

Optimizing Paste Formulation for Improving the Performances of CMOS-Based MO_x Chemiresistors Prepared by Ink-Jet Printing [†]

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Abstract: CMOS-based devices and the control of the materials properties by nanotechnology enabled significant progresses in the field of metal chemiresistors for gas sensing applications both in terms of miniaturization and performances (e.g., gas sensitivity). In this regard, ink-jet printing is a powerful technique to achieve high-volume production and meet the emerging consumer market demands. The paste formulation is an obvious aspect to consider for achieving a viscosity range suitable for ink-jet printing. More importantly, it is often an underestimated task which impacts the gas response of the resulting chemiresistors in terms of sensitivity, cross-sensitivity and baseline drift. In this manuscript, the effects on the film morphology and gas response upon removing ethyl-cellulose from the paste formulation is reported. Improvements in terms of sensitivity and baseline drift were observed.

Keywords: metal-oxide chemiresistors; ink-jet printing; paste formulation; gas sensors; sensors drift

1. Introduction

Metal oxide (MO_x) chemiresistors have drawn considerable academic and commercial interest as gas sensors because of attractive attributes such as low-cost and compatibility with CMOS fabrication processes [1,2]. However, cross-sensitivity and sensor drift perhaps remain two of the main challenges which have not been fully resolved [3,4]. In this regard, sensor drift is a complex phenomenon and factors such as microheater temperature fluctuations and changes in the MO_x chemical and electrical properties during operation may contribute to drift [3,4]. Paste formulation is a key step in the preparation of MO_x chemiresistors since it allows the transfer of the metal oxide on the substrates by means of thick-films deposition techniques such as ink-jet printing [3,4]. This step is often overlooked due to the assumption that the formulation does not impact on the resulting sensors. In fact, it is worth to note that for instance organic stabilizers and polymeric resins such as ethyl-cellulose are often added to the formulation in order to tune the viscosity of the paste and avoid phase separation. An annealing step is then accomplished after the deposition in order to combust these additives and thermo-chemical analysis can provide a useful insight in order to design an appropriate temperature profile to achieve the sought degradation of the polymer. However, residual content of carbon even at trace levels may contribute to the slow-drift characteristics often experienced with chemiresistors. In particular, this manuscript investigates whether the presence or

absence of ethyl-cellulose in the ink-jet formulation employed for the preparation of MOx chemiresistors impacts on the sensors characteristics.

2. Materials and Methods

CMOS-based devices were prepared as described elsewhere [5] and employed as substrates. Chemiresistors were produced by depositing a metal oxide paste by ink-jet printing. Pd-doped tin oxide or a composite of tin oxide and indium oxide were employed as metal oxides. The paste was obtained by ball-milling (PM-100, Retsch) the powder together with a high-boiling temperature solvent with and without polymeric additives, e.g., ethyl-cellulose. An identical in-situ annealing step was performed on the chemiresistors by operating the embedded microheater independently from the formulation of the metal oxide paste. Driving and readout electronics were built in-house and are based on available documentation [6]. Simultaneous Differential Thermal Analysis (TGA) and Differential Scanning Calorimetry (DSC) were performed using SDT Q600 (TA instruments). The top morphology of the metal oxide films was investigated by means of Scanning Electron Microscopy (Jeol 5800LV SEM). Gas and ambient air bench-top tests were performed by operating devices at the same temperature and monitoring resistive output. Single gas exposures of CH₄ (1500 ppm), NO₂ (0.1 ppm), acetone (0.75 ppm), toluene (50 ppm), CO (50 ppm), ethanol (50 ppm) and H₂ (100 ppm) were alternated to synthetic air (N₂:O₂ ratio of 80:20) using an in-house built gas rig system [5]. Relative humidity was maintained at 50% during all the gas sequences. Gas sensitivity was calculated as ratio of R_a/R_g or R_g/R_a for reducing or oxidizing gases, respectively. R_a and R_g stand for the sensor resistance as measured in air and during a gas exposure.

