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# Tailoring and characterization of porous hierarchical nanostructured p type thin film of Cu-Al-Oxide for the detection of pollutant gases

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## Abstract

An experimental approach for the detection of harmful gases in presence of humidity has been applied for gas sensors based on p-type Cu-Al-Oxide thin films. The impact of deposition conditions on the surface, morphology and sensing properties of the semiconducting oxide thin films are investigated. Cu-Al-Oxide thin film with higher resistance can be applied as p-type resistive gas sensor for the detection of pollutant gases. Thin films were characterized by X-Ray Diffraction, scanning electron microscope, and Raman spectroscopy. We observed that inert atmosphere and deposition temperature play the important role to affect the structural and surface morphology of Cu-Al-Oxide thin films. Sensitivity of nanostructured thin films towards reducing and oxidizing gas are studied as a function of gas concentration and operating temperature.

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*Keywords:* Delafossite; Cu-Al-Oxide; p-type transparent conducting oxides; gas sensor; RF sputtering;

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## 1. Introduction

In past one decade, thin film, nanobelts and nanowire based on p-type transparent conducting oxide materials have

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attracted significant research interest in the field of chemical gas sensing and nano electronic devices.

Semiconductor metal oxides (SMOX) show a different activities and sensing abilities appeared differently in relation to more common n-type gas sensors, like $SnO_2$, $In_2O_3$, ZnO [1, 2] and might be used for the production of gas sensors that show diverse novel functionalities. In recent few years p-type semiconductors oxides like NiO, CuO, and $Cr_2O_3$ [3] have been reported for chemical gas sensing while the p-type ternary metal oxides have been tested at very small level. There are lots of ternary oxide materials ($CuMO_2$, M=Al, Cr, Y) which can be utilized for gas sensing application. In 1997 Kawazoe introduced a transparent conducting oxide (TCO) $CuAlO_2$ thin film with delafossite phase that showed p-type conductivity [4]. The use of copper delafossite thin films for gas sensing is still little exploited, with only two reports on a rhombohedral phase of $CuAlO_2$, where the researchers reported a specific and reversible reaction to ozone gas at room temperature [5, 6].

The defect chemistry such as vacancies, interstitials play a vital role in delivering the p-type conductivity for $CuAlO_2$ thin films [7, 8]. A metal deficiency (or abundance oxygen) should prompt the defects inside the materials, and this deviation from the stoichiometric arrangement of the components can happen by controlling the preparation conditions of the material. The vicinity of oxygen throughout the deposition process and a post deposition oxygen-annealing treatment of the films can enhance the p-type conductivity of these materials. Hamada et al. [8] pointed out that oxygen interstitial induces deep levels while copper vacancy induces no deep levels in the band gap. In present letter we deposited Cu-Al-Oxide thin films by RF magnetron sputtering from 2” $CuAlO_2$ target in inert Ar atmosphere and studied the influence of the deposition temperature on the structural, morphological and gas-sensing properties. The thin films with a suitable resistivity were tested with respect to pollutant gases like acetone, ethanol, CO, and ozone.

## 2. Experimental

The 2” $CuAlO_2$ target (CAO) was tailored using a solid-state synthesis at 1100 °C in argon from a mixture of the nanoboehmite AlOOH.xH2O (99.99%, Sky Spring Nanomaterials, Houston, Texas) and $Cu_2O$ (99.9%, Alfa Aesar, Karlsruhe, Germany) reagents[9]. Prior to deposition, target was sputtered for 10min to avoid the contamination. Thin films were deposited by RF magnetron sputtering on silicon and (2mm x 2mm) alumina substrates, starting from a ternary oxide target ($CuAlO_2$) with a 2” diameter. 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 10 mm × 10 mm alumina substrates for the XRD analysis and on 2 mm × 2 mm alumina substrates for gas sensing, SEM and electrical characterization. Interdigitated Pt contacts and a backside Pt heater were deposited by sputtering after the deposition of the sensing layers. The deposition was conducted at 300°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.

Cu-Al-Oxide thin films were fabricated on the $Al_2O_3$ substrates and equipped with interdigitated Pt contacts and backside Pt heaters were used. The volt–amperometric technique at constant bias (1V direct-current) was applied to the sensing film and the electrical current was measured by a picoammeter Keithley model 486. The system was used to dynamically reproduce environmental conditions in a controlled and repeatable way is based on volumetric mixing through mass flow controllers and certified bottles. The ozonized air was produced by a thermo-stated UV lamp discharge (ANSYCO). All characterizations were performed keeping the ambient at a temperature of 20°C, at atmospheric pressure, and at 50% relative humidity (RH).

