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Ozone Sensitive Properties of Thin Films of Nanocrystalline Silicon Carbide

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In this paper, we investigated the ability of nanocrystalline SiC films to detect ozone in an air mixture under atmospheric pressure for ozone concentrations of 0.1 mg/m^3 (maximum allowable concentration) and 4.0 mg/m^3. The ozone sensitivity coefficient S (O_3) was estimated by the formula S (O_3) = (R_g – R_a)/R_a, where R_g and R_a are respectively the film resistances in the presence and absence of ozone in the air atmosphere. The volume flow rate of the ozone-air mixture was 2 l/min. The temperature dependence of the ozone sensitivity coefficient S (O_3) was studied in the temperature range 100-450 °C. It was found that the maximum values of S (O_3) + 0.71 and – 0.80 were observed at temperatures of 280 °C and 330 °C, respectively, for both concentrations of ozone. Moreover, S (O_3) had a positive sign for a temperature of 280 °C and a negative value for 330 °C. The different polarity of the change in the film resistance at given temperatures was due to the different ratio of redox reactions of ozone with atmospheric gases on the surface of nc-SiC films. Both temperatures can be used for detecting ozone with sensors on nc-SiC films, however, from the point of view of reducing energy consumption, operating temperature of 280 °C looks more preferable.

Keywords: Ozone sensors, Silicon carbide, Nanocrystalline film, Electrical resistance, Temperature ozone sensitivity.

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1. INTRODUCTION

In recent years, scientists of the leading countries of the world have been paying more and more attention to solving global environmental problems on the planet, including air pollution and global warming. One of the factors that negatively affect these processes is the presence of ozone in the lower atmospheric layers. This is the result of the widespread use of ozone in many important industrial processes, such as the purification of drinking water and soil, the disinfection of plant and animal products, tissue bleaching, the complete oxidation of gases in the production of various organic chemicals, the sterilization of medical supplies, etc. [1, 2]. Especially relevant in our time that ozone can be used to destroy the new coronavirus and disinfection [3]. Therefore, the used ozone technologies require the development and production of reliable instruments for measuring ozone concentration [2, 4]. While expensive stationary spectrometers can be used in laboratory studies, portable monitoring devices for measuring high, medium, and low (about maximum admissible concentration of ~ 0.1 mg/m^3) ozone concentrations are required for mass monitoring of ozone. The most common portable sensors available on the market are based on the principle of ozone absorption of ultraviolet radiation at a wavelength of 254 nm, the accuracy and reliability of which is constantly being improved [4, 5]. Portable semiconductor ozone sensors based on metal oxides are also proved to be quite good [4, 6-8]. But the ever-increasing demands on reliability, lifetime, miniaturization, lower power consumption and increased sensitivity of portable ozone measuring instruments stimulate the development of new-generation semiconductor sensors based on materials whose properties meet growing requirements.

In the present work, we investigated the ozone sensitivity properties of thin films of nanocrystalline silicon carbide (nc-SiC), which has higher reliability and resistance to external influences compared to metal oxides. The work continued the gas sensitivity researches of nc-SiC films, the results of which were published earlier [9, 10].

2. MATERIALS AND METHODS

Thin layers of nc-SiC films on leucosapphire substrates were prepared by the method of direct deposition of carbon and silicon ions with an energy of 100-120 eV at the substrate temperature of 1000 °C [11]. Films deposited under these conditions contained a mixture of nanocrystals of cubic and rhombohedral polytypes [12]. The sizes of nanocrystals varied in the range 5-50 nm [12]. The structural characteristics of the films obtained under the indicated conditions were studied in detail earlier [12]. Fig. 1 shows an electron microscope image of a typical portion of an nc-SiC film. The films possessed an electronic type of conductivity.

The film thickness was in the range 500-1000 nm. For resistive measurements, Au/Ni 5×3 mm^2 rectangular contact pads were applied at a distance of 2 mm between the contact boundaries. The resistance of the films at room temperature was in the range 130-150 MΩ. A resistive heater of the substrate with films could provide a working temperature of the sample up to 600 °C. A sample with a film was installed in a sealed cylindrical chamber with a volume of ~ 60 cm^3 through which an ozone-air mixture was pumped. To generate ozone, we used an original ozone-air mixture generator based on a barrier discharge using an inverse half-bridge circuit, which provided an output ozone concentration in the range from 0.1 mg/m^3 to 4.3 mg/m^3 with a volume flow rate of the ozone-air mixture of 2 l/min. The ozone-air generator was connected to the sample cham-

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ber using a polyvinyl chloride tube that did not interact with ozone. The ozone concentration in the air atmosphere in the sample area was measured using the Cyclone-5.31 instrument [13] with a measurement accuracy of 0.01 mg/m^3. The degree of ozone effect was determined by comparing the electrical conductivity of the films in air and in the air-ozone mixture at a certain ozone concentration at given film temperatures in the range of 100-500 °C. The block diagram of the measurement setup is shown in Fig. 2.