3. Results and Discussion

Figure 1 shows the DTA trace of the ethyl-cellulose dissolved in a high-boiling point solvent and Figure 2 shows the DTA/DSC traces of the ink-jet paste formulated with and without ethyl-cellulose. These graphs suggest that the solvent is fully removed when the temperature reaches ~190–210 °C and that the onset temperature for the decomposition of polymer occurs at ~280 °C. It should be noted that according to Figure 1 the total weight loss measured at 500 °C is equal to 99.92%, i.e., a residue of 0.08%. The latter may seem as a small value, however, it corresponds to 1.6% of the content of ethyl-cellulose initially present. We hypothesize that this carbonaceous residue may further combust during the operations of the sensors thus contributing to the slow drift characteristics of the resistive baseline of the prepared MOx sensors. Figure 3 compares the SEM images of the morphology of the films produced without ethyl-cellulose and with increasing loading of the polymer. This figure does not highlight significant differences in term of film porosity and particle granularity although a slightly larger inter-particles spacing seems apparent with the highest ethyl-cellulose loading. It is important to note that similar conclusions on the film morphology withstand independently of the metal oxide used in the paste formulation, i.e., SnO₂/In₂O₃ and Pd-SnO₂.

A SnO₂/In₂O₃ composite was employed as metal oxide.

Figure 4 compares bench-top tests of devices prepared with and without ethyl-cellulose. A couple of conclusions can be drawn. Firstly, the baseline resistance of the resin-free sensors (i.e., without the ethyl cellulose) as measured after ~21 days of monitoring is significantly larger than the other ones, i.e., ~2 and ~1 MΩ, respectively. Secondly, sensors prepared without the use of ethyl-cellulose seem to reach a stable plateau in as shorter time. This is well illustrated in Figure 5a where the traces are normalized by dividing the sensor resistance by the value after 24 h. Finally, the large spikes which are present in the resistance traces of devices prepared with ethyl-cellulose are instead absent when the polymer was not employed in the formulation. This seems to suggest that the resin-free sensors are less sensitive to oxidizing gas events. In this regard, Figure 5b reports the sensitivity of the sensors towards the tested gas and it may be concluded that the sensors prepared without ethyl-cellulose have greater responses to reducing gases although response to NO₂ seems unchanged.

