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Abstract

Annealed Gallium-Doped Zinc Oxide (ZnO:Ga) Thin Films for Sub-ppm NO_2 Sensing †

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Abstract: In this work, gallium-doped zinc oxide was deposited with a Radio Frequency Magnetron sputtering method on test platforms. The NO_2 sensing properties of the resulting devices were studied. The sensing properties of ZnO:Ga thin films were successfully stabilized through annealing in dry air, and then improved by either a thinning of the layer or an increase in the roughness of the substrate. The sensing response with an Rgas/Rair of 15 for 100 ppb of NO_2 under 50% humidity was obtained, with a response time below 10 min.

Keywords: NO_2 sensing; thin films; RF sputtering; GZO; annealing

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1. Introduction

Resistive gas sensors based on Metal Oxide Semiconductors (MOSs) are a promising solution for cheap, reliable, and highly sensitive gas sensors. Among them, ZnO has interesting characteristics for such application thanks to its large band gap and its high chemical stability. RF magnetron sputtering is a widely used process in the Incorporated Circuit industry, well fit for mass production, and allows for control over the microstructure of the thin films deposited. The present work shows high NO_2 sensing properties of ZnO:Ga thin films integrated on test platforms, as well as an improvement of the sensitive layers through structure modifications.

2. Materials and Methods

Ga-doped ZnO thin films (4% in cation sites) with thicknesses of 12, 25, 50, and 100 nm were deposited at room temperature on simplified test platforms by RF magnetron sputtering with an Ar plasma. The as-deposited ZnO:Ga thin films were first characterized in terms of structure, grain size, and total thickness by Grazing Incidence X-ray (GIXRD), AFM, SEM, TEM, and profilometry. The resulting devices were annealed in synthetic air for 4 h at 500 °C, 600 °C, and 700 °C, respectively. The influence of layer thickness and annealing temperature on the gas sensing properties was studied.

The test platforms used for these experiments were produced through classic lithography in a clean room. A 600 nm layer of SiO_2 was thermally grown on a silicon wafer for electric isolation. Pt electrodes for electric contact were deposited on top. The thermal SiO_2 was very smooth. To increase the roughness of the platform, an alternative platform was designed with the addition of a layer of 300 nm of SiO_2 obtained with PECVD, providing a much rougher surface.

The sensing properties of the produced devices were examined with a dilution gas test bench in synthetic air at 250 °C with a humidity level of 50%. This temperature was previously found to be the optimum temperature for NO_2 sensing for the studied ZnO:Ga material [1,2]. The devices were first electrically stabilized for 10 h in these conditions before the injection of a set of 6 pulses of NO_2 at 100 ppb (2 h in NO_2, 2 h in synthetic air). The electric resistance was measured at the beginning and at the end of each injection, providing a measurement of the electrical response to gas as Rgas/Rair. In the meantime, the response time was calculated as the time needed for a device to reach 90% of its final response value.

3. Discussion

The structural and microstructural analysis of the thin films show columnar growth, as shown in Figure 1, and has a preferential orientation along the (002) plane. A recrystallization phenomenon was observed for the samples annealed above 600 °C, which might explain the increase in the sensing properties but not why the devices annealed at 700 °C did not show as-good results.

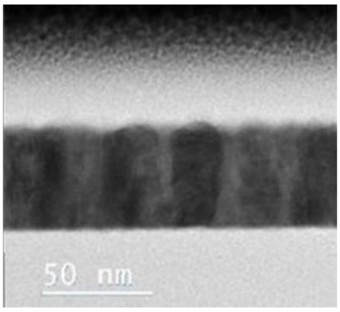

Figure 1. STEM capture of a 50 nm thick ZnO:Ga thin film deposited by RF sputtering on a Si substrate covered by smooth thermal SiO_2.

The experiments on the gas dilution test bench showed that the annealing stabilized the sensing properties of the devices. The devices annealed at 600 °C showed a sensitivity improvement, with an Rgas/Rair response of nine, whereas devices annealed at other temperatures or not annealed at all were measured with a response between 2.5 and 3. The response time, however, was never impacted and was recorded as roughly 80 min for all devices.

The NO_2 sensing properties of four test substrates coated with ZnO:Ga with a thickness of 12, 25, 50, and 100 nm, each annealed at 600 °C for 4 h, were compared. Both the response and the response time were greatly improved for thinner films. Films of 12 nm and 25 nm showed a response value of Rgas/Rair equal to 15, and their response time was measured at around 10 min.

The NO_2 sensing properties of a 50 nm thin film of ZnO:Ga deposited on a rough test platform were studied after annealing at 600 °C. Compared to a similar device obtained on a smooth test platform, its electric resistivity and gas response were identical, but its response time was five times shorter.

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