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Research Article

The Chemresistive Properties of SiC Nanocrystalline Films with Different Conductivity Type

A. V. Semenov,[1] **D. V. Lubov,**[1] **and A. A. Kozlovskyi**[2]

[1]*National Technical University "Kharkiv Polytechnic Institute", 2, Kyrpychova str., Kharkiv 61002, Ukraine*
[2]*Institute for Single Crystals NAS of Ukraine, Nauky Ave. 60, Kharkiv 61001, Ukraine*

Correspondence should be addressed to A. V. Semenov; savladi@ukr.net

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We have demonstrated the ability of thin nanocrystalline SiC films with various types of conductivity to detect oxidative (O_2), reducing gases (CO, CH_4) with the maximum allowable concentrations for human safety. It was shown that n-nc-SiC films with electronic conductivity had a higher gas sensitivity S_n than p-nc-SiC films with hole conductivity sensivity S_p to the action of gases in a wide concentration range. So, for the maximum permissible concentrations of O_2 (3%), CO (0.1%), CH_4 (10%) the sensitivity ratio of the films S_n/S_p was 2.9; 4.8 and 10, respectively. For research, we used a simple resistor geometry optimizing which it is possible to significantly increase the sensitivity of films to gases in order to detect extremely low gas concentrations. Thus, based on nc-SiC films, it is possible to develop high-temperature gas sensors to detect reactive gases in a wide range of concentrations, including threshold allowable values.

1. Introduction

Silicon carbide (SiC) has high potential as an electronic semiconductor material for a new generation of high-temperature sensors and power electronics devices. Based on single-crystal silicon carbide, a wide range of chemical sensors of various designs [1, 2] was developed including capacitors [3], field effect transistors [4], Schottky diodes [5, 6]. The high sensitivity of SiC sensors to many toxic and dangerous gases makes them indispensable for monitoring the gas atmosphere in high temperature (> 800°C) processes in space, aviation, automotive, chemical and physical reactors [7]. These applications require sensor's reliable operation in various difficult conditions: from cryogenic temperatures to more than 800°C, from chemically inert media to highly aggressive engine emissions and from the detection of one gas in a wide range of concentrations in inert media to the detection of several gases in narrower ranges of concentration in the presence of interfering gases. At the same time high sensitivity, long-term stability, good reproducibility are necessary. The combination of these requirements was achieved on the sensors developed on monocrystalline SiC [1, 7]. However, the high cost of technology for SiC monocrystalline sensors limits their wide application.

Some additional possibilities for increasing sensitivity and reducing response time, along with a decrease in the cost of technology are opening with the use of layers of nanocrystalline SiC [8, 9] obtained on the basis of nanoscale powder SiC with an organic bundle. Despite the fact that the concentration of SiC nanocrystals in such composite layers was not very high already in the first articles the prospects of application of layers of nanocrystalline SiC as gas sensors in difficult conditions were shown [8, 9]. Significantly higher concentration of SiC nanocrystals is present in the films obtained by the method of direct ion deposition [10].

Therefore, the use of nanocrystalline SiC (nc-SiC) films for the development of gas sensors can significantly expand the market of SiC-based devices. Earlier we presented the first results of the study of chemical resistance sensitivity of thin nc-SiC films to air atmosphere gases [11]. In this work we continued these studies on thin nc-SiC films with different types of conductivity to optimize their gas sensing properties.

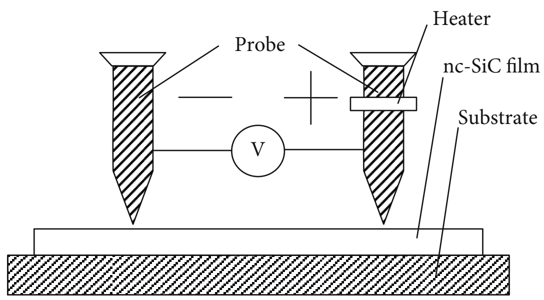


Figure 1: Scheme for measuring the type of conductivity in nc-SiC films by the thermal probe method.

