

Evaluation of In₂O₃ Prepared by the Delayed Ignition Combustion Process as a Gas Sensor

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ABSTRACT

In the data analytics era, the development of superior metal oxide semiconductor (MOS) gas sensors is of paramount importance. In this paper, we report an analysis of 35nm thick indium oxide films prepared using two simple, solution-based methodologies: a traditional sol-gel process (benchmark), and Delayed Ignition of Combustion (DICO), a more recent process that we are evaluating for gas sensing. The latter process offers a route to MOS thin films at lower cure temperatures, using ionic oxidizers and organic ignition fuels. We find that the radically different chemical reactions between sol-gel chemistry and DICO lead to the formation of In₂O₃ with very different morphologies, and consequently with significantly different gas sensitivity. The significantly smaller grain size yielded by DICO is critical to enhance In₂O₃ gas sensitivity. The latter result, in conjunction with the versatility and low temperature associated with the DICO process clearly show the high potential of the latter for gas sensing applications.

Keywords: gas sensing, indium oxide, sol-gel, delayed ignition combustion.

1 INTRODUCTION

With the explosion of data analytics over the last years, there is a dramatic push for the development of superior sensors of all kinds, especially when associated with Internet of Things (IoT) applications. Gas phase sensing is a good example, with applications in healthcare, food and environment safety, as well as Homeland security that require sensors with very fast response and high sensitivity, among many other requirements [1]. In this context, the most studied sensors are chemiresistors, where the change in resistance in the presence of an analyte can be correlated to the analyte concentration. Within this class of sensors, MOS are excellent candidates and are currently found in a variety of low-cost gas sensors on the market. Commercial MOS sensors typically employ a thick sensing layer (several microns) with a rather unsophisticated and random morphology. In order to maximize MOS performance, it is critical to i) find simple, alternative ways to prepare MOS materials at the *nanoscale* with a controlled and optimized structure and ii) establish structure-property relationships.

In this paper, we report on the preparation of indium oxide for the detection of acetone, a volatile organic compound (VOC) connected to diabetes conditions when detected in high concentrations in the human breath [2]. In₂O₃ thin films were prepared using two simple and inexpensive solution-based processes: a traditional sol-gel approach, used as a benchmark, and a less conventional process referred to as delayed ignition of combustion (DICO). The latter is a highly exothermic process that has similarities to CVD combustion and spray pyrolysis [3] but with differences such as a significantly lower deposition temperature (350^oC vs. 850^oC), making it very industry-friendly and cost effective. DICO for thin films was only recently reported in the literature [4], and to our knowledge has not been considered for formation of gas sensors. Here we show that, while sol-gel derived In₂O₃ had a relatively modest sensitivity to low concentrations of acetone as previously reported [5,6], preparing In₂O₃ by DICO led to 30-60% improvement in sensitivity (Figure 1). An in-depth characterization of the film morphologies by TEM and x-ray techniques led to the conclusion that, despite differences in porosity, smaller grain size in the DICO film was the main factor responsible for the increased sensitivity to acetone. This provides clear evidence that controlling the final MOS morphology is of paramount importance in the development of superior, industry compatible thin film sensors. It also shows the great potential of the DICO process for MOS preparation: metal salts convert to an oxide in a fast, highly exothermic process with low ignition temperature, i.e. ideal thermodynamic nucleation conditions to obtain small, yet stable grains, hence high gas sensitivity.

2 EXPERIMENTAL

2.1 Solution preparation

Two different solution-based systems leading to the formation of In₂O₃ were auditioned: one using traditional sol-gel reactions, the other one following the DICO protocol, previously described by T.J. Marks [7]. All chemicals were purchased and used as received.

The sol-gel solution was prepared by dissolving 2.2g of indium(III) chloride in 30 mL of 2-methoxyethanol, under stirring. After 2 hours, 0.27 g of water was added. The solution was deposited after 24 hours of aging. For the DICO solution, 772.2 mg of indium(III) nitrate hydrate

were dissolved in 4mL of 2-methoxy ethanol. After full dissolution of the nitrate, 0.4mL of acetylaceton was added as the organic fuel and the solution was stirred for 30 minutes, before adding 228 uL of 14.5M ammonium hydroxide. The formulation was further stirred overnight.

2.2 Solution deposition and bake

Cr/Pt (5/50nm) interdigitated electrodes (IDE) in a comb-comb geometry were deposited by e-beam lithography onto Si/SiO_x (oxide ~1 μm thick) wafers. The latter were cleaned using an oxygen plasma just prior to solution deposition. Both solutions were spin-deposited on the IDE substrates at 1500 rpm for 30 seconds. Following deposition, the samples were baked under different conditions, depending on the process: sol-gel specimens were heated to 400°C using a multi-step temperature profile with slow ramp rates, and kept at 400 °C for 2 hours. On the other hand, DICO films were quickly heated to 350°C and held at 350 °C for 1 hour. The final film thickness was 35nm for both sol-gel and DICO films, and Rutherford Backscattering Spectrometry (RBS) analysis indicated that both films are In₂O₃.

