Gas sensitive properties of β-Ga_2O_3 thin films deposited and annealed at high temperature.

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Abstract: The gas-sensitive properties of thin films of β-Ga_2O_3 deposited by RF magnetron sputtering with heating of the substrate to 650 °C were studied. Some of the samples were subjected to additional high-temperature annealing at a temperature of 900 °C. As a result, for samples subjected to addi-tional annealing, the response when exposed to 1% H_2 increased by 5 once, sensitivity to hydro-gen-containing gases appeared. These samples are also characterized by good long-term stability compared to samples without high-temperature annealing. The improvement in gas-sensitive characteristics is explained by a decrease in oxygen vacancies and a decrease in current density by 4 orders of magnitude.

Introduction. Active development of resistive gas sensors based on β-Ga_2O_3 began in the 80-90s of the last century. Thanks to advances in the synthesis of semiconductor materials, resistive gas sensors based on β-Ga_2O_3 have been widely developed. Compared to many metal oxide semiconductors (SnO_2, In_2O_3, WO_3 and ZnO), the using of Ga_2O_3 as a sensitive layer makes it possible to create gas sensors that are stable at high operating temperatures and low oxygen concentrations, weakly affected by environmental humidity and characterized by high stability of characteristics. These advantages are key in the development of gas analytical systems for extreme operating conditions (elevated ambient temperatures, high concentrations of water vapor, changes in oxy-gen concentration over a wide range).

The magnetron sputtering method is widely used to form thin films of metal oxide semiconductors. RF magnetron sputtering has several advantages over other methods: low cost, ease of control, good adhesion, wide variety of materials and high sputtering speed. To improve the crystallinity of films obtained by this method, it is necessary to anneal at T > 800 °C. When annealing T < 800 °C, amorphous and a mixture of Ga_2O_3 phases are observed. The gas-sensitive properties of Ga_2O_3 thin films obtained by high-temperature magnetron sputtering have not yet been studied. In this work, β-Ga_2O_3 samples obtained by RF magnetron sputtering at a substrate temperature of 650 °C and subsequent high-temperature annealing of 900 °C were studied.

Materials and methods. β-Ga_2O_3 with a thickness of 300 nm was deposited by radio frequency magnetron sputtering of a (5N) oxide target in an argon plasma onto sapphire with a thickness of 0.43 mm. The substrate temperature during film deposition was 650 ºC (GO-650). The plate was additionally annealed at a temperature of 900 ºC (GO-650+900). Pt contacts of various topologies were formed on the surface of the films.

Measurements I-V characteristics and time dependences of the sample current when exposed to various gases were carried out with a Keithley 2636A source-meter in a sealed Nextron MPS-CHH microprobe station. As the target gases H_2, CO_2, CO, NO_2 and O_2 were chosen. The applied voltage to the sample electrodes was 5 V.

Results. Main Samples GO-650 and GO-650+900 have high resistance even at T < 300 °C, the current in the samples at 5 V is no more than pA. The current increases with in-creasing temperature from 300 to 600 °C, and from 400 to 750 °C for samples GO-650 and GO-650+900 by 3 orders of magnitude, respectively. In Fig. 1 shows the dependence of responses to fixed H_2 concentrations on temperature for GO-650 and GO-650+900 thin films. Exposure to reducing gases H_2, CH_4, NH_3 and CO results in a reversible increase in current through the samples. Response to reducing gases $S_g = I_g/I_{air}$. Exposure to O_2, NO_2 leads to a reversible decrease in the current through the GO-650 and GO-650+900 samples. Response to these gases $S_{ox} = I_{air}/I_{ox}$. The curves in Fig. 1 are characterized by the presence of maxima S_{MAX} at a certain temperature T_{MAX}. The response of GO-650 films when stored in a sealed bag after exposure to H_2 changes significantly. This results in a significant increase in response. Such a drift of gas-sensitive characteristics over time is typical for thin films of metal oxides and semiconductors. For samples GO-650+900 such a pattern is not observed, the response deviates from the average value in small areas (Fig. 2).