For measurement, two concentrations of ozone in air were used: 0.1 mg/m^3 (maximum allowable concentration of ozone) and 4.0 mg/m^3. The gas sensitivity coefficient was estimated by the formula $S\,(O_3) = (R_g - R_a)/R_a$, where R_g and R_a are the film resistances in the presence and absence of ozone in the air atmosphere, respectively.

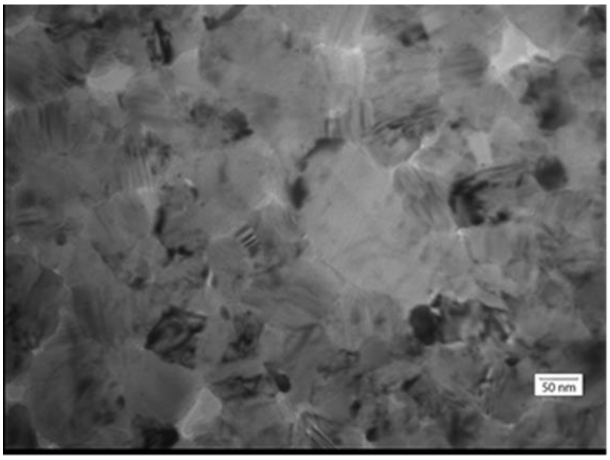


Fig. 1 – Transmission electron microscopy image of the nc-SiC film

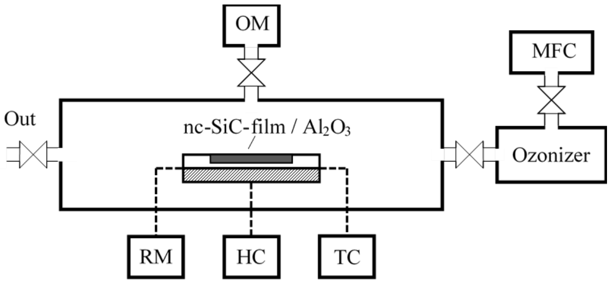


Fig. 2 – Block diagram of the nc-SiC film ozone sensitivity measurement setup: OM – ozone meter, MFC – mass flow control, RM – resistance meter, HC – heater control, TC – temperature control

3. RESULTS AND DISCUSSION

The sensitivity of nc-SiC films to ozone was measured over a wide temperature range of the films in order to determine the optimal operating temperature for gas detection. At the same time, we understood that temperature is an important parameter for both a semiconductor nc-SiC film and the state of ozone molecules. As the temperature of the film rises, its resistance decreases exponentially. As for ozone, the temperature determines the rate of its decomposition and the reaction constant with other substances. Fig. 3 shows the temperature dependence of the resistance of an nc-SiC film measured in air.

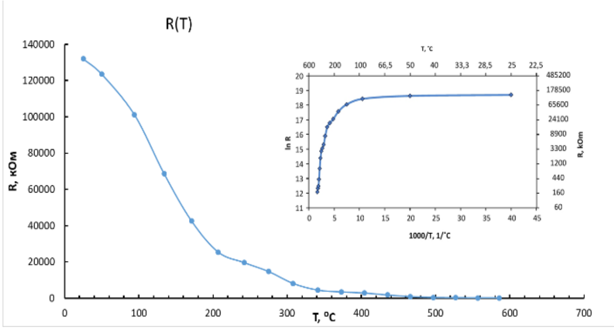


Fig. 3 – Dependence of the resistance of the nc-SiC film on the temperature measured in air. The same dependence in Arrhenius coordinates is shown in the inset

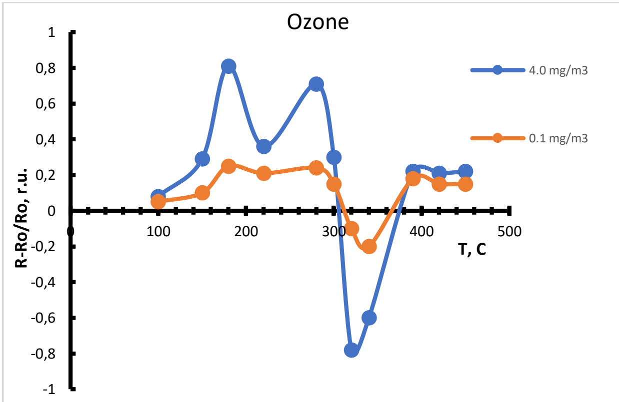


Fig. 4 – Gas sensing results of the nc-SiC film towards ozone concentration of 0.1 mg/m^3 and 4.0 mg/m^3 versus temperature