2.3 Electrical and sensing measurements

A probe station coupled to a heating plate was used to carry out two-point probe current measurements of the sensing films. The latter is used to assess the MOS resistance at operating temperature (300°C) as well as to implement a current burn-in (300°C at 2V overnight under dry air) to ensure device stabilization prior to sensing experiment. During operation, the active device region is located below a gas delivery tube. A local environment that completely envelopes the IDE and the surrounding area is created under a gas flow.

Known concentrations of acetone (30 – 3000 ppb) are achieved using a calibrated Owlston permeation oven. Dry air (RH <2 %) is used as the carrier gas and for additional dilution. A constant flow of 450 sccm impinges on the sample.

3 RESULTS & DISCUSSION

Both In₂O₃ films prepared by sol-gel or DICO were exposed to three different acetone concentrations, going by steps from high to low: 2.7ppm, 1ppm and 300ppb. After measuring the response at one concentration, dry air was used to recover the baseline of the MOS device. The sensing response of the two In₂O₃ films is shown in Figure 1 and represented as the sensitivity *S* of the MOS device, defined by $S=R_{air}/R_{gas}$. The experimental procedures were tuned to prepare films with similar thickness in order to make direct comparisons possible. First, it is worth noting that the raw sensing data show a decrease in resistance for both films and all analyte concentrations, which is consistent with the reducing effect (electron donating) of

acetone. Nevertheless, after converting the resistance measurements to sensitivity values (Fig. 1), it is observed that, even though response time and recovery time are very similar for both films, the DICO film exhibits a significantly higher sensitivity than the sol-gel film for all acetone concentrations tested.

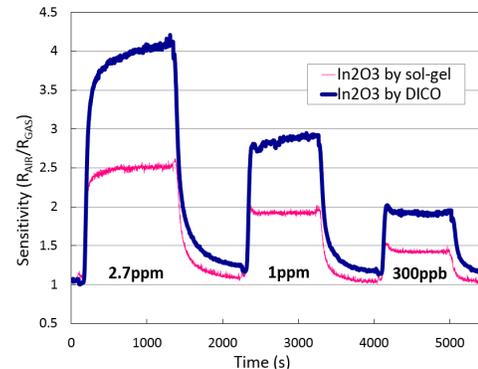


Figure 1: Response of In₂O₃ by sol-gel and DICO to various low concentrations of acetone.

The sensitivity improvement ranges from 30 to 60%, with more improvement observed for higher analyte concentration. This is a significant achievement as In₂O₃ reportedly responds with modest sensitivity to acetone [5,6]. Although differences in sensitivity may be surprising as both films have similar composition and thicknesses, they can be rationalized by differences in morphology. TEM cross-sectional images of both films are shown in Figure 2. The size, crystallinity and packing/arrangement of the In₂O₃ grains are dramatically different for the two films: while the sol-gel film (Fig. 2a) shows grains ~15-20nm in diameter with large interstitial porosity, the DICO film (Fig. 2b), on the other hand, shows significantly smaller grains (6-8nm) that are highly packed, with no discernible interstitial voids. These differences in crystallinity and density were then further investigated by x-ray reflectivity (XRR) and x-ray diffraction (XRD), respectively (Fig. 3).

The XRR scans (Fig. 3a) clearly show a shift of the critical angle Θ_c towards lower values for the sol-gel film. Since the critical angle value is directly proportional to the film density, the results indicate that the sol-gel film is much less dense than the DICO film, a conclusion in excellent agreement with what was observed on Figure 2. The fit of the XRR data for the DICO film returned a density value of 5.15g/cm³, while that of the sol-gel film, less accurate due to the absence of Kiessig fringes on the XRR scan, allows only an estimation of the density value in the range 3-4g/cm³. It is worth noting that both values are lower than the theoretical density of single crystalline In₂O₃ (7.18g/cm³). This could be due to two main factors: incomplete DICO or sol-gel reactions, i.e. incomplete indium precursor conversion to oxide, or the presence of pores in the films. While the former cannot be completely ruled out, it is clear that it is not the primary explanation for the lower density values as the RBS compositional analysis (not shown here) only found traces of chloride and nitrogen

