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p-Type copper aluminum oxide thin films for gas-sensing applications

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ABSTRACT

In this study we deposited new, ternary thin films of copper aluminum oxide with *p*-type and *n*-type behavior using RF magnetron sputtering for use as chemical gas sensors. *p*-Type materials are known to be good catalysts and can be combined with the well-known *n*-type materials for chemiresistive sensors application. Copper aluminum oxide in the delafossite phase $CuAlO_2$ is a ternary oxide that has generated interest as a transparent *p*-type conducting material, while in the spinel phase $CuAl_2O_4$ is known to be *n*-type. We demonstrated that thin films of copper aluminum oxide with the proper resistance can be successfully applied as *p*- and *n*-type resistive gas sensors for ozone detection. We have studied the sputtering deposition conditions from a $CuAlO_2$ sintered target by changing the substrate temperature in inert Ar atmosphere. In addition, post-deposition annealing in O_2 atmospheres was also tested. XRD, SEM and Raman investigations were used to characterize the thin films. Selected films with mixed phases of $CuAlO_2$, $CuAl_2O_4$ and CuO were tested for gas sensing as resistive chemical sensors, showing promising results with ozone, acetone and ethanol.

1. Introduction

Over the past 10 years research on chemical gas sensors has been focused on the use of *p*-type metal oxides. These materials exhibit a wide range of catalytic activities and sensing capabilities compared to the more conventional *n*-type gas sensors, like ZnO [1] or SnO_2 [2], and can be used for the fabrication of gas sensors that exhibit various novel functionalities. Research on chemiresistors fabricated using binary *p*-type semiconductors such as NiO, CuO, Cr_2O_3 [3–6] has been widely reported in recent years, in contrast to the *p*-type ternary compounds, which have received little attention until now.

A ternary compound investigated mainly for its application as a transparent conducting oxide is $CuAlO_2$ in the delafossite phase: it has a direct band gap of 3.5 eV and *p*-type conductivity along with a good optical transparency (transmittance close to 80% in the visible range) [7]. It can be obtained by many techniques, such as laser ablation [8], pulsed-laser deposition [9], sputtering [10–12] and the sol–gel process [13].

The application of copper aluminum oxide to the field of chemical sensing has received very little attention, with only one report in the literature about a rhombohedral phase of $CuAlO_2$, where the authors reported a selective and reversible response to ozone gas at room temperature, but at a relatively high concentration of 0.1% [14].

The quasi-binary phase diagram of the system CuO/Al_2O_3 [15] points out that delafossite $CuAlO_2$ should be formed in reaction of spinel $CuAl_2O_4$ and CuO phases above 1003 °C. Since the $CuAlO_2$ is a metastable phase, its conversion to $CuAl_2O_4$ and CuO below the phase boundary at 1003 °C (at 0.21 atm O_2) could not be completely avoided [9,15]. From the aspect of sensor properties, the presence of both $CuAl_2O_4$ and CuO phases, besides the $CuAlO_2$, in tested samples could be important: spinel $CuAl_2O_4$ is an *n*-type material and insulator [16], and the CuO is an interesting *p*-type material for gas sensing [4,5]. The use of sol–gel-prepared, spinel, $CuAl_2O_4$ and Sr-doped $CuAl_2O_4$ pellets has been reported for the sensing of VOCs [17].

Even if the use of the delafossite phase could be of interest for gas sensing applications, engineering constraints for a resistive chemical gas sensor are posed by the very high conductance observed in the pure delafossite phase. The optimum resistance for a chemiresistive gas sensor at the working temperature between 200 and 500 °C is in the range 10 kΩ–1 GΩ. In this respect, mixture of phases, can unfavorably/beneficially affect the electrical and functional properties of the material [18,19].

In this work we prepared Cu—Al—O films by RF magnetron sputtering from a $CuAlO_2$ sintered target and studied the influence of deposition temperature and the subsequent annealing treatments

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on the structural, morphological and gas-sensing properties. The transparent thin films were analyzed by UV–vis, SEM, XRD, micro Raman and four-point measurements to gain an insight into the correlation between the structure and the resistivity. Mixture of CuO, $CuAlO_2$ and $CuAl_2O_4$ was observed in the sensing films.

Selected thin films with a suitable resistivity were deposited on an appropriate transducer and tested with respect to pollutant gases like ozone and CO, and interfering ones like acetone and ethanol. By properly selecting the deposition protocol we were able to obtain brand new *p*-type and *n*-type thin films with the correct range of resistance, to be applied as innovative gas sensors for ozone detection.

2. Experimental

2.1. Target and thin-film preparation

For the fabrication of the $CuAlO_2$ target (CAO), the $CuAlO_2$ powder was prepared using a solid-state synthesis at 1100 °C in argon from a mixture of the nano-boehmite $AlOOH{\cdot}xH_2O$ (99.99%, Sky Spring Nanomaterials, Houston, TX) and Cu_2O (99.9%, Alfa Aesar, Karlsruhe, Germany) reagents.

The as-calcined powder was uniaxially pressed at 100 MPa, subsequently cold isostatically pressed, and then sintered at 1100 °C in air, followed by a holding time of 2 h, with heating and cooling rates of 5 °C/min. Further processing details can be found in [20]. The CAO ceramic target of 48 mm in diameter had an 87% relative density. The structural and microstructural analyses of a ceramic sample sintered at the same time (see Fig. 1) revealed that the sample was a single-phase delafossite and had a dense microstructure with a uniform distribution of the porosity within the delafossite matrix.

