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MANUFACTURABILITY OF GAS SENSOR WITH ZnO NANOPARTICLES SUSPENSION DEPOSITED BY INK JET PRINTING

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ABSTRACT

Zinc oxide is used in many applications thanks to its various characteristics as well as photoresistivity, piezoelectricity, wide band gap for power components but also its capability for gas detection. In this article, we first present new process based on ZnO nanoparticles from Sigma Aldrich manufacturer; a stable ink obtained by mixing 10% weight of commercial powder with ethylene glycol, has been deposited by ink-jet printing on a silicon oxide substrate covered by platinum interdigitated electrodes. To obtain homogeneous deposits of nanoparticles, the working area of the sensor was bounded by functionalisation by the n-Octadecyltrichlorosilane. These deposits were optimized at 65°C.

Then, the study was focused on the correlation between parameters of deposit and global resistance and gas sensitivity: conductivity for different operating temperatures under methane and isopropyl alcohol vapours. The best results have been obtained for thicknesses in the range of 0.5 and 2.5 µm. The ZnO resistance is stable under gas from 200°C and the relative sensitivity to methane and isopropyl alcohol are maximum and opposite at 225°C and 300°C respectively. This work shows that ink-jet is a promising technique to manufacture a new generation of low cost gas sensors at lower temperature deposition.

1 INTRODUCTION

Many metal oxides as well as SnO₂, WO₃, In₂O₃ but also ZnO are well known for their capability to detect reductive and/or oxidative gases. Their semi-conducting behavior is affected by gas adsorption that changes their resistance value. These physical and chemical phenomena, widely explain in literature [1-3], occur at high temperature level from 200°C to 450°C. Moreover, it is also proved that the sensor sensitivity is strongly improved when the nanoparticle size is reduced around the debye length [4].

Unfortunately, the distribution of nanoparticles is not still made in a homogeneous and uniform way; formation of agglomerates, due to the Van Der Waals strengths, occurs. The intensity of this phenomenon is conversely proportional with the dimension of particles [5]. The synthesis of nanoparticles is widely developed in literature [6] and constitutes important studies. Moreover, the behavior of the sensing layer could be affected by ageing with cracks and dislocation for thin layers (<2µm).

In this work, we are only interested in ZnO sensing layer. This oxide was widely used as thin layer in various applications such as optics and photonics but also in cosmetics, medicine (bio sensors), gas sensors (SAW) or ferroelectric memories. The methods of synthesis and deposit known are the ones quoted previously [6] to which it is necessary to add the other methods as CVD process [7], sputtering [8], or pulsed laser deposition (PLD) [9]. It also exists the electro-spray method [10] that uses a sol-gel solution. Finally, the ink-jet printing method has been also quoted in [11] by using also a sol-gel solution. In this article we describe a method of deposit of nanoparticles in suspension in the ethylene glycol by ink jet, at low temperature (65°C) ; this method is absolutely innovative for low cost gas sensor application.

We describe the process of deposit to obtain very well located films on the top of the active part of detector. Then, we validate the feasibility of the method by the study of the ZnO layer sensitivity to methane and isopropyl alcohol vapors according to the temperature and to the thickness of films. The most significant advantages of this method are:

- No annealing at high temperature after synthesis as with all sol-gel solutions
- only two ingredients (nanoparticles of zinc oxide and ethylene glycol);
- no additive to adjust the viscosity;
- simplicity and speed of implementation (put in suspension and homogenization by ultra sonic wave);
- good control of the dispersal of particles over the substrate;
- absence of cracks in films;
- direct writing without any other technological stage before characterization (i.e. photolithography).

2 TECHNOLOGY

2.1. Realization of metallic electrodes

From a standard silicon substrate (4"), a thin layer of SiO_2 is deposited by PECVD (5000 Å) just for electrical insulation. Then, interdigitated Ti/Pt electrodes are deposited by e-beam evaporation (1500 Å). The lithography is made by the lift-off technique. The device is shown in figure 1.

