Investigation of gas-sensitive properties of cobalt oxide films

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Abstract. This paper presents a study of the gas-sensitive properties of cobalt oxide films formed by rapid thermal annealing on a sitall substrate. Cobalt films were formed on a pre-cleaned sitall substrate by vacuum thermal evaporation. The thickness of the deposited films was 470 nm. Rapid thermal annealing (RTA) was used to form cobalt oxide films. RTA of cobalt films was carried out at temperatures of 500°C, 600°C and 700°C. The resistivity of the films after RTA at 500°C, 600°C and 700°C was 3.6 × 10–2 Ohm·cm, 1.2 × 103 Ohm·cm and 5.8 × 103 Ohm·cm, respectively. The surface morphology of the obtained films was investigated by the AFM method. The gas sensitivity of cobalt oxide films was studied for gases like CO, NO2, CH4, C3H6O (vapors of acetone), C3H8O (vapors of isopropyl) and NH3·H2O (vapors of ammonium hydroxide 25%). The gas sensitivity was measured at 300°C. The results of gas sensitivity measurements showed significantly lower sensitivity to gases such as CO, NO2 and CH4. It was found that cobalt oxide films have good sensitivity to gases such as C3H6O, NH3·H2O and C3H8O. Sensitive elements based on cobalt oxide films are interesting as gas sensor elements for the detection of C3H6O, NH3·H2O and C3H8O.

1. Introduction

Currently, metal oxides are one of the most promising materials for use as a sensitive layer in gas sensors due to a number of advantages such as high gas sensitivity, selectivity, low cost, short response and recovery time, etc. Metal oxide gas sensors have all these advantages that make them promising for use in various fields of gas analysis [1-8]. Sensor elements based on metal oxides are capable of detecting a large number of toxic and explosive gases. The principle of operation of metal oxide gas sensors is based on a change in electrical resistance as a result of the adsorption of gas molecules on the surface of the sensitive layer [9-11].

One of the promising metal oxide gas sensors is a gas sensor based on cobalt oxide. This is due to the fact that cobalt oxide has a good response to a large number of industrial gases, selectivity and long-term use [1-2].

There are two main types of cobalt oxide, Co3O4 and CoO. Both cobalt oxides are p-type semiconductors [2]. There are various methods for the formation of cobalt oxide on a dielectric substrate [12-19]. One of the promising methods is rapid thermal annealing (RTA) by halogen lamps in air. The main advantages of rapid thermal annealing are high-speed processing of semiconductor wafers and various microstructures, relatively low energy consumption, low cost, cost of equipment and its operation, high heating rate, wide heating range, reproducibility and uniformity of processing, high productivity and small sizes of equipment for rapid thermal annealing.
The use of RTA allows us to form a cobalt oxide film from a cobalt metal film. The deposition of metal films on a substrate by vacuum thermal evaporation with subsequent annealing these films by RTA allows us to achieve good results in the formation of cobalt oxide films.

2. Experiment details
Cobalt films were formed on a pre-cleaned sitall substrate by vacuum thermal evaporation (UVN-72).

The thickness of cobalt films was 470 nm. Electrical properties were measured using the Hall effect measurement system HMS-3000 (Ecopia Corp., Korea). The resistance of the formed cobalt films was 2.43 Ohm, and their resistivity was $5.48 \times 10^{-5}$ Ohm·cm. The resistivity of the formed cobalt oxide films was investigated after rapid thermal annealing. The measurement results are presented in table 1.

| Cobalt oxide film | Resistance, Ohm | Resistivity, Ohm·cm |
|-------------------|-----------------|---------------------|
| RTA at 500°C      | $1.6 \times 10^3$ | $3.6 \times 10^2$    |
| RTA at 600°C      | $5.6 \times 10^3$ | $1.2 \times 10^3$    |
| RTA at 700°C      | $2.6 \times 10^3$ | $5.8 \times 10^3$    |

Table 1. The dependence of resistance and resistivity on rapid thermal annealing temperature.

The gas sensitivity of cobalt oxide films formed by RTA was studied for gases like CO, NO$_2$, CH$_4$, C$_3$H$_6$O (vapors of acetone), C$_3$H$_8$O (vapors of isopropyl) and NH$_3$·H$_2$O (vapors of ammonium hydroxide 25%). The gas sensitivity of thin cobalt oxide films was measured at a temperature of 300°C (for all the measurements). The gas sensitivity coefficient $S$ (%) was determined by the following equation:

$$ S = \left( \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} \right) \times 100 $$

where $R_{\text{gas}}$ – film resistance in the presence of gas, $R_{\text{air}}$ – film resistance in the air.
3. Results and discussion

The morphology of the surface of cobalt films without annealing and with RTA annealing was investigated by the AFM method using the Ntegra Vita probe nanolaboratory, figure 2. Figure 2 (a) shows the surface morphology of the film of metallic cobalt without annealing. The surface morphology of the films formed by rapid thermal annealing at 500°C, 600°C and 700°C is shown in figures 2 (b), (c) and (d), respectively. From the results, it can be seen that the use of RTA makes it possible to substantially change the surface of the film, to significantly increase its roughness and grain size in comparison with a film of metallic cobalt. It was found that the average surface roughness for a film without annealing is 3.5 nm, and for films after RTA at 500 °C, 600 °C, and 700 °C the average surface roughness is 28.9 nm, 25.9 nm, and 18.7 nm, respectively.

![Figure 2](image)

**Figure 2.** The morphology of the surface of the Co film without annealing (a) and after RTA at temperatures of 500°C (b), 600°C (c) and 700°C (d).

Figure 3 shows the response of cobalt oxide films formed by RTA at 500°C, 600°C and 700°C. From the results, it can be seen that the cobalt oxide films are most sensitive to C$_2$H$_5$O vapors compared to other gases. In addition, cobalt oxide films show good sensitivity to NH$_3$·H$_2$O
vapors (vapors of ammonium hydroxide 25%) and to C₃H₈O vapors. The results obtained are in good agreement with published data [1].

![Graph showing gas response vs. annealing temperature](image)

**Figure 3.** The dependence of the response of cobalt oxide films on the annealing temperature and various gases.

4. Conclusion
In summary, it was found that cobalt oxide films, which were formed by rapid thermal annealing, show significantly lower sensitivity to gases such as CO, NO₂ and CH₄. The cobalt oxide films formed by RTA at 500°C show the highest gas response, and only response to CO was slightly lower than the response of films formed by RTA at 600°C and 700°C.

Based on these results, it can be concluded that cobalt oxide films formed by RTA have good sensitivity. Cobalt oxide films are interesting as gas sensor elements for the detection of C₃H₆O, NH₃·H₂O and C₃H₈O.

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