Despite the poor long-term stability of the GO-650 samples, all samples have good temporary stability over the course of a single experiment. Fig. 3 shows the time dependences of the current under 5-fold exposure to 1% of H_2. The selectivity of thin films was measured. The temperature dependences of the response for various gases for GO-650+900 thin films are presented in Fig 4. The concentration of CH_4, CO_2 and O_2 was 1 vol. %, the concentration of CO and NH_3 was 0.2 vol. %. GO-650 thin films do not respond well to other gases. GO-650+900 samples have a high response to H_2, NH_3 and CH_4.

Conclusion. For the first time, the gas-sensitive properties of β-Ga_2O_3 structures obtained by RF magnetron sputtering with heating of the substrate followed by high-temperature annealing were studied. Thin films of GO-650 had a response to hydrogen 3-4 times lower and had a long-term drift of characteristics in comparison with samples of GO-650+900. High-temperature annealing and the formation of interdigitated contacts, GO-650+900 thin films became more stable and the responses increased several times. As a result of annealing in air at T = 900 °C, the number of vacancies in GO-650+900 samples decreases, the current density decreases by 4 orders of magnitude, and stability increases.

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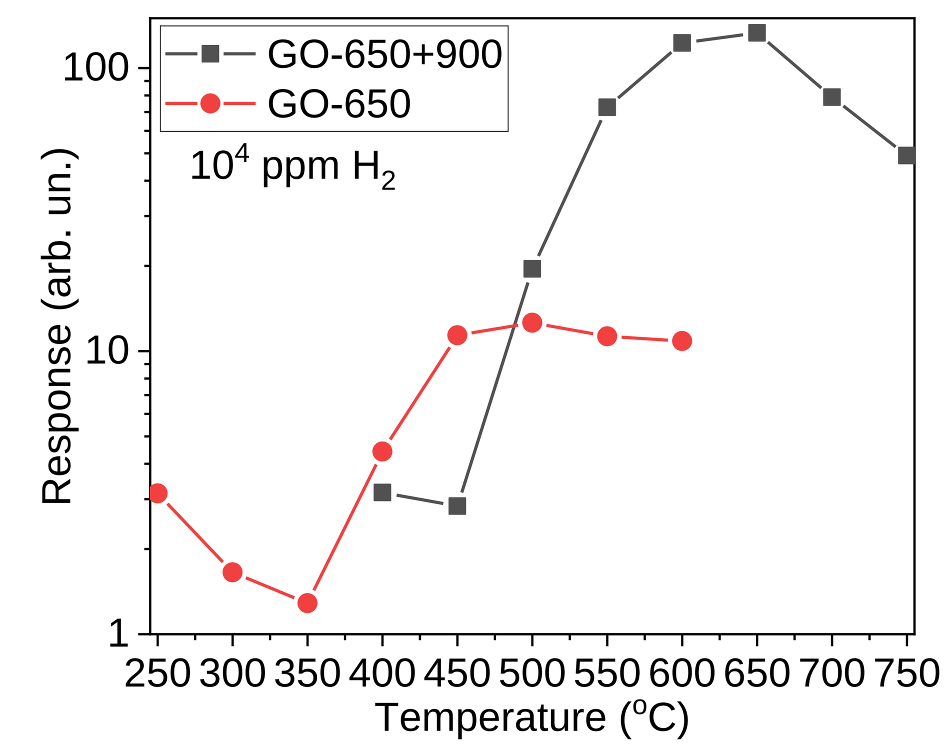

Fig. 1. Dependence of the response of GO-650 and GO-650+900 at 10^4 ppm H_2 on the operating temperature.

