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Abstract

Cu Ferrospinel Thin Films for Sub-ppm NO_2 Sensing †

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Abstract: The paper reports the synthesis and characterization of a copper ferrospinel thin layer. The thin layer (25 nm) was synthesized by RF sputtering of a pure $CuFe_2O_4$ target. The material structure and microstructure were characterized using X-ray diffraction and transmission electron microscopy. Simplified test substrates were microfabricated with interdigitated Pt electrodes to investigate electrical properties in a controlled atmosphere. The sensitive layer was stabilized by annealing at 550 °C under air. NO_2 responses at a low concentration (<1 ppm) and 50% relative humidity were measured between 100 and 500 °C. The optimal response was obtained at 250 °C.

Keywords: ferrospinel; semiconducting oxide; thin layer; RF sputtering; gas sensors; NO_2 sensing

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1. Introduction

Nitrogen dioxide (NO_2) is a toxic gas produced by industrial and domestic use, in particular by internal combustion engines used in vehicles. NO_2 is dangerous for human health, with a threshold limit value (TLV) of 0.5 ppm. Many sensing technologies are being developed; among them, metal oxide semiconductor gas sensors are the most widely used for NO_2 detection [1]. Copper ferrospinel is an interesting candidate thanks to its electrical and reactional properties. Indeed, $CuFe_2O_4$ is used as a catalyst in particular for the removal of NOx emitted from diesel exhaust [2].

2. Materials and Methods

Twenty-five nm thin layers were elaborated by RF sputtering at 2 Pa under argon on various substrates and annealed at 550 °C under air. The structural properties were studied by X-ray diffraction (XRD) in grazing incidence (α = 1°), transmission electron microscopy (TEM) and Raman spectroscopy. Microstructure analysis was performed using scanning electron microscopy (SEM). The gas-sensing performance was studied using simplified test substrates with Pt interdigitated electrodes (Figure 1) to measure the resistance variation under clean and polluted air. The test substrate was introduced on a heating chuck in a small chamber in which the atmosphere was well controlled.

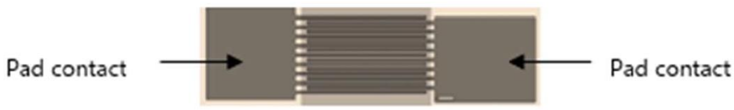

Figure 1. Electrical microdevice design used for sensing performance evaluation with 16 Pt electrodes of 100 μm width. The distance between each electrode is 50 μm.

3. Discussion

XRD analysis on a thin layer deposited on a substrate without electrodes (Figure 2) reveals a quadratic $CuFe_2O_4$ pattern (JCPDS card 034-0425) at room temperature. No additional phases were detected. Transmission Electronic Microscopy confirms the XRD results.

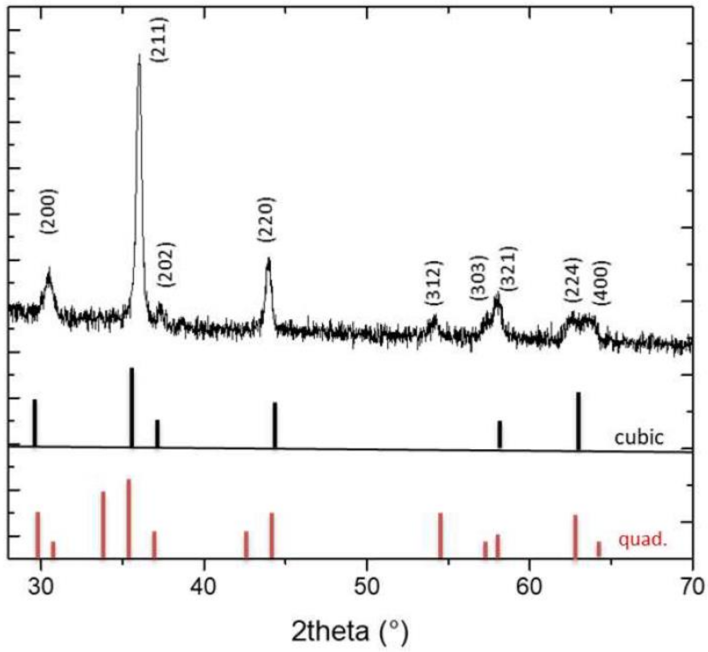

Figure 2. XRD pattern of copper ferrospinel thin film.

Structural properties were also investigated under temperature since the sensing performances are measured at high temperatures. The literature shows structural distortions when $CuFe_2O_4$ is heated, due to a cooperative Jahn–Teller effect [3]. High temperature XRD analysis was performed and revealed that elaborated ferrospinel thin film turns into a cubic structure above 350 °C.

The resistance behavior under air and NO_2 at 250 ppb was investigated at different temperatures in isothermal mode. As the NO_2 is an oxidizing gas, the resistance increased, meaning that the material is an n-type semiconductor. The R_{NO_2}/R_{air} ratio was calculated at each temperature and is represented in Figure 3. The best response was obtained at 250 °C and decreased above that temperature (Figure 3). Furthermore, above 450 °C the response was reversed; the copper ferrospinel film behaved like a p-type semiconductor. Gas-sensing performances seem to depend on structural properties, since the structural transition starts at 350 °C.

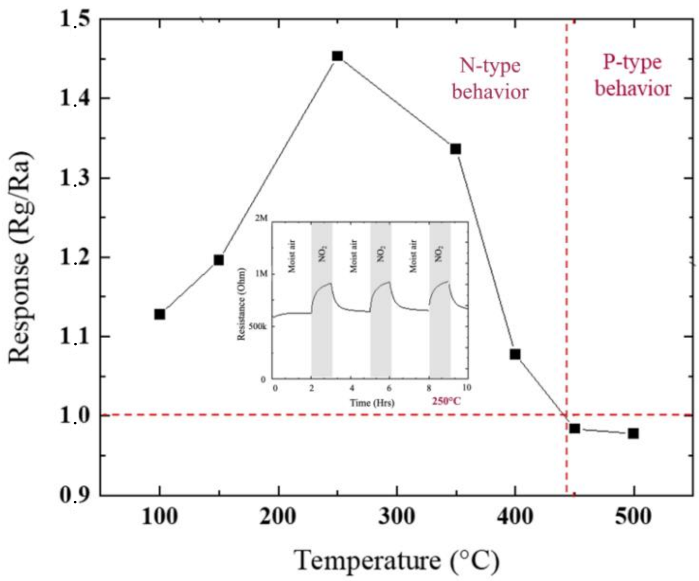

Figure 3. NO_2-sensing performance.

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