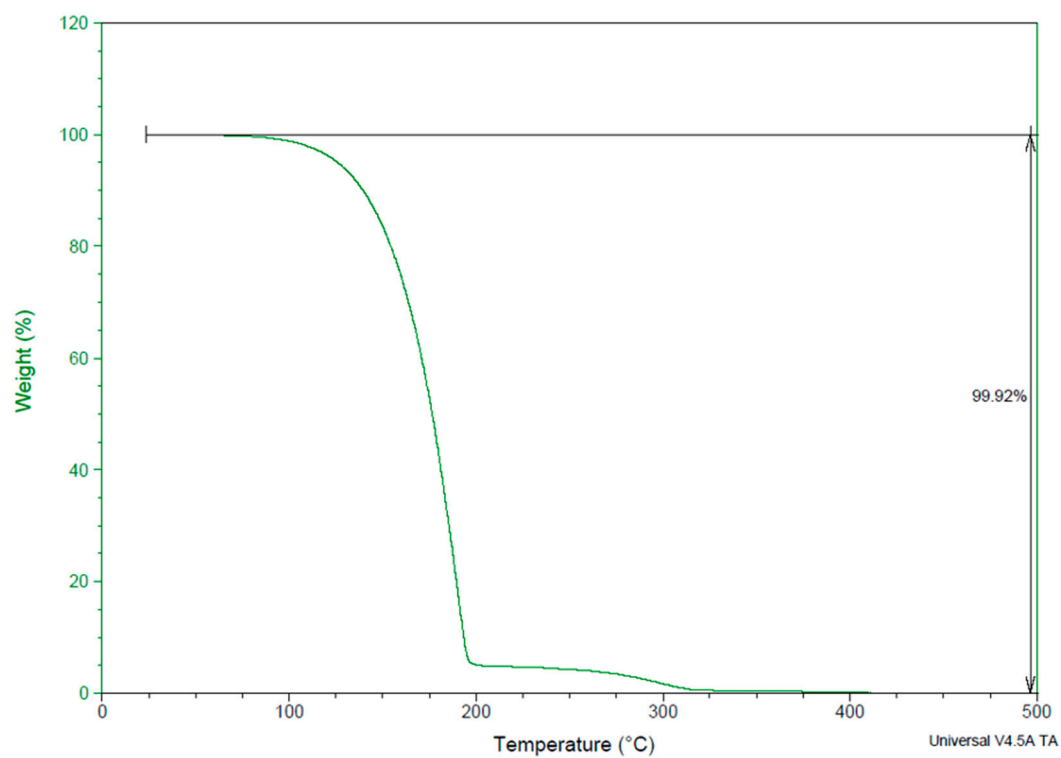
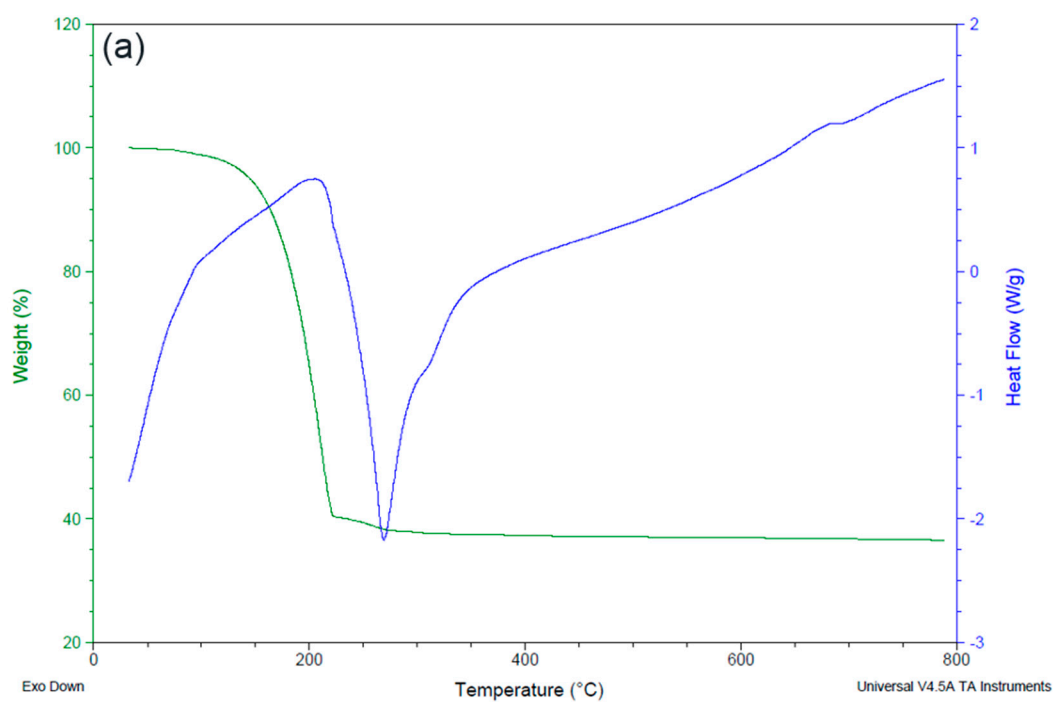


Figure 1. (—) TGA of ethyl-cellulose dissolved in a high-boiling point solvent.



