and reducing (CH_4, CO) gases and found that n-nc-SiC films with electronic conductivity provide for all gases a significantly greater response than p-nc-SiC films, which is reflected in the diagram in **Fig. 1**.

Similar results are known for other semiconductors with hole conductivity [23, 24]. The lower speed and magnitude of the response in *p*-semiconductors is explained by differences in the mechanisms and kinetics of electron and hole conductivities in semiconductors. For example, the mobility of holes in all SiC polytypes is an order of magnitude less than the mobility of electrons [25, 26]. The advantage of semiconductors with electronic conductivity in the magnitude of the response to reactions with gas molecules is clearly confirmed by the fact that the overwhelming majority of semiconductor sensors are based on *n*-semiconductors [25]. Also, a significant factor is the more accessible technologies for doping semiconductors with donor impurities. The prepared samples of both series of nc-SiC films had a thickness in the range of 100—200 nm, rectangular Au/Ni contact pads with an area of 5×3 mm with a distance of 2 mm between them. The initial resistance of the samples was in the range of 100—120 MΩ. Both series of nc-SiC films on sapphire substrates were exposed to gases simultaneously in one chamber. The measurement scheme is shown in **Fig. 2**. The working temperature of the samples was 500°C. When measuring ozone, the working temperature was 280°C [26]. The samples were exposed to interaction with oxidizing O_2, O_3 and reducing CO, CH_4 gases in concentration ranges, the lower limits of which are accepted in many countries as critical for human health and life: O_2 — 5%, O_3 — 0.1 mg/m^3, CO — 0,04%, CH_4 — 10% [27].

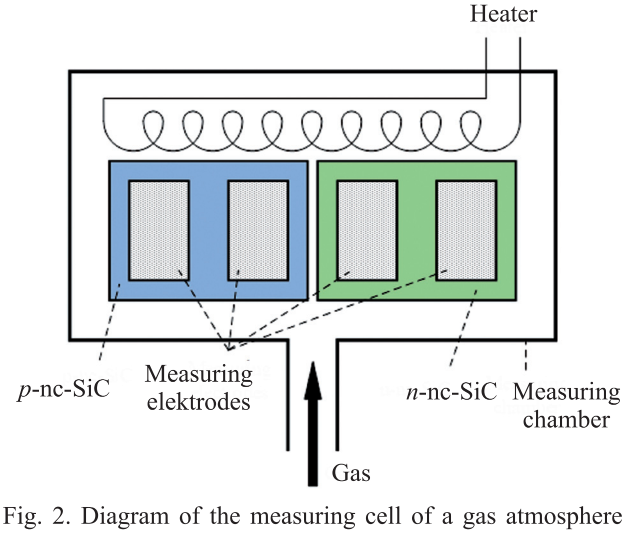

Fig. 2. Diagram of the measuring cell of a gas atmosphere sensor with two sensitive components based on nc-SiC films with *n*- and *p*-conductivity

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Results and discussion

Fig. 3 show the dependences of changes in the relative resistance R/R_0, where R and R_0 are the resistance after and before the action of the gas, samples of n-nc-SiC and p-nc-SiC films under the action of oxidative O_2, O_3 and reducing CO, CH_4 gases.

The fundamental influence of chemically active gases on the electrical resistance of semiconductors is well known [26]. Under the action of oxidizing gases, which reduce the concentration of electrons and reduce their mobility, the resistance of a semiconductor with electronic conductivity increases, and in a semiconductor with hole conductivity, the resistance, respectively, decreases. The action of reducing gases is the opposite. Their interaction with a semiconductor with electronic conductivity increases the concentration of electrons and therefore the resistance decreases, and in a semiconductor with hole conductivity, accordingly, the resistance increases. The presented dependences of the relative resistances of n-nc-SiC and p-nc-SiC films under the action of oxidizing O_2, O_3, and reducing CO, CH_4 gases fully correspond to the fundamental mechanisms of interaction. The figures show that the relative resistance R/R_0 of n-nc-SiC samples under the action of oxidizing O_2, O_3 gases becomes greater than 1 and increases with increasing gas concentration. And when nc-SiC films interact with reducing CO, CH_4 gases, the relative resistance R/R_0 becomes less than 1 with a subsequent decrease with the gas concentration. And in samples of p-nc-SiC films with hole conductivity, the effect of gases on resistance is opposite.