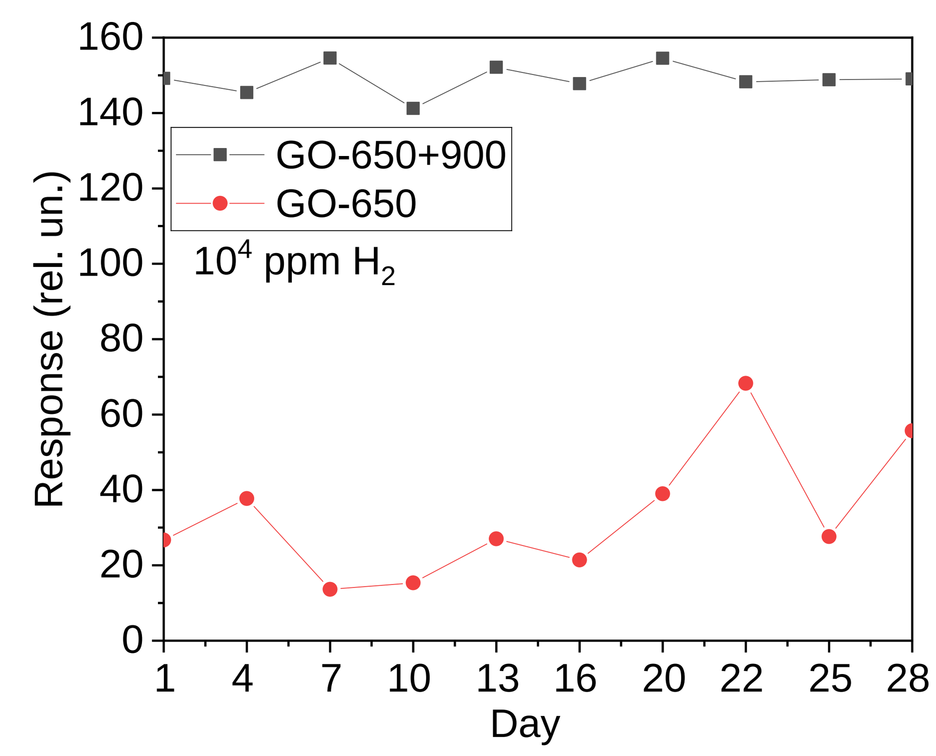

Fig. 2. Long-term stability under the exposure to a fixed hydrogen concentration.