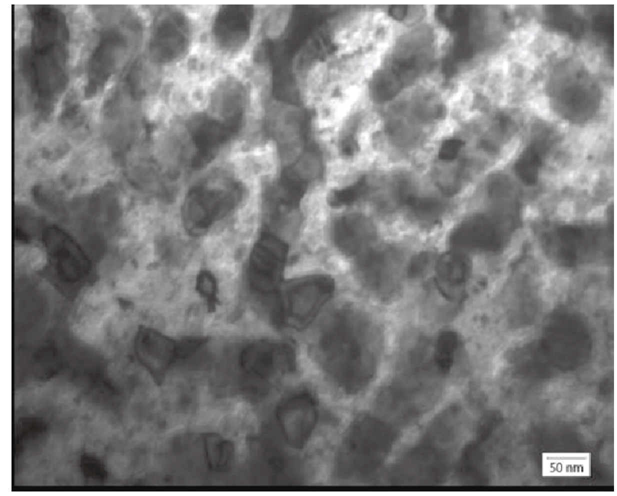
2. Materials and Methods

Crystalline silicon carbide is a universal semiconductor in terms of the possibility of changing the types of conductivity with a slight mismatch in stoichiometry, that is, to exhibit self-doping. Excess Si in SiC leads to donor doping, i.e. to electronic conduction. Excess C in SiC creates acceptor centers and leads to hole conductivity [12, 13]. It is technologically difficult to realize controlled nonstoichiometry for self-doping at growing single-crystal SiC, which occurs under thermodynamic conditions close to equilibrium, but can be carried out under nonequilibrium conditions by the deposition of carbon and silicon ions with an energy of~ 100 eV by direct ion deposition method [10].

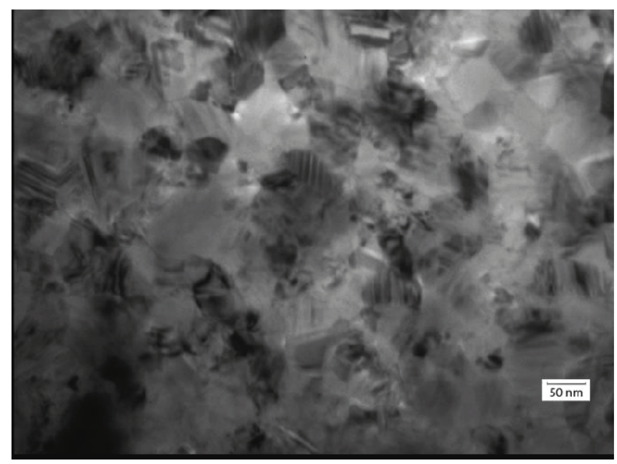
Excess silicon or carbon in the films is provided during deposition by changing the composition of the ion flow [14]. Using the capabilities of this method for self-doping, two series of nc-SiC films of a mixture of cubic and rhombohedral polytypes with different types of conductivity were prepared on sapphire substrates. One series of films designated n-nc-SiC had electronic conductivity.

Another series of films designated p-nc-SiC had hole conductivity. The type of conductivity in the films was determined by the sign of the Seebeck thermoelectric coefficient using a thermal probe [15]. Measurement circuit presented in Figure 1. A positive sign of the potential of a heated probe indicated electronic conductivity and vice versa. In this case, the concentration of charge carriers was not measured. At the same time, samples were prepared with close resistances (~ 2 MΩ) at the same thicknesses and contact pads in order to ensure close charge carrier concentrations. The sizes of nanocrystals in the films varied in the range 5–50 nm [10]. Figure 2 shows Transmission Electron Microscopy image of typical sections of the nc-SiC films of both series.

Films thicknesses were in the range of 200 – 300 nm. For resistive measurements Au/Ni contacts area of $7 \times 5\,\text{mm}^2$ were applied. The working temperature of the films was previously estimated from the temperature of desorption of the atmospheric layer on nc-SiC films in vacuum [11]; therefore, we used this value of 500°C. The gas sensing properties of the films to gases was determined by exposing the films in an atmosphere of an air mixture of oxygen O_2 of various concentrations, carbon monoxide CO, methane CH_4. It should be noted that most studies of the properties of gas semiconductor sensors focused on the sensitivity of sensors to



(a)



(b)

Figure 2: Transmission Electron Microscopy image of the nc-SiC films with different types of conductivity, a) n-nc-SiC – electronic conductivity, b) p-nc-SiC – hole conductivity.

extremely small concentrations of chemical media, which is a very important signal property of sensors. At the same time, there are few articles on the properties of semiconductor sensors that measure extremely large or small maximum permissible concentrations of active gases.