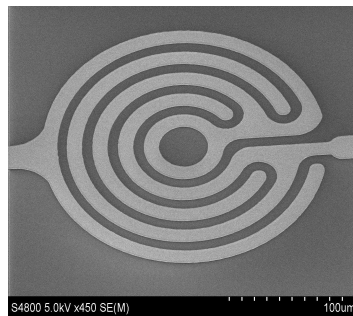


Figure 1. SEM image of one of Ti/Pt electrode designs

2.2. Surface treatment

The oxidized wafer is stewed at 150°C during one hour; 2.7µm of resin AZ1529 (from Clariant) are deposited by spin coating; follow-up by a pre-baking at 105°C during 1min. After exposition to UV light, the development is made in the AZ developer during 30 seconds followed by cleaning and drying under nitrogen. A hard bake is made at 115°C during 1 min. The wafer is then immersed in a solution of OTS (2 % in volume) in the hanging trichloroethylene during 2min. This operation is followed by successive rinsing in trichloroethylene, acetone and DI water. A drying in the nitrogen flow is followed by a dehydration baking 10min in furnace at 120°C. The quality of the surface functionalization is checked by contact angle measurements. Typically the treated region by OTS gives a contact angle of 107° with a drop of water while the untreated region give angles from 25 to 60° (on Silica and on platinum electrodes).

2.3. Sensing layer deposition

2.3.1. Material for Ink synthesis

The Zinc oxide used here is a commercial material provided by Sigma-Aldrich company. It consists of ZnO nanoparticles with diameter size between 50 and 70nm. Ink preparation and surface treatment is realized in our laboratory with commercialized products as ethylene glycol, octadecyltrichlorosilane and bi-ethylene glycol, also provided by Sigma-Aldrich Co.. It is important to notice extreme purity of these materials from 90% (octadecyl trichlorosilane) to 99,8% (anhydrate ethylene glycol). The trichloroethylene used for cleaning has a MOS quality level.

2.3.2. Equipments

The Ink-jet machine used is a "drop on demand" type, manufactured by Altatech. The principle of this machine is described in the fig.2.