More interesting and useful data calculated from the presented dependencies are shown in the Table. In addition to the numerical values of the relative resistances for each gas concentration of both series of samples, the rows $|\Delta R/R_0|$ (where $\Delta R = R - R_0$) show the changes in relative resistances under the action of gases in percent, which clearly shows the differences in the gas sensitivity of nc-SiC films with electron and hole conductivity. We decided to use the fact that the polarity of changes in the resistances of nc-SiC films with electron and hole conductivity is different. And thus, the difference in the simultaneous change in relative resistance for two nc-SiC films with electron and hole conductivity $(R/R_0)_n - (R/R_0)_p$ will be greater than the change for one sample of any conductivity.

This value is indicated by Δ and is presented in the Table as a percentage. It can be seen that Δ for all the given concentrations is greater, and in some cases substantially greater, than the change in the resistance of any one sample of the film with any conductivity. For critical gas concentrations C_{CR} the excess of Δ was 38% for O_2 (C_{CR} = 5%), 19% for O_3 (C_{CR} = 0,1 mg/m^3), 30% for CO (C_{CR} = 0,04%), 57% for CH_4 (C_{CR} = 10%).

Thus, the use of the combination of two nc-SiC films with electron and hole conductivity as a gas-sensitive

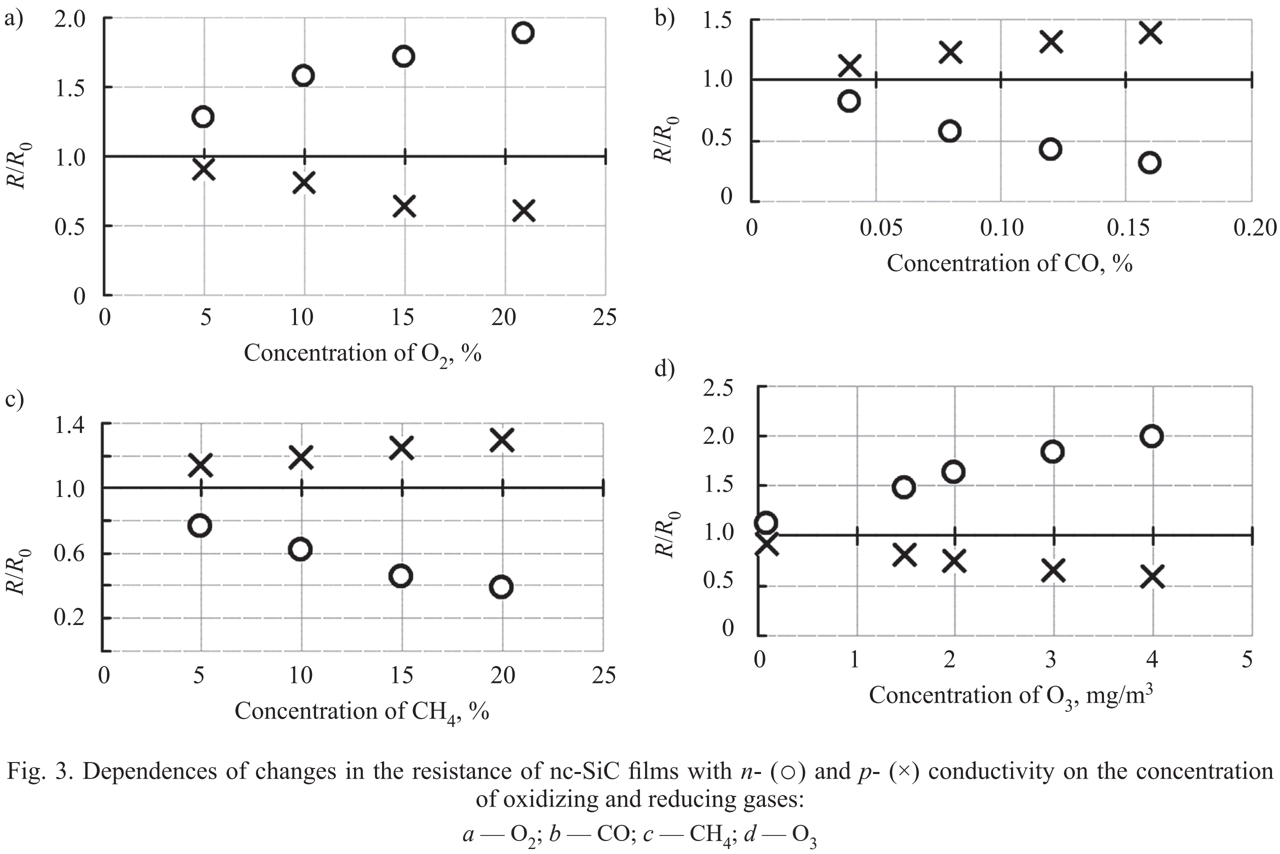

Fig. 3. Dependences of changes in the resistance of nc-SiC films with n- (○) and p- (×) conductivity on the concentration of oxidizing and reducing gases:
a — O_2; *b* — CO; *c* — CH_4; *d* — O_3

Dependences of changes in the resistance of nc-SiC films of n- and p-conductivity from the concentration of oxidizing and reducing gases

Parameter		Concentration								
		O_2, %				CO, %				
		5	10	15	20	0,04	0,08	0,12	0,16	
n-nc-SiC	R/R_0	1,28	1,57	1,71	1,88	0,82	0,57	0,42	0,31	
	$\lvert\Delta R/R_0\rvert$, %	28	57	71	88	18	43	58	69	
p-nc-SiC	R/R_0	0,9	0,81	0,64	0,61	1,12	1,22	1,31	1,39	
	$\lvert\Delta R/R_0\rvert$, %	10	19	36	39	12	22	31	39	
Δ, %		38	76	107	127	30	65	89	108	
		CH_4, %				O_3, mg/m^3				
		5	10	15	20	0,1	1,5	2,0	3,0	4,0
n-nc-SiC	R/R_0	0,76	0,62	0,45	0,38	1,11	1,47	1,63	1,83	1,98
	$\lvert\Delta R/R_0\rvert$, %	24	38	55	62	11	47	63	83	98