Therefore, in the work the sensitivity of films to the maximum concentrations of gases admissible for human health was studied, the measurement of which by semiconductor sensors was practically not reflected in the published works. For human health, not only the content of harmful gas components in the air is important, but also the absolute partial pressure of O_2, the minimum acceptable value for human life is defined at~ 7000 Pa (weight content of O_2~ $0.29\,\text{g/m}^3$). This corresponds to the concentration of O_2 at atmospheric pressure of~ 3% by volume. Below this value, human metabolism is disturbed [16]. Therefore, we studied the sensitivity of nc-SiC films to oxygen in the concentration range from normal~ 21% to a threshold value of~ 3% at atmospheric pressure. In addition, from the point of view of the maximum allowable concentration for human safety and health, the

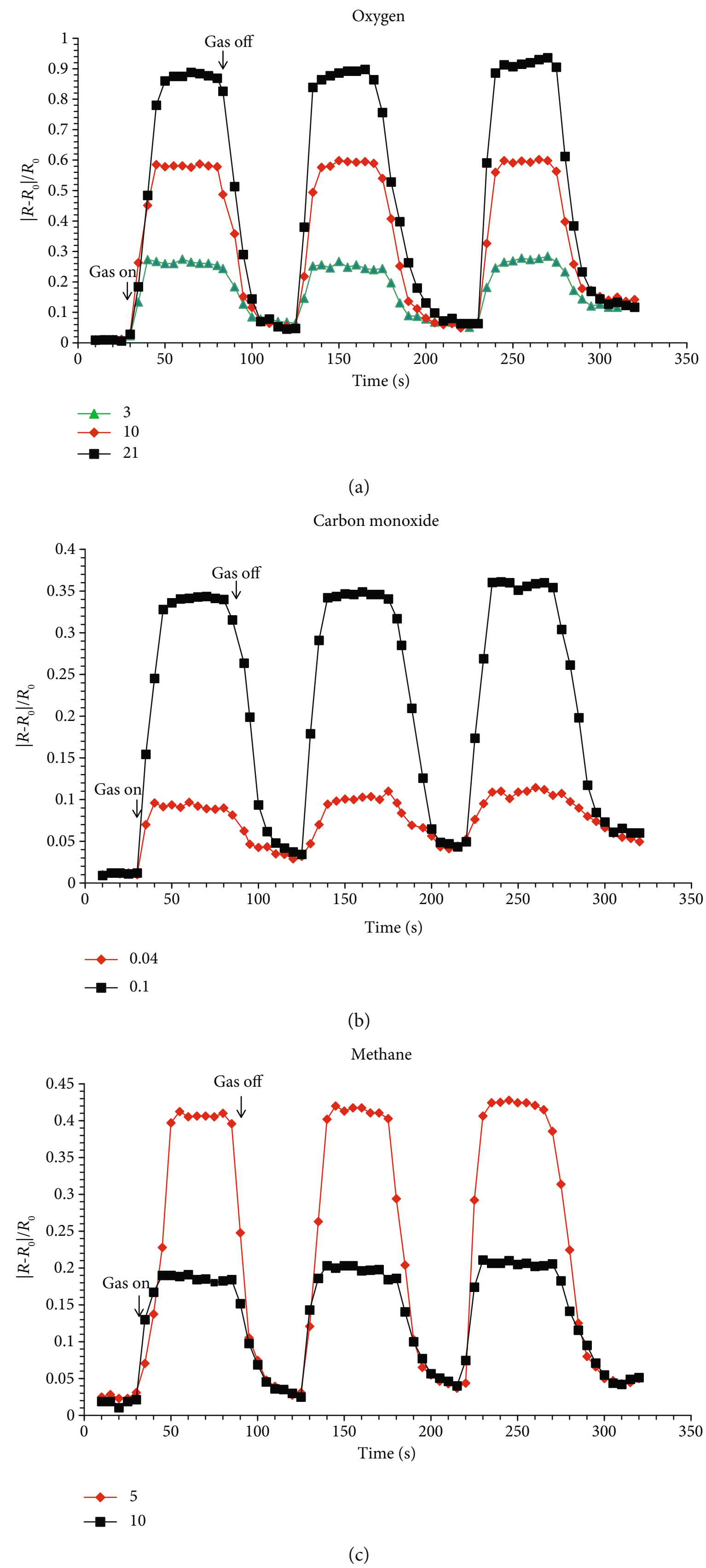


FIGURE 3: Gas sensing results of n-nc-SiC films towards a) oxygen concentration of 21%, 10%, 3%, b) carbon monoxide concentration of 0.1%, 0.04%, c) methane concentration of 10%, 5%. Testing temperature – 500°C. The numbers on the insert indicate the gas concentration.