It can be seen from the above dependence that the resistance of the nc-SiC film in the temperature range 100-450 °C varies from ~ 130 MΩ to ~ 400 KΩ. Fig. 4 shows the dependence of the ozone sensitivity coefficient $S\,(O_3)$ of the nc-SiC film measured at a sample temperature in the range 100-450 °C.

It can be seen from the graphs that the temperature dependences of $S\,(O_3)$ of the films under the action of ozone have a complex form with maxima and minima. The $S\,(O_3)$ curves for two different O_3 concentrations have similar extrema on the curves, which indicates the identical physicochemical processes of interactions of ozone with the nc-SiC film and atmospheric gas. Therefore, we will consider the $S\,(O_3)$ curve for an ozone concentration of 4.0 mg/m^3, on which the features are more pronounced. On the curve, $S\,(O_3)$ maxima are observed in the temperature range 180, 290, 390 °C. The minima are also observed, which means that the film resistance decreases in the temperature range 220, 330-340 °C.

What physicochemical processes can cause the observed changes in the resistance of nc-SiC films with electronic conductivity depending on temperature? Ozone is a very strong oxidizing agent, and its direct effect on the conductivity of the film leads to a decrease in charge carriers and, consequently, to an increase in resistance. We presume that the increase in resistance in the region of 100 °C is associated with the direct effect of film oxidation by ozone. As a result, the electron concentration in the conductive layer decreases. At the same time, ozone molecules are metastable complexes and, when the temperature rises above 150 °C, they quickly decompose with the formation of molecular and atomic oxygen [14]

$$O_3 + O \rightarrow 2O_2.$$

The data on the lifetime of the ozone molecule at various temperatures in Table 1 say that a real direct measurement of ozone is possible up to temperatures in the region of 250 °C.

Table 1 – Half-life of ozone [14]

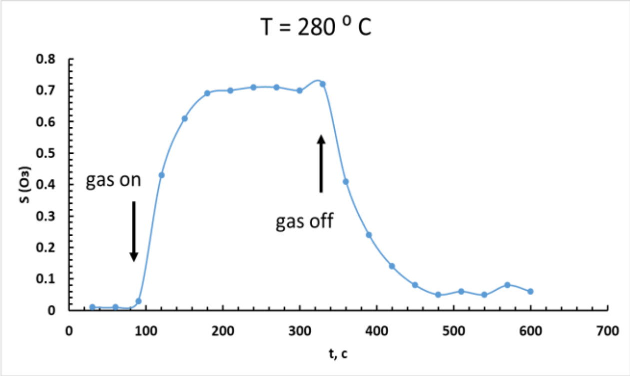
Temperature (°C)	Half-life
– 50	3 months
– 35	18 days
– 25	8 days
20	3 days
120	1.5 hours
250	1.5 seconds

Moreover, it should be noted that many substances, including silicon [15] and carbon [16], located on the surface of nc-SiC films, are catalysts for the decomposition of ozone at temperatures ranging from room temperature that can lead to an even greater reduction in ozone life compared to table data. We presume that the increase in resistance with a maximum in the region of 180 °C is due to the combined action of strong oxidizing agents – ozone and its decomposition product oxygen. The observed decrease in resistance after 180 °C with a minimum in the region of 220 °C can be associated with two processes: the number of formed oxygen molecules saturates, i.e. ozone completely decomposed, and the second process – atmospheric nitrogen began to oxidize with the formation of an active NO molecule, which exhibits reducing properties in the presence of a strong oxidizing agent [17].

The action of a reducing gas on the oxide layer of a film with electronic conductivity leads to a decrease in resistance due to an increase in the concentration of electrons in the surface layers of the film. A further rise in resistance to 280 °C may be due to an increase in the influx of fresh oxygen to the film surface due to increased desorption of molecular oxygen and nitrogen [18]. A large drop in resistance to a minimum in the region of 330-340 °C, in our opinion, is associated with an increase in the rate of formation of the active form of nitric oxide NO_x and its reducing effect on the oxide layer of the film. A further increase in temperature causes the formation of less active nitrogen oxides NO_2, N_2O_5 and others. And the total effect of the gases is balanced by oxidative (O_2, O) and reducing (NO_x) reactions on the film surface. Taking into account the results obtained and our ideas about the influence of temperature on the processes of interaction of ozone with an nc-SiC film, we chose 280 °C and 330 °C as the operating temperatures. Fig. 5 shows the dependences of the ozone sensitivity coefficient of the films at operating temperatures of 280 °C and 330 °C for an ozone concentration of 4 mg/m^3 in the air mixture.