p-nc-SiC	R/R_0	1,14	1,19	1,24	1,29	0,92	0,81	0,74	0,65	0,59
	$\lvert\Delta R/R_0\rvert$, %	14	19	24	29	8	19	26	35	41
Δ, %		38	57	79	91	19	66	89	118	139

component can provide an increase in the sensitivity of sensors operating under extreme conditions.

Conclusion

The authors have developed a method for increasing the sensitivity of a gas sensor based on nanocrystalline SiC films by using a scheme of a two-component sensitive element, one of which is an *n*-nc-SiC film with electronic conductivity, and the second is an *p*-nc-SiC film with hole conductivity. It is shown that due to the opposite polarity of changes in resistance in the films under the simultaneous action of gases, the difference in relative resistance changes Δ in the n-nc-SiC and p-nc-SiC films will always be greater than in each film separately. So for critical gas concentrations, the excess of Δ (%) was 38 for O_2 (5%), 19 for O_3 (0,1 mg/m^3), 30 for CO (0,04%), 57 for CH_4 (10%). The authors did not aim to carefully optimize the characteristics of gas-sensitive properties of *p*-nc-SiC and *n*-nc-SiC films, but only showed the gain in sensitivity when using a complementary pair of these films for gas analysis. Thus expediency of using a two-component sensing element of a gas sensor based on nc-SiC films with electron and hole conduction is shown. A two-component gas sensor with increased sensitivity based on nc-SiC films can form the basis of a new line of instruments for analyzing aggressive gases in extreme conditions.

REFERENCES

1. Mehmood F., Ahmad S., Kim D.H. Design and implementation of an interworking IoT platform and marketplace in could of things. *Sustainability*, 2019, vol. 11, iss. 21, p. 5952. https://doi.org/10.3390/su11215952

2. Arafat M., Haseeb A.S.M.A., Akbar S.A. Quadir M.Z. In-situ fabricated gas sensors based on one dimensional core-shell TiO_2-Al_2O_3 nanostructures. *Sensors and Actuators B: Chemical*, 2017, vol. 238, pp. 972–984. https://doi.org/10.1016/j.snb.2016.07.135

3. Jaisutti R., Lee M., Kim J. et al. Ultrasensitive room-temperature operable gas sensors using p-type Na: ZnO nanoflowers for diabetes detection. *ACS Applied Materials & Interfaces*, 2017, vol. 9, iss. 10, pp. 8796–8804. https://doi.org/10.1021/acsami.7b00673