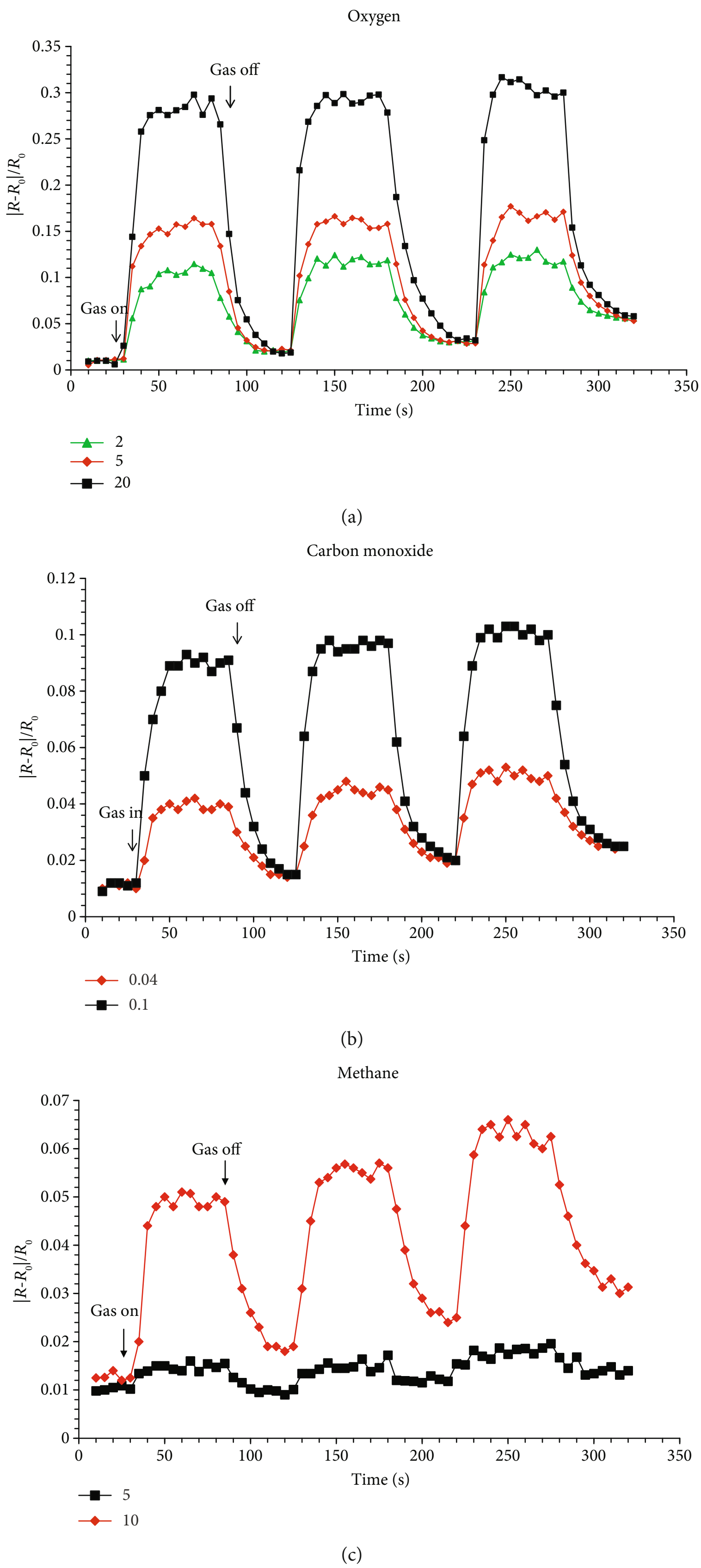


Figure 4: Gas sensing results of p-nc-SiC films towards a) oxygen concentration of 20%, 10%, 3%, b) carbon monoxide concentration of 0.1%, 0.04%, c) methane concentration of 10%, 5%. Testing temperature 500°C. The numbers on the insert indicate the gas concentration.

sensitivity of films to concentrations of carbon monoxide in the range of 0.04 - 0.1% and methane from a concentration of 5% to explosive 10% was studied. The measurements were performed by inflating an air mixture with various concentrations of the gases into the sample chamber. To measure the sensitivity of the film to oxygen, a nitrogen-oxygen mixture of various concentrations filled the previously evacuated sample chamber to a pressure of 10^{-1} Pa. The time of action gas was held at about 50 seconds. The gas inlet and evacuation was repeated at least three times. Previously, it was established that the effect of N_2 on the electrical conductivity of films is neutral [11]. Therefore, the effect of a mixture of N_2 and O_2 is assigned only to the impact of O_2. The gas sensitivity coefficient was estimated by the formula $S = (|R_0 - R|/R_0)$, where R_0 and R are the film resistance in the absence and presence of a chemically active atmosphere, respectively.