It can be seen from the graphs that both temperatures are working and provide close maximum values of the ozone sensitivity coefficient, but of different polarity: for 280 °C S_{max} = 0.71, for 330 °C S_{max} = – 0.80. It should be noted that the established operating temperatures of nc-SiC films for ozone detection are close to the operating temperatures of ozone sensors on semiconductor films of nanocrystalline metal oxides set in the range of 250-400 °C [19].

Close temperatures indicate identical physicochemical processes of ozone interaction with thin layers of nanocrystalline semiconductors.



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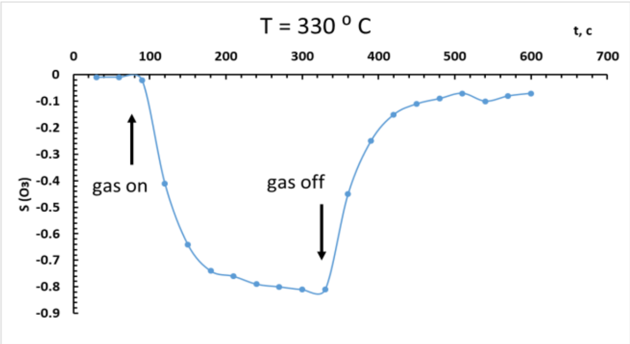

b

Fig. 5 – Ozone sensitivity of nc-SiC films at various operating temperatures: a) 280 °C, b) 330 °C. Ozone concentration in the air mixture is 4.0 mg/m^3

4. CONCLUSIONS

In this paper, we demonstrated the ability of nanocrystalline SiC films to detect ozone in an air mixture for an ozone concentration of 0.1 mg/m^3 (maximum allowable concentration) and 4.0 mg/m^3. The temperature dependence of the ozone sensitivity coefficient S (O_3) was studied in the temperature range 100-450 °C. It was found that the maximum values of S (O_3) + 0.71 and – 0.80 were observed at temperatures of 280 °C and 330 °C, respectively. Moreover, for a temperature of 280 °C S (O_3) had a positive sign and a negative value for a temperature of 330 °C. The different polarity of the change in the film resistance at given temperatures was due to the different ratio of redox reactions on the surface of nc-SiC films. Both temperatures can be used for detecting ozone with sensors on nc-SiC films, however, from the point of view of reducing energy consumption, 280 °C should be used as the operating temperature. Thus, highly reliable ozone sensors can be created on the basis of nc-SiC layers for operation in heavy conditions.

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Озоночутливі властивості тонких плівок нанокристалічного карбіду кремнію

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У роботі ми дослідили здатність нанокристалічних плівок SiC виявляти озон у атмосферній суміші під атмосферним тиском за концентраціями озону 0,1 мг/м^3 (максимально допустима концентрація) та 4,0 мг/м^3. Коефіцієнт чутливості до озону S (O_3) оцінювали за формулою S (O_3) = (R_g – R_a)/R_a, де R_g і R_a – плівкові опори при наявності та відсутності озону в атмосфері повітря відповідно. Об'ємна витрата озоно-повітряної суміші становила 2 л/хв. Вивчено температурну залежність коефіцієнта чутливості до озону S (O_3) в інтервалі температур 100-450 °C. Було встановлено, що максимальні значення S (O_3) + 0,71 та – 0,80 спостерігалися при температурах 280 °C та 330 °C відповідно для обох концентрацій озону. Крім того, встановлено, що S (O_3) мав позитивний знак при температурі 280 °C і негативне значення при 330 °C. Різна полярність зміни опору плівки при заданих температурах була обумовлена різним співвідношенням окислювально-відновлювальні реакції озону з атмосферними газами на поверхні плівок nc-SiC. Обидві температури можна використовувати для детектування озону за допомогою датчиків на плівках nc-SiC, однак, з точки зору зниження споживання енергії, температура 280 °C виглядає більш переважно.

Ключові слова: Сенсор озону, Карбід кремнію, Нанокристалічні плівки, Електричний опір, Температурна залежність.