The thin films were deposited by RF magnetron sputtering on various substrates, starting from a ternary oxide target ($CuAlO_2$) with a 2-inch diameter, described above. The substrates were carefully washed in acetone, dried with synthetic air and kept in a deposition chamber at the desired temperature and a vacuum of 0.1 Pa for 30 min prior to the deposition. The films were deposited on glass slides for the UV–vis analysis, on 10 mm × 10 mm alumina substrates for the XRD analysis, and on 2 mm × 2 mm alumina substrates for the SEM and electrical characterization, gas sensing and Raman measurements. Interdigitated Pt contacts and a backside Pt heater were deposited by sputtering after the deposition of the sensing layers.

The deposition was conducted at room temperature (RT), 200 °C and 400 °C, in an inert (Ar) atmosphere, under a constant RF power of 100 W, a total gas pressure of 1 Pa and a deposition time of 60 min. The film thickness was approximately 200 nm. Next, the annealing treatment at 1000 °C in O_2 was applied. The thermal treatment was made in a ceramic tubular furnace. Prior to the annealing, the tube was evacuated to 400 Pa, and then as the gas was fluxed into the tube the pressure was increased to 2×10^3 Pa. The thermal treatments were performed according to the following procedure: from ambient temperature to 110 °C at 1°/min, followed by a plateau at 1000 °C for 1 h, and then back to room temperature.

Table 1
Preparation conditions of samples deposited by RF sputtering on alumina substrates in an Ar atmosphere at 100 W, with a deposition time of 60′ and a pressure of 1 Pa for the sensing tests. Samples were analyzed by XRD, micro-Raman and SEM.

Sample code	Deposition conditions	Substrate temperature
A	100 W, 60′, 10×10^{-3} mbar	RT
B	100 W, 60′, 10×10^{-3} mbar	200 °C
C	100 W, 60′, 10×10^{-3} mbar	400 °C
D	100 W, 60′, 10×10^{-3} mbar	200 °C + annealing 1000 °C in O_2

The as deposited thin films were transparent (90% transmittance) with a slightly brown color.

The effect of post-deposition annealing in O_2 at 1000 °C on the thin film conductance was investigated: the only film with a readable resistance after annealing was the one prepared at 200 °C. It showed a resistance in the range from 10^{10} Ω to 10^9 Ω, at working temperatures between 300 °C and 500 °C. Increase in the resistances of the thin film is ascribable to the increase of spinel phase amount due to annealing at high temperature, as will be shown in Section 3.1. Thermal annealing decreases the conductivity of samples deposited at other temperatures below 10^{-12} S, the picoammeter detection limit with standard coaxial cables, even when operated at high working temperature.

Table 1 lists the thin films selected for gas testing, along with the deposition conditions. All the films were deposited on alumina substrates.

Before the sensing measurements, controlled aging was performed on the sensing films listed in Table 1 by keeping them at 500 °C in ambient air for 2 weeks, using the backside heater. This procedure is commonly used to avoid any resistance drift during the sensor testing, due to a variation in the grain size or the phase in the sensor film induced by the working temperature. To simulate the aging effect observed on the sensors, the thin films deposited on the 10 mm × 10 mm substrate for the XRD were purposely annealed at 500 °C in humid air for 36 h. SEM, XRD and Raman measurements were performed on the thin films before and after the aging to obtain a better insight into the morphological and the compositional changes, and simultaneously connect them to the sensing properties.

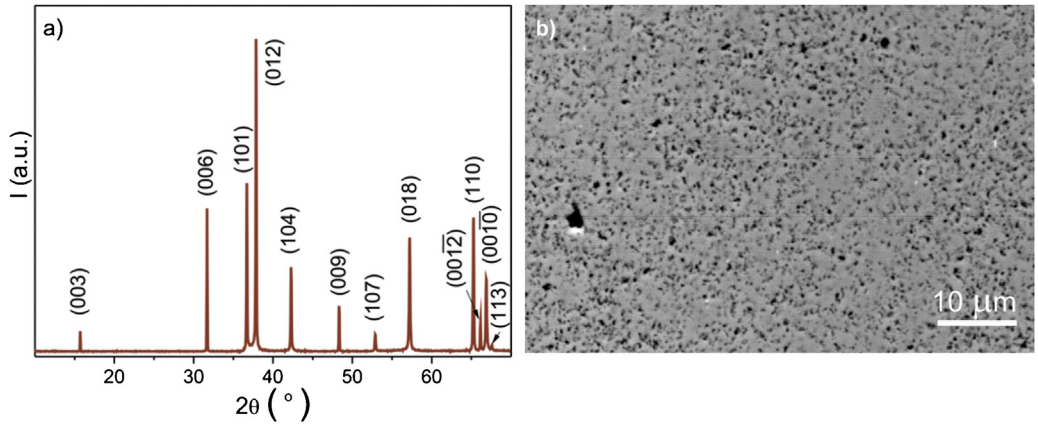

Fig. 1. XRD pattern (a) and SEM micrograph (b) of the sintered $CuAlO_2$ sample.