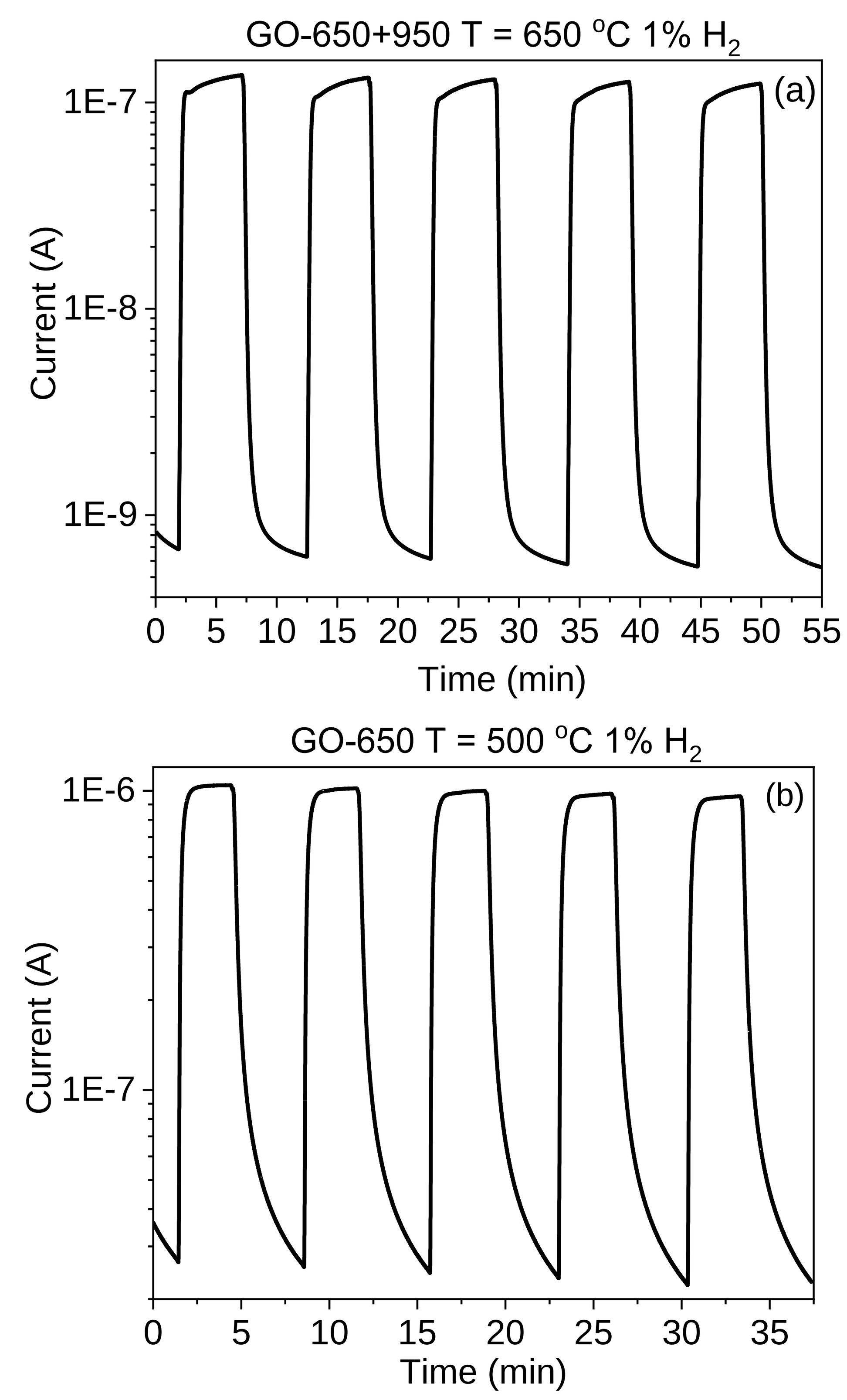

Fig. 3. Time dependences of the current through the samples under fivefold exposure to 1% of H_2.

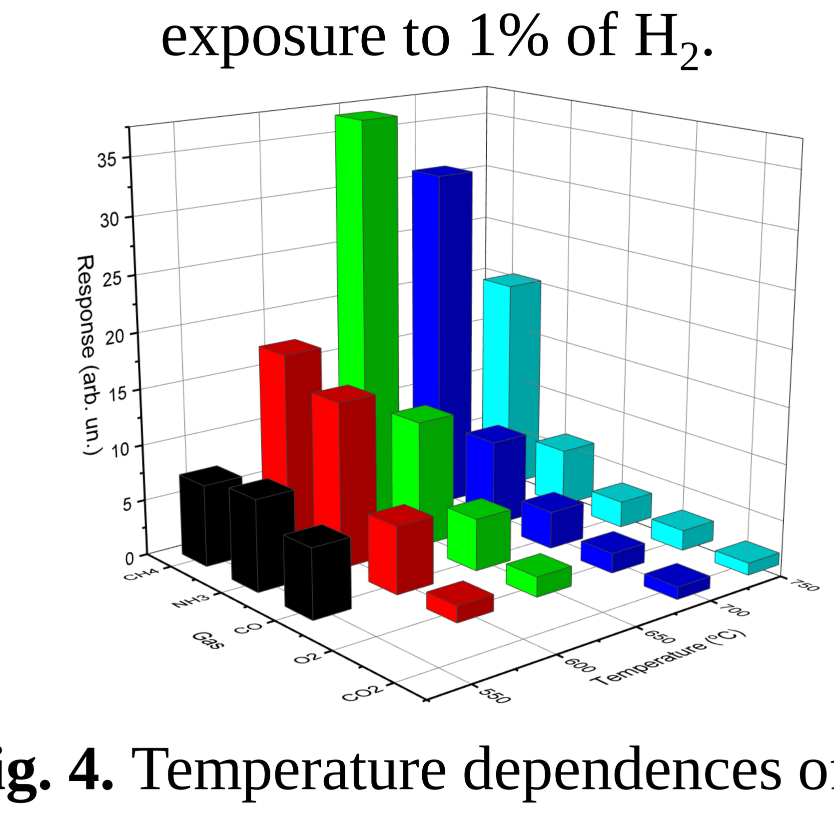

Fig. 4. Temperature dependences of the response to various gases and for thin films GO-650+900.