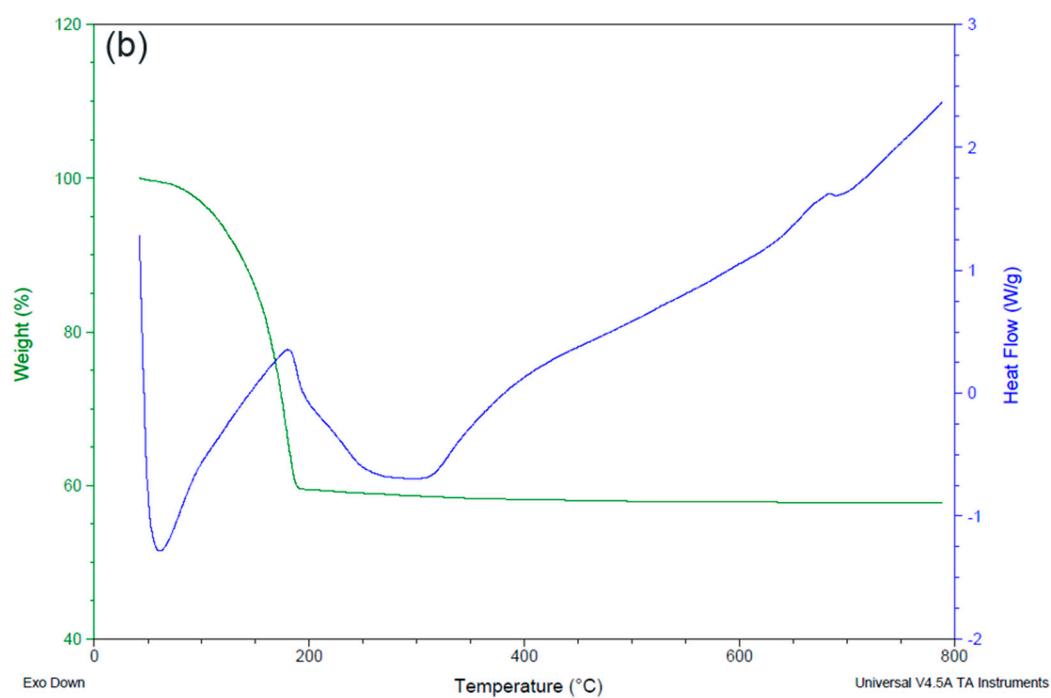
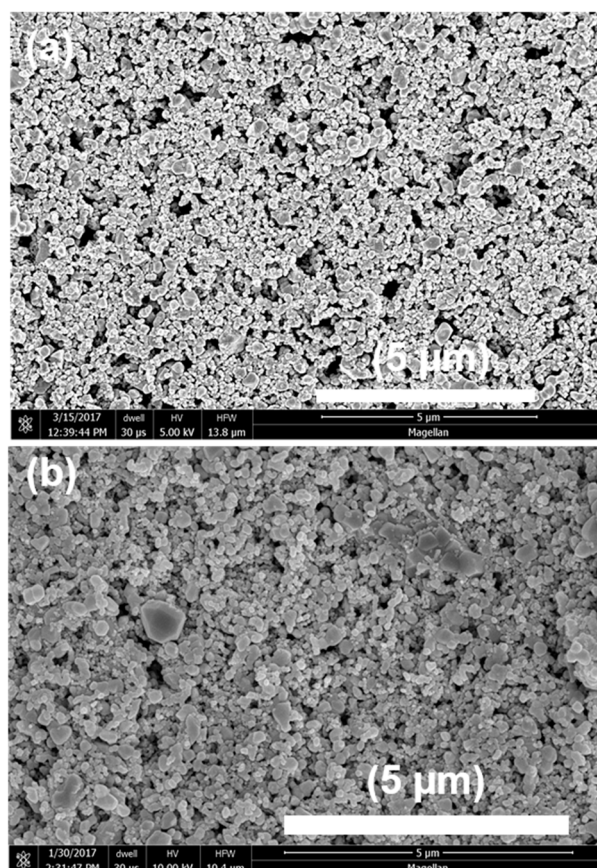


Figure 2. (—) TGA and (—) DSC of ink-jet pastes formulated (a) with and (b) without ethyl-cellulose.



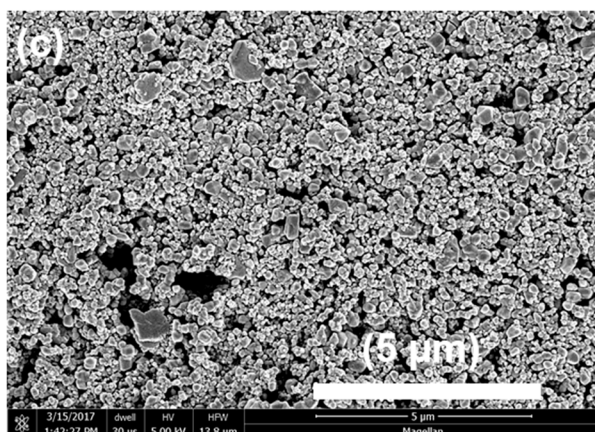


Figure 3. SEM images of a $\text{SnO}_2/\text{In}_2\text{O}_3$ composite films deposited from pastes formulated (a) without and (b) with ethyl-cellulose and (c) with double % loading compared to (b).