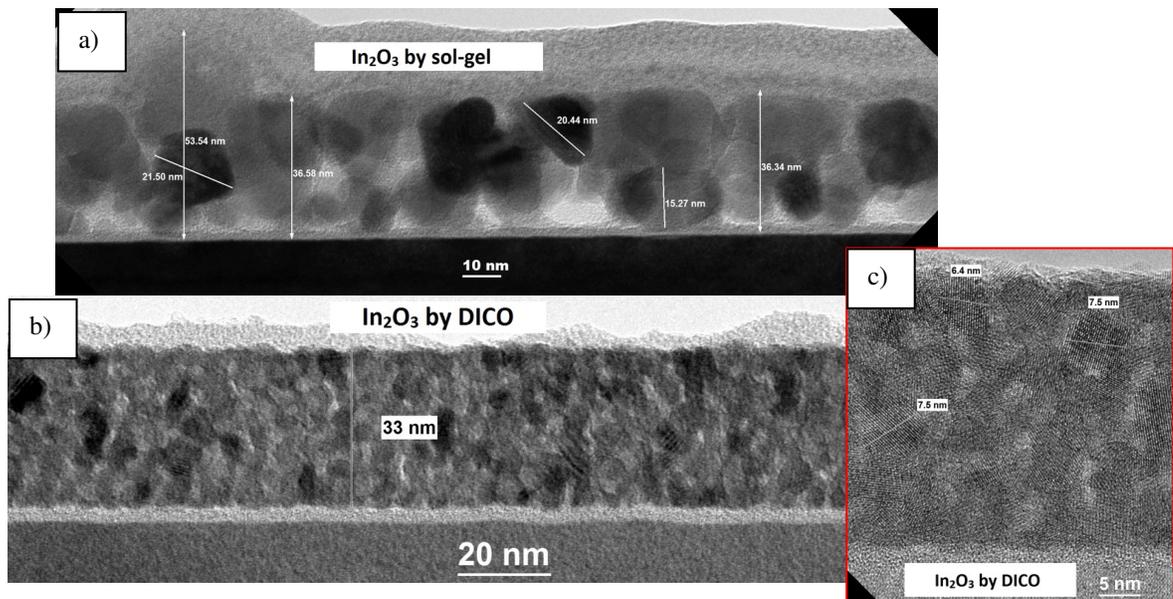


Fig. 2: TEM cross sections of a) In_2O_3 by sol-gel (x100k), b) In_2O_3 by DICO (x100k), c) In_2O_3 by DICO (x250k)

in the final sol-gel and DICO films, respectively. Consequently, we can conclude that i) the porous volume in the sol-gel film is larger than that of the DICO film and ii) even though no interstitial porosity is visible on Fig. 2b) and 2c), there is some free volume present in the DICO film. Based on the latter conclusions, one would expect the sensitivity of the porous sol-gel film to be higher than that of the DICO sample, as more accessible surface area is known to increase MOS sensors sensitivity through increased and facilitated surface reactions [8]. Interestingly, the opposite effect was observed, which points to a difference in crystallinity as the reason for the increased sensitivity. The XRD scans are presented in Fig. 3b): the peaks observed on both scans appear at similar diffraction angles with similar relative intensities, indicating that the crystalline phase is the same in both films and therefore not the differentiating factor. The crystallographic analysis indicates that the structure is cubic, with Ia-3 space group, typical of indium (III) oxide. A difference between the scans is related to the relative peak widths which appear much larger in the case of the DICO films. Using the Debye-Scherrer equation, and the most intense peak of each scan (30.6°), the calculated crystallite sizes are 7nm and 18nm for the DICO and the sol-gel films respectively, which is in excellent agreement with the grain size measured on the TEM pictures in Fig. 1. Altogether, these results indicate that i) the significant difference in grain size is substantially responsible for the superior sensitivity of the DICO film and ii) sensitivity is more impacted by the size of the crystallites than by interstitial porosity. It is worth noting that higher sensitivity with smaller grains has been reported before [9,10]. This phenomena can be explained by smaller interstitial voids, therefore enhancing electrons hopping between grains.

