TiO₂ films can serve as oxygen sensors for controlling the nitrogen potential in the process of nitrocarburizing. In contrast to conventional semiconductor-base oxygen sensors that lose stability under extreme thermal and chemical conditions in nitriding and carburizing atmospheres, TiO₂ films obtained by the sol-gel method offer a promising alternative. In the present work TiO₂ films with a density of about 80% and a grain size of 30 – 50 nm are deposited by the sol-gel technology. Steel substrates and commercial substrates from Al₂O₃ aluminum oxide with platinum electrodes are coated and calcinated. In order to preserve the sensitive element of the sensor a special casing is constructed for operation under conditions very close to the atmosphere of nitrocarburizing. The sensitive element consists of an Al₂O₃ substrate with built-in Pt-electrodes, which is coated by a thin sol-gel TiO₂ film. The direct current in the furnace is measured for nitrocarburizing in various mixtures (N₂, O₂, H₂, and NH₃) at a temperature of 500 – 600°C. A linear dependence log [R] – log [pO₂], where R is the electrical resistivity, is obtained for the films in the studied range of partial pressure of oxygen pO₂ independently of the presence of NH₃ or H₂ in the atmosphere. The dependence log [R] – log [pO₂] for a nitriding furnace with a capacity of 90 liters is shown to be stable with 3% scattering per month.
factors depends on the composition of the gas mixture and the temperature and affects the number of free electrons that can be evaluated by measuring the conductivity. The functional design of the semiconductor gas analyzer is presented in Fig. 1.

METHODS OF STUDY

Titania films were obtained by the sol-gel technology using titanium tetraisopropoxide (TTIP, Ti[OCH(CH₃)₂]₄), 2-butanol (CH₃(COH)(C₂H₅)), acetic acid (HAc, CH₃COOH), acetylaceton (AcAc, CH₃COOH₂COCH₃), polyethylene glycol 400 (PEG), and distilled water. TTIP and 2-butanol were mixed in a beaker. AcAc was added as a chelating agent. The molar ratio of TTIP to AcAc was 1 : 1. Water and HAc were added to the sol for hydrolysis and stabilization. The initial components were mixed to obtain a transparent solution. The drying control additive (sol A) was PEG. The second sol (sol B) was prepared on the basis of sol A with the addition of organic binders. The process of sol preparation is described in detail in [5, 8].

We measured the conductivity of two types of specimen, i.e., TiO₂-SA and TiO₂-SA-IDS. To prepare specimens of group TiO₂-SA, TiO₂ was deposited onto polished sheets of alumina 2 × 20 mm² in size by dipping with constant pullout speed. After drying of the sol for several minutes the specimens were heat treated at 600°C for 10 min. The deposition of the coating and the heat treatment were repeated 5 – 6 times to form a layer about 1 μm thick. Electric contacts in the form of plates from steel AISI 304 were pressed into one of the surfaces.

Successive stages of the process of deposition of a TiO₂ coating are presented in Fig. 2. At first a specimen is coated with a thin film of sol by dipping, spinning, draining, or dropping. The quality and thickness of the film depend on the viscosity. Controlled transverse “linking” of the molecules of titanium alcoholate (TTIP) in the processes of deposition and drying yields a compact gel-like film. With growth in the heat treatment temperature such a film acquires the properties of a ceramic during pyrolysis, sintering, and crystallization.

Specimens of TiO₂-SA-IDS were fabricated on commercial Al₂O₃ substrates 3.5 × 3.5 mm in size [6] with Pt electrodes 1 μm high and 20 μm wide, which were arranged in an interdigital manner at a distance of 50 μm from each other, and a 30-Ω Pt-heater mounted in the bottom zone of the substrate (see Fig. 3a). The coating was deposited on the substrate by dropping the sol from a Pasteur pipette, after which it was dried in air for several minutes. The final treatment consisted of 10-min heating at 600°C. The deposition of the coating and the heat treatment were repeated five times. This produced a multilayer sol-gel TiO₂ coating with drying cracks, which is presented in Fig. 3b.