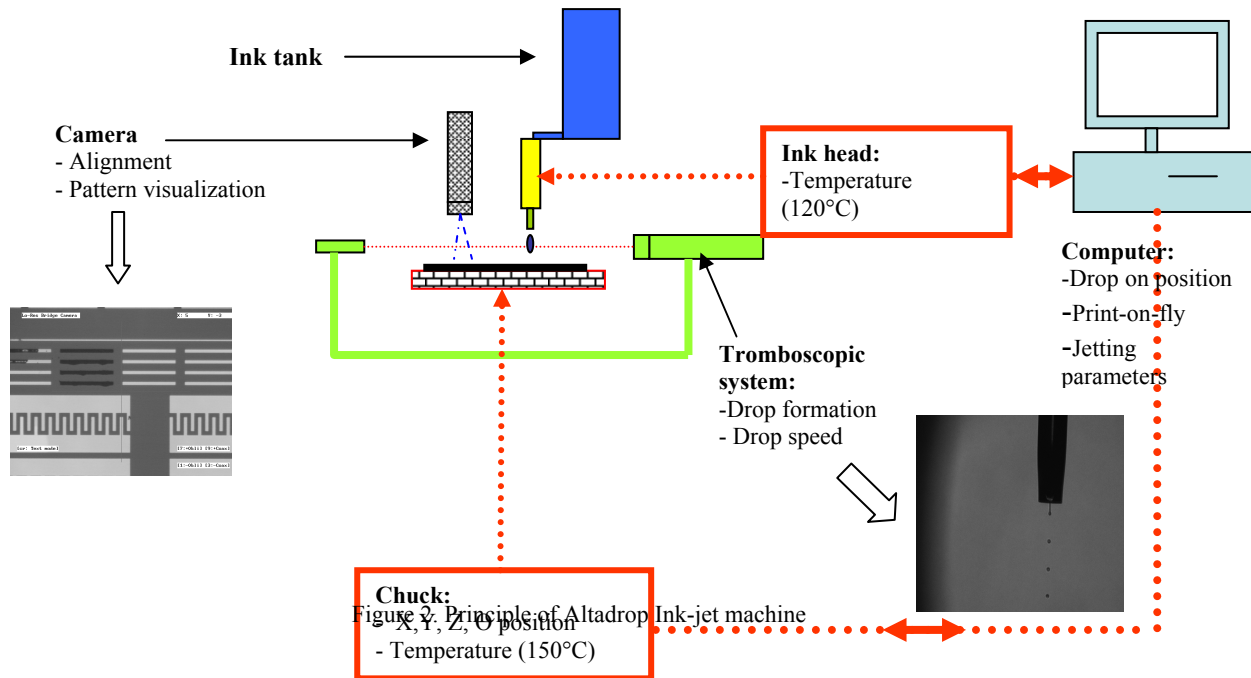


Figure 2. Principle of Altatech Ink-jet machine

This machine consists of a system of wafer automatic transfer with an automatic alignment with a precision of ± 4 microns. The chuck can be warmed until 150°C and accept wafers up to 6 inches of diameter. The heads of mono ink jet buzzards are made by the Microphone Fab company. The temperature of heads can be carried until 120°C to decrease the ink viscosity. The movement of the chuck has also a $\pm 4\mu\text{m}$ -precision. A display camera allows to centre the jet on a target and to make an observation after jetting. A trombosopic system allows to visualize the drops formation and to measure their ejected speed. The own setup is driven by a computer: chuck moving and jetting parameters to control drop formation and the printing modes (drop on position, print-on fly). The density meter Jobin Yvon Horiba LA-950V2 of Horiba Jobin-Yvon is a granulometer with diffraction laser. It allows determining the size and the distribution of particles in suspension in a liquid. The range of measure is between 0.01 μm and 3000 μm . This device allows the analysis of the quality of the suspensions. The ultrasonic probe (Biblioblock Vibra Cell) is used for the dispersal of nanoparticles in the ethylene glycol. A maximal power of 500W is available with a function of pulsed power which allows, by rest of time, to avoid a too important rise of temperature.

2.3.3. Generalities on ink-jet deposition technique

There are different approaches to write lines or to draw structures in microtechnology. The method "print-on fly" which is the one which is used in printing office in which, the substrate and the head move in a continuous way; drops are ejected according to drawing generation parameters. The writing is very fast and all the drawn designs will have the same parameters of deposit. This method is thus adapted to an already well optimized process. The second method is "the drop one position". In that case, each design is treated in a individual way, with its own parameters.

If we observe now the impact of a drop which arrives on a surface, complex phenomena take place and made the object of numerous studies [12-13]. The mechanism of deposit of a drop can be separated in two stages:

- a stage in which the kinetic energy is dissipated;
- a stage in which the drop will have to spread out on the surface and the diameter of which will depend on energy interactions between the surface and the ink. In these two stages, it is often necessary to add a third one which is the evaporation of the solvent. In the simplest case, the width of a line is given by the formula (1) [13]:

$$W = (\theta d^3/6p) / (\theta / 4 \sin^2 \theta - \cos \theta / 4 \sin \theta)^{1/2} \quad (1)$$

Where W represents the width of the line, θ the contact angle that makes the drop with the substrate, p the distance between 2 drops and d the diameter of the drop. This formula shows that the smallest line width will be obtained with a maximum value of the contact angle. Unfortunately, increasing contact angle leads to instability of the line [13]; instead of a continuous line, then we obtain ink dots more or less separated. The figure 3 shows this phenomenon.

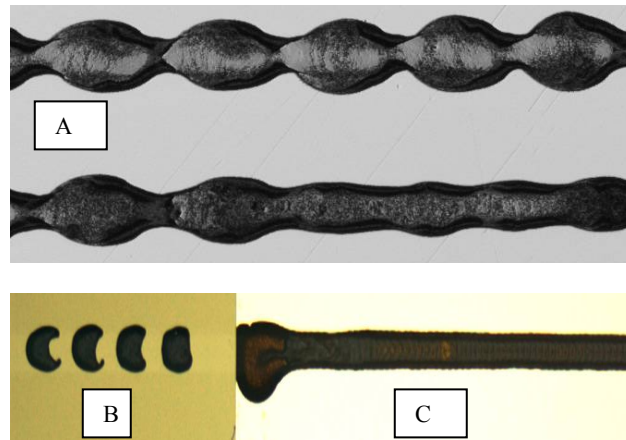


Figure 3. Photographies from optical microscope of different deposits with different contact angles: A : $\theta = 70^\circ$; B : $\theta = 90^\circ$; C : $\theta = 40^\circ$.

In case A, the contact angle is about 70° . The instability of the writing leads to the formation of a “pearl necklace”. In case B, the contact angle is 90° ; at this value, we only have separated dots: it is not possible to write line continuously. In case C, the contact angle is 40° . In this case, we can obtain a continuous line.

These results were obtained with an ink which consists of ZnO in the ethylene glycol. The distance between two drops was $30 \mu\text{m}$ and the temperature of the substrate was about 110°C to obtain an almost immediate evaporation of the ethylene glycol. In this example, the diameter of the open head of ejection was $50 \mu\text{m}$. We also measured the diameter of the drops which was around $60 \mu\text{m}$ with the same parameters of drop formation and the width of the line was near $80 \mu\text{m}$.

2.3