4. Wu J., Tao K., Guo Y. et al. A 3D chemically modified graphene hydrogel for fast, highly sensitive, and selective gas sensor. *Advanced Science*, 2016, vol. 4, iss. 3, pp. 1–9. https://doi.org/10.1002/advs.201600319

5. Song Z., Wei Z., Wang B. et al. Sensitive room-temperature H_2S gas sensors employing SnO_2 quantum wire/reduced graphene oxide nanocomposites. *Chemistry of Materials*, 2016, vol. 28, iss. 4, pp. 1205–1212. https://doi.org/10.1021/acs.chemmater.5b04850

6. Hien H.T., Giang H.T., Hieu N.V. et al. Elaboration of Pd-nanoparticle decorated polyaniline films for room temperature NH_3 gas sensors. *Sensors and Actuators B: Chemical*, 2017, vol. 249, pp. 348–356. https://doi.org/10.1016/j.snb.2017.04.115

7. Mun S., Park Y., Lee Y.K., Sung M.M. Highly sensitive ammonia gas sensor based on single-crystal poly(3-hexylthiophene) (P3HT) organic field effect transistor. *Langmuir*, 2017, vol. 33, iss. 47, pp.13554–13560. https://doi.org/10.1021/acs.langmuir.7b02466

8. Capano M.A., Trew R.J. Silicon carbide electronic materials and devices. *MRS Bulletin*, 1997, vol. 22. iss. 3, pp. 19–23. https://doi.org/10.1557/S0883769400032711

9. Spetz A.L, Savage S. Advances in SiC field effect gas sensors. In: Choyke W.J., Matsunami H., Pensl G. (eds) *Silicon Carbide. Recent Major Advances*, Germany, Berlin, Springer, 2004, pp. 869–896. https://doi.org/10.1007/978-3-642-18870-1_36

10. Zolper J.C., Skowronski M. Advances in silicon carbide electronics. *MRS Bulletin*, 2005, vol. 30, iss. 4, pp. 273–278. https://doi.org/10.1557/mrs2005.73

11. Neudeck P.G., Okojie R.S., Chen L. High-temperature electronics – a role for wide bandgap semiconductors? *Proceedings of the IEEE*, 2002, vol. 90, iss. 6, pp. 1065–1076. https://doi.org/10.1109/JPROC.2002.1021571

12. Gaiardoa A., Belluttib P., Fabbria B. et al. Sensing properties of nanocrystalline silicon carbide in wet condition. *17th IMCS University*

of Vienna, 2018, Austria, pp. 612-613. https://doi.org/10.5162/IMCS2018/P1NM.18

13. Sultan A., Ahmad S., Mohammad F. A highly sensitive chlorine gas sensor and enhanced thermal DC electrical conductivity from polypyrrole/silicon carbide nanocomposites. *RSC Advances*, 2016, vol. 6, pp. 84200-84208. https://doi.org/10.1039/C6RA12613H

14. Semenov A.V., Puzikov V.M., Dobrotvorskaya M.V. et al. Nanocrystalline SiC films prepared by direct deposition of carbon and silicon ions. *Thin Solid Films*, 2008, vol. 516, iss. 10, pp. 2899–2903. https://doi.org/10.1016/j.tsf.2007.05.059

15. Kozlovskyi A., Semenov A., Skorik S. Electron transport in nanocrystalline SiC films obtained by direct ion deposition. *Superlattices and Microstructures*, 2016, vol. 100, pp. 596–604. https://doi.org/10.1016/j.spmi.2016.10.013

16. Semenov A., Kozlovskyi A., Skorik S., Lubov D. Gas sensing properties of nanocrystalline silicon carbide films. *Micro and Nano System Letters*, 2019, vol. 7, iss. 6, pp. 1–5. https://doi.org/10.1186/s40486-019-0084-7

17. Semenov A.V., Lubov D.V., Kozlovskyi A.A. The Chemresistive properties of SiC nanocrystalline films with different conductivity type. *Journal of Sensors*, 2020, article ID 7587314, pp. 1–6. https://doi.org/10.1155/2020/7587314

18. Taki Y., Kitiwan M., Katsui H., Goto T. Electrical and thermal properties of off-stoichiometric SiC prepared by spark plasma sintering. *Journal of Asian Ceramic Societies*, 2018, vol. 6, iss. 1, pp. 95–101. https://doi.org/10.1080/21870764.2018.1446490

