Investigation of Titanium Oxide Film on Sapphire Substrate for Gas Sensor

Y V Klunnikova¹, S P Malyukov¹, A V Sayenko¹, M I Tolstunov²

¹ Institute of Nanotechnology, Electronics and Electronic Equipment Engineering, Southern Federal University, Taganrog 347928, Russia
² Institute of Chemistry, Southern Federal University, Rostov-on-Don 344006, Russia

Abstract. We study the surface structure of titanium oxide (TiO₂) film on sapphire substrate obtained by laser annealing (wavelength of 1064 nm). The film was studied by powder x-ray diffractometry. The obtained TiO₂ films can be used as a sensitive material for gas sensors.

1. Introduction
There is a wide range of gas sensor designs due to their importance in various fields of technology (mainly for prevention of fire and explosions, when working with explosive and poisonous gases, and to monitor the environmental situation in large cities).

The principal inorganic materials with gas sensitive properties used in gas sensors are metal oxides which have semiconductor properties and a bandgap width about 3-4 eV. The oxides of tin (SnO₂), tungsten (WO₃), zinc (ZnO), indium (In₂O₃), copper (Cu₂O, CuO), titanium (TiO₂), iron (Fe₂O₃) and their combinations are the most widely used among gas sensitive materials. One of the important features of gas sensors based on titanium oxide (TiO₂) is the possibility of using them at high temperatures due to the high chemical stability of the film [1-4].

2. Investigation of titanium oxide films on sapphire substrate
The film-forming solution of tetraethoxytitanium (Ti(OC₂H₅)₄) was deposited on a sapphire substrate with a thickness of 500 μm by centrifugation (centrifuge SPIN NXG-P1, rotor rotation speed of 2000-3000 rpm, application time of 30 s).

The use of sapphire substrate allows subsequent laser annealing of the gas sensitive material. Sapphire substrates cause high adhesion strength to the gas sensitive material and have a high melting point, high chemical and radiation resistance, high hardness and transparency, which leads to the quality and stability improvement of the gas sensitive material [5-8]. After film pre-drying in the oven at 100-120 °C for 15-20 minutes (the solvent and hydrolysis products are removed from the film) laser annealing is carried out using the radiation of a pulsed solid-state Nd:YAG laser with a wavelength of 1064 nm (temperature on film surface of 500-600 °C, laser beam scanning rate of 1-10 mm/s) needed to modify the crystalline and defective structure and improve the quality and stability of the gas sensitive material. The use of laser annealing makes it possible to shorten the technological time of obtaining a gas sensitive material in comparison with existing methods (for example, with annealing in a muffle furnace) [9-10].

The main benefits of gas sensor development on sapphire substrate with TiO₂ film are lowering of working temperature, high selectivity to detectable gases, and increased stability in time. Reaching these goals calls for employing modern tendencies of gas sensor construction as gas sensing materials.
Improving sensing characteristics and lowering working temperatures is possible in obtaining thin (50-300 nm) gas sensing films that have nanostructure with unique properties.

Figure 1 shows the technological route of titanium dioxide gas sensitive material formation.

Contents, structure and properties of solution and derivative films are determined by both chemical processes in the solution and physical-chemical processes, which occur in subsequent operation and depend on:
- chemical composition of source components in the solution;
- solution preparation order;
- solution aging time;
- methods and patterns of film infliction;
- methods of thermal treatment (drying and annealing).

**Figure 1.** The technological route of titanium dioxide gas sensitive material formation

The proposed method [10] assumes obtaining a thin film gas sensing material based on titanium dioxide (TiO$_2$) on a 20×20×0.5 mm sapphire substrate. A thin (100-250 nm) TiO$_2$ film with platinum electrodes (50-200 nm) is inflicted onto the top surface, while a film (300-400 nm) resistive Ni heater is formed on the bottom side.

The topology and 3D visualization of top and bottom surfaces of the sensitive material of gas sensor are shown in Figure 2.
The phase composition of the thin-film structure was investigated by powder X-ray diffractometry [11]. We used ARLXTRA, Thermo ARL diffractometer to perform X-ray phase analysis of obtained thin films. Qualitative analysis of the phase composition was performed using an open database (card index) COD (Crystallography Open Database) and Match program. The X-ray roentgenogram of the obtained film, reflexes of the standardized roentgenogram and Miller indices are shown in Figure 3. We have chosen the x-ray roentgenogram for titanium oxide with the structure of rutile (card No. 99-207-1134) for the reference. We can see from the obtained data that the reflexes of the standard sample coincide with the reflexes of the resulting film. Therefore, the material has a phase composition similar to the rutile modification of titanium oxide.

By varying the composition and structure, as well as the porosity and the thickness of the gas sensitive layer, we can control the sensitivity and selectivity of the sensor to various external components. The
surface morphology of TiO$_2$ film on sapphire substrate (scanning electron microscopy) is shown in figure 4. The average crystallite size is 15 – 25 nm. The dimensions of crystallites have a direct impact on the width of the forbidden zone of a titanium oxide thin film.

![Image](image.png)

**Figure 4.** The surface morphology of TiO$_2$ film on sapphire substrate

3. Investigation results
We have obtained the gas-sensitive material from a film-forming solution of tetraethoxytitanium on the sapphire substrate by laser annealing. We have determined that laser radiation allows to modify the crystalline and defective structure of materials, improve the quality of the oxide, reproducibility of the film parameters and their stability, as well as increase the production capacity of gas sensitive elements. The proposed method for the titanium oxide (TiO$_2$) film obtaining can be used to produce gas sensors for fire alarms and detecting concentrations of hazardous, toxic and harmful substances [2, 4, 10].

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