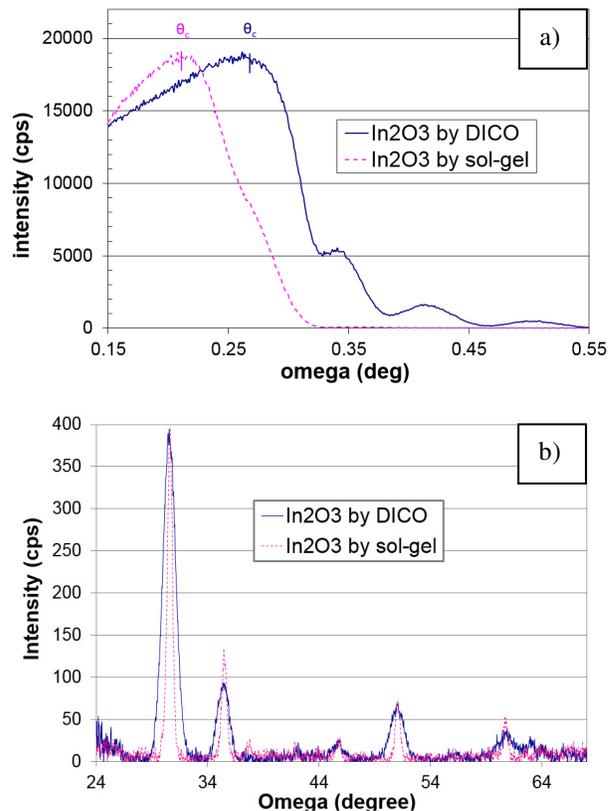
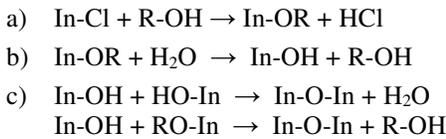


Fig. 3: a) x-ray reflectivity scans and b) x-ray diffraction scans of In_2O_3 by sol-gel and DICO

In order to understand why the DICO derived film produced smaller grains than the conventional sol-gel film, it is necessary to look at the fundamental chemical reactions characteristic for each of the two processes. Sol-gel chemistry, also referred to as “soft” chemistry, involves

a) ligand exchange, b) hydrolysis and c) condensation reactions of a metal salt:



These reactions are thermally driven but readily start at room temperature (RT), therefore a sol-gel solution is continuously evolving towards the formation of an oxide, with time. Nevertheless, the reactions are endothermic thus slow at RT, and getting complete precursor conversion to oxide form at a reasonable rate requires energy to be provided to the system, typically in the form of heat. This is illustrated on Figure 4 showing the thermogravimetric analysis (TGA) of the 24h old sol-gel solution recorded from RT to 700C at 10C/min.

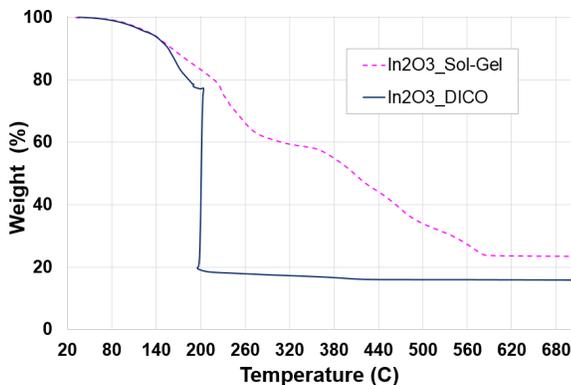
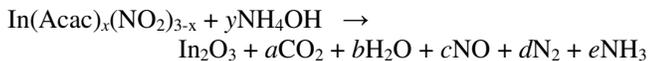


Figure 4: Thermogravimetric analysis of the 24h old sol-gel and the DICO solutions.

The weight loss of the sol-gel solution, is substantially due to the evaporation of the products formed during precursor conversion to oxide form: the decrease in mass is slow and steady until 580C and confirms that the conversion is ultimately limited by the energy input to the system. Hence, bake conditions for sol-gel materials are commonly 400C or more, for extended periods (i.e. hours). In the case of crystalline materials, these conditions favor crystallite growth.

On the other hand, the DICO reaction is a localized combustion, i.e. a redox reaction between a fuel and an oxidizer:



To start the combustion process, an ignition step is necessary. It is reported that for indium nitrate, ignition takes place at around 200C[11], which is also what we have experimentally observed in the TGA analysis of the DICO solution (Fig. 4). The initial weight loss of ~22% is due to solvent evaporation, and the extremely sharp drop in weight at 200C indicates ignition. The combustion reaction

proceeds rapidly: as it is localized and highly exothermic it does not require any additional external energy input for metal salt conversion to oxide. This is again confirmed by the TGA data where, after the sharp drop at 200C, the weight remains constant irrespective of the temperature. This fast, uncontrolled conversion at low temperatures favors rapid nucleation over growth, hence yielding smaller crystal grains than a conventional sol-gel process.

4 CONCLUSION

Sub-ppm acetone sensing of indium oxide thin films prepared via sol-gel and DICO solution-based processes was investigated. In-depth morphological characterization of the respective films suggested that the smaller grains of the DICO film are responsible for the 30-60% higher sensitivity to acetone. Altogether, these results validate the great potential of the DICO process to produce highly sensitive MOS sensors because the highly exothermic, localized combustion leads to the formation of smaller grain sizes in the film.

5 ACKNOWLEDGMENTS

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