19. Gadzira M., Gnesin G., Mykhaylyk O. et al. Solid solution of carbon in β-SiC. *Materials Letters*, 1998, vol. 35, iss. 5–6, pp. 277–282. https://doi.org/10.1016/S0167-577X(97)00263-2

20. Semenov A.V., Puzikov V.M., Golubova E.P. et al. Low-temperature production of silicon carbide films of different polytypes. *Semiconductors*, 2009, vol. 43, iss. 5, pp. 685–689. http://dx.doi.org/10.1134/S1063782609050273

21. Birnie, D. P., & Kingery, W. D. , The limit of non-stoichiometry in silicon carbide. *Journal of Materials Science*, 1990, vol. 25, iss. 6, pp. 2827–2834. doi:10.1007/bf00584888

22. Platzek D., Karpinski G., Stiewe C. et al. Potential-Seebeck-microprobe (PSM): measuring the spatial resolution of the Seeb.eck coefficient and the electric potential. *ICT 2005. 24th International Conference on Thermoelectrics*. https://doi.org/10.1109/ICT.2005.1519875

23. Cheong K.Y., Silicon carbide (SiC) as non-volatile random access memory (NVRAM) material. *JURUTERA*, 2005, pp. 10-16.

24. Yoon J.W., Kim H.J., Jeong H.M., Lee J.H. Gas sensing characteristics of p-type Cr2O3 and Co3O4 nanofibers depending on inter-particle connectivity. *Sensors and Actuators B: Chemical*, 2016, vol. 202, pp. 263–271. http://dx.doi.org/10.1016/j.snb.2014.05.081

25. Nikolic M.V., Milovanovic V., Vasiljevic Z.Z., Stamenkovic Z. Semiconductor gas sensors: materials, technology, design, and application. *Sensors*, 2020, vol. 20, iss. 22, 6694. https://doi.org/10.3390/s20226694

26. George F.F., Leon M.C., Ayo A., Russell B. Metal oxide semiconductor gas sensors in environmental monitoring. *Sensors*, 2010, vol. 10, iss. 6, pp. 5469-5502. https://doi.org/10.3390/s100605469

27. Semenov A.V., Lubov D.V., Makhonin M.V., Ozone Sensitive Properties of Thin Films of Nanocrystalline Silicon Carbide. *Journal of Nano- and Electronic Physics*, 2020, vol. 12, iss. 5, p. 05016. https://doi.org/10.21272/jnep.12(5).05016

28. Hall S.A. Airborne contaminants. *Occupational Health Practice*, 1973.

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НОВИЙ ПІДХІД ДО ПІДВИЩЕННЯ ЧУТЛИВОСТІ ГАЗОВОГО СЕНСОРА НА ОСНОВІ ПЛІВОК НАНОКРИСТАЛІЧНОГО КАРБІДУ КРЕМНІЮ

Останнім часом гостро стоїть проблема пошуку нових функціональних напівпровідникових матеріалів для створення високочутливих газових сенсорів, які слабо змінюють свої властивості в умовах жорстких зовнішніх впливів. Завдання поліпшення характеристик газочутливих матеріалів постійно знаходяться в центрі уваги розробників приладів. Наноструктуровані SiC матеріали, при більш низькій вартості, проявляють високу стабільність властивостей і підвищену газову чутливість в порівнянні з об'ємними SiC матеріалами, завдяки значно більшій площі поверхні взаємодії з аналізованих газом

У роботі досліджено можливість збільшення чутливості газового сенсора на основі плівок нанокристалічного SiC, шляхом використання схеми двох компонентного чутливого елемента, один з яких є плівка n-nc-SiC з електронною провідністю, а другий плівка p-nc-SiC з дірковою провідністю. Завдяки протилежній полярності зміни опору під час дії газу різниця між величинами зміни відносних опорів плівок n-nc-SiC та p-nc-SiC завжди буде більше, ніж у кожній плівці окремо. Встановлено доцільність використання двокомпонентного чутливого елемента газового сенсора на основі плівок nc-SiC з електронною та дірковою провідностями. Двокомпонентний газовий сенсор з підвищеною чутливістю на основі nc-SiC плівок може бути основою лінійки нових приладів для аналізу агресивних газів в екстремальних умовах.

Ключові слова: нанокристалічні плівки SiC, газовий сенсор, чутливість до газу, електронна провідність, діркова провідність.

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