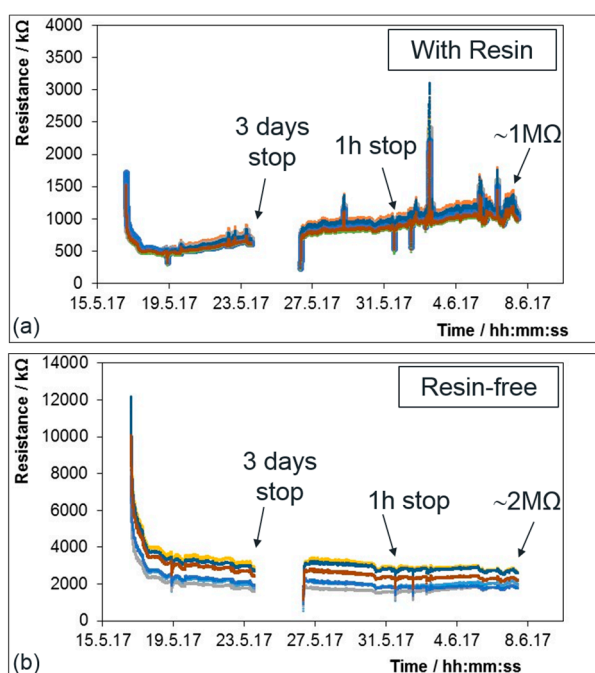


Figure 4. (a) Electrical baseline of Pd-doped SnO_2 chemiresistors prepared using formulation (a) with and (b) without ethyl-cellulose.

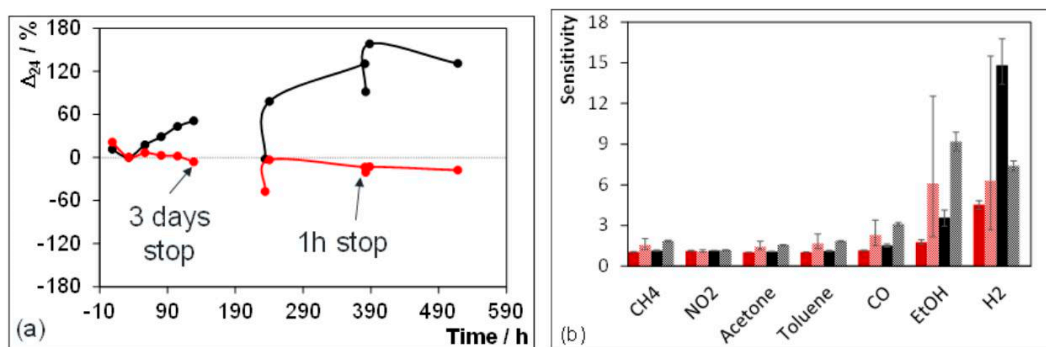


Figure 5. (a) Resistance changes derived from Figure 4 normalized using its value at 24 h. Graph report the normalized traces of sensors prepared (—) with and (—) without ethyl-cellulose. (b) Sensitivity for sensors prepared from a formulation containing ethyl-cellulose and annealed at 720 °C (red) and 500 °C (black) and from a formulation without resin and annealed at 720 °C (pink) and 500 °C (grey). The type of gas employed during the gas testing is indicated below the bars.

4. Conclusions and Future Work

The work in this manuscript highlights that improvements in terms of the sensitivity and the baseline drift of MOx sensors may be obtained by removing the polymers added to stabilize the ink-jet paste. In particular, the incomplete combustion of the resin may produce a carbon residue which contributes to slow-drift dynamics. Future work has to address the de-coupling of paste viscosity from the MOx solid loading in order to remove any possible carbon residue and afford a suitable paste viscosity while retaining an identical thickness of the film.

Author Contributions: C.Z. conceived, designed, performed the experiments and wrote the paper; L.J. and A.H. analyzed the data; Z.A. designed the CMOS-based chemiresistors; W.S. and M.C. supported the design of experiments and the drawing of conclusions.

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