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Abstract

Cu Ferros spinel Thin Films for Sub-ppm NO₂ Sensing[†]

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Abstract: The paper reports the synthesis and characterization of a copper ferros spinel thin layer. The thin layer (25 nm) was synthesized by RF sputtering of a pure CuFe₂O₄ 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. NO₂ 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: ferros spinel; semiconducting oxide; thin layer; RF sputtering; gas sensors; NO₂ sensing

1. Introduction

Nitrogen dioxide (NO₂) is a toxic gas produced by industrial and domestic use, in particular by internal combustion engines used in vehicles. NO₂ 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 NO₂ detection [1]. Copper ferros spinel is an interesting candidate thanks to its electrical and reactional properties. Indeed, CuFe₂O₄ is used as a catalyst in particular for the removal of NO_x 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 ($\alpha = 1^\circ$), 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 CuFe₂O₄ pattern (JCPDS card 034-0425) at room temperature. No additional phases were detected. Transmission Electronic Microscopy confirms the XRD results.



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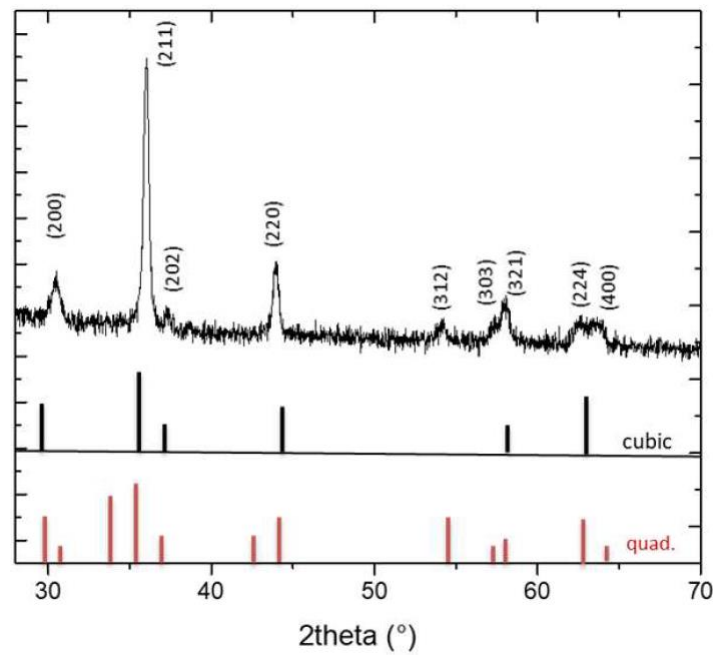


Figure 2. XRD pattern of copper ferros spinel thin film.

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 ferros spinel thin film turns into a cubic structure above $350\text{ }^\circ\text{C}$.

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 $R_{\text{NO}_2}/R_{\text{air}}$ ratio was calculated at each temperature and is represented in Figure 3. The best response was obtained at $250\text{ }^\circ\text{C}$ and decreased above that temperature (Figure 3). Furthermore, above $450\text{ }^\circ\text{C}$ the response was reversed; the copper ferros spinel film behaved like a p-type semiconductor. Gas-sensing performances seem to depend on structural properties, since the structural transition starts at $350\text{ }^\circ\text{C}$.

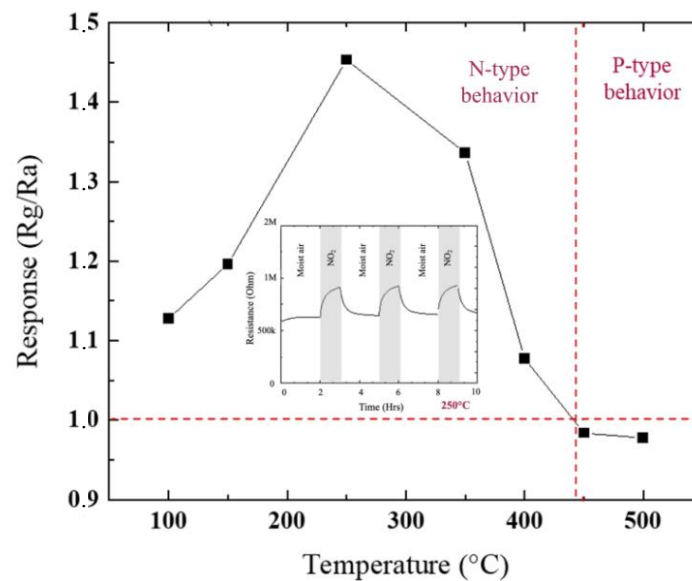


Figure 3. NO_2 -sensing performance.

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