## 3. Results and Discussion

### *3.1 Surface morphology and phase determination of the thin films*

The surface morphology and phase determination of the as-deposited and aged thin films screened for the gas sensing were investigated by FE-SEM and XRD technique. The surface morphology of thin film was observed by FE-SEM at 10keV accelerating voltages at 100KX magnification and the as-deposited thin films are presented in

Figure 1 with the schematic diagram of transducer. The as-deposited film was composed of multiple phases of copper and aluminum oxides. The presence of the delafossite $CuAlO_2$ (PDF 00-040-1037, hexagonal phase, P63/mmc) and metallic Cu (PDF 00-003-1005, cubic phase, Fm3m) was determined by the XRD (image not shown). The as-deposited thin film was annealed at 500 °C for 36 hours in air to simulate the effect of "real" ageing during the sensor study and characterized by XRD. Only CuO oxide phase was observed after annealing.

Micro-Raman spectroscopy was performed on sample mounted for gas sensing on the TO-5 case after the sensing tests. Only CuO Raman signal with typical vibration at 295, 345, 631, 1100-1200 $cm^{-1}$[10,11] was observed on the tested sensing film which is in an agreement with XRD result.

Figure 1: (Left) SEM image of nanostructured p type thin film of Cu-Al-Oxide sensing layer is deposited by RF sputtering with schematic diagram of sensing thin film. (Right) Raman signal of aged sensing thin film used for sensor and the CuO monoclinic phase can be detected.

### 3.2 *Sensing study of thin film*

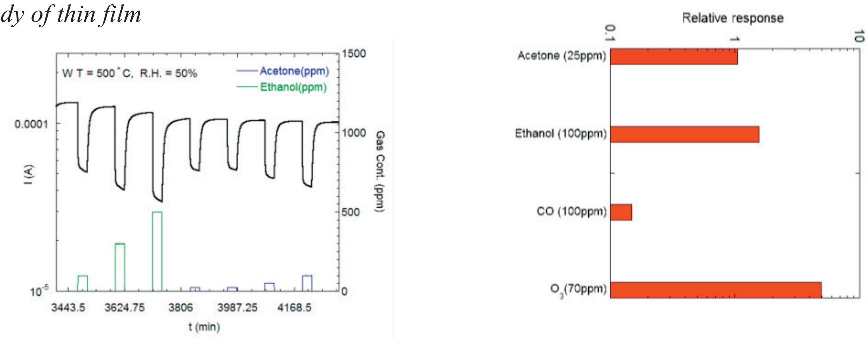

Figure 2: (Left) Dynamic response curve of sensor tested for acetone and ethanol in air with 50% RH at the working temperature of 500°C; (Right) the response curve corresponding to acetone 25ppm, ethanol 100ppm, CO 100ppm and $O_3$ 70ppm.

The sensing films were tested for the detection of reducing gases, like acetone (25-50-100ppm), ethanol (100-300-500ppm), CO (100-300-500ppm) diluted in humid air at a 50% RH. The maximum response for acetone and ethanol was observed at 500°C while low response was recorded towards CO. The dynamic response indicates that the as-deposited sensors exhibit p-type behavior for the gas sensing at optimum working temperature at 500°C and (Right) column plot shows the optimum response corresponding to different gases. In case of p-type oxide material, M. Hübner et al. pointed out that oxygen ionosorption induces the appearance of a surface accumulation layer, which has a higher concentration of free charge carriers (holes) and a higher conductivity (a lower resistivity). It might be possible to have a lower resistance path around the grains and parallel to the surface[12]. Response and recovery times towards 25ppm of acetone are 225s and 315s while for 100ppm of ethanol are 330s and 360s at 500°C working temperature.

Cu-Al-Oxide thin film tested for ozone at operating temperature from 150°C to 500°C and showed the p-type behaviour. Figure 3(Left) shows the dynamic response curve of sensor towards $O_3$ at optimum working temperature at 300°C with 50% R.H. and (Right) calibration curve for 70ppb of $O_3$ shows the optimum response at 300°C working temperature corresponding to 70ppb of $O_3$. Ozone absorption extracts electrons from the oxide and an enhancement in the holes concentration appeared near the surface. The resistivity of the thin film decreases after the exposure to ozone. Response and recovery time towards 70ppm of $O_3$ are 2415s and 465s at 300°C. The result shows that Cu-Al-Oxide thin film has good potential to detect the low concentration of ozone gas.

Figure 3: (Left) Dynamic response of sensor tested for ozone (70ppb) and (Right) the calibration curve for 70ppb of $O_3$.

## 4. Conclusions

We prepared Cu-Al-Oxide thin film with interesting morphology composed polycrystalline wires as revealed by SEM microscopy. The chemical sensor based on thin films deposited in an inert atmosphere and aged at 500°C showed p-type behavior. Raman analysis performed on the tested film confirmed the CuO phase only which is a p-type material. The response to reducing gases like ethanol, acetone and CO was observed to be lower than the response to ozone and the optimum operating temperature for reducing gases is 500°C. Thin film shows a good response to 70ppb of ozone R =4.9 at 300°C. The result shows that Cu-Al-Oxide thin films can be used as p-type MOX for production of gas sensor to detect the low concentration of ozone gas.

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