3. Results and Discussion

Figure 3 presents the results of measurements of the effect of chemically active gases with concentrations, including the limiting ones, on the resistance of n-nc-SiC films with electronic conductivity.

Figure 3 shows the modules of the relative changes in the resistance of the n-nc-SiC films. Graph 3a shows the relative changes in the resistance of the film under conditions of exposure to oxygen with concentrations of 3, 10 and 21%. The absolute changes in resistance for various gases differed not only in magnitude, but also in sign. When exposed to oxygen, the resistance of the n-nc-SiC films increased, and when exposed to carbon monoxide and methane, the resistance decreased. This is due to the different mechanism of action of oxidizing (O_2) and reducing (CO, CH_4) gases on the conduction channels of n-nc-SiC films with electron conductivity. The absolute values of the reaction also varied greatly. The greatest deviation in resistance was observed under the action of oxygen at atmospheric concentration (21%) ($S = 0.9$), and the relative changes in S were equal to 0.6 and 0.2 at a concentration of 10% and at a threshold concentration 3%, respectively. The decrease in the relative change in resistance S under the action of the threshold concentration (0.1%) of carbon monoxide was 0.38 and the decrease in the relative change in resistance under the action of the threshold concentration of methane (10%) was $S = 0.4$. The results of gas sensitivity measurements of p-nc-SiC films presented in Figure 4. On p-nc-SiC films with hole conductivity a lower sensitivity of the resistance to the action of gases was observed. So, when the p-nc-SiC film was exposed to oxygen at atmospheric concentration (21%), the change in relative resistance S was 0.28, and at a threshold oxygen concentration (3%) $S = 0.1$. And S was 0.16 at an oxygen concentration of 10%.

Under the action of reducing gases CO, CH_4 with limiting concentrations (CO -0.1%) and (CH_4-10%) the resistance increased with relative changes of 0.08 and 0.04, respectively. When the films were exposed to CO and CH_4 gases with concentrations of 0.04% and 5%, the changes in S were 0.03 and 0.005, respectively. Figure 5 shows the comparative characteristics of the sensitivity of n-nc-SiC and p-nc-SiC films to the limiting concentrations of O_2 (3%), CO (0.1%), and CH_4 (10%) gases. The comparative diagram shows that films with electronic conductivity have a higher sensitivity to the action of both oxidizing and reducing gases. We believe that this is due to differences in the mechanisms of conductivity in films with different structural features of self-doping.

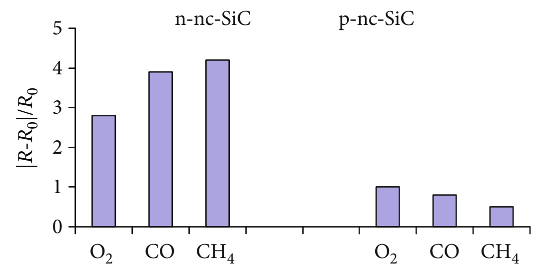


Figure 5: The comparative characteristics of the gas sensitivity of n-nc-SiC and p-nc-SiC films to the limiting concentrations of O_2 (3%), CO (0.1%), and CH_4 (10%).

We previously determined that in the films with an electronic type of conductivity there are several conduction channels that can respond differently to chemisorption of active gases [11]. The mechanisms of conductivity in p-nc-SiC films with hole conductivity have not yet been studied in detail, and, we believe, this will be a task in our future studies.

4. Conclusion

In this work, we demonstrated the ability of nanocrystalline SiC films with various types of conductivity to detect oxidative (O_2), reducing gases (CO, CH_4) with maximum permissible concentrations for human safety. It has been shown that n-nc-SiC films with electronic conductivity have a higher sensitivity than p-nc-SiC films with hole conductivity to the action of gases of threshold concentrations. For concentration O_2 (3%) gas sensitivity coefficient was 2.9 times greater; for CO (0.1%) - 4.8 times; for CH_4 (10%) - 10 times. Thus, the use of nc-SiC films with electronic conductivity is more preferable for the analysis of O_2, CO, CH_4 in a wide concentration range, including the maximum permissible ones.

Data Availability

The datasets supporting the conclusions of this article are included within the article.

Conflicts of Interest

The authors declare that they have no competing interests.

Authors' Contributions

A-S developed a method for producing nc-SiC films and proposed a concept for using nc-SiC films of different conductivity for sensors, and wrote the overall manuscript. D-L performed the experiments for obtaining films and performed measurements of the films gas sensivity. A-K performed measurements of the electrophysical characteristics of films and assisted in writing the manuscript. All authors read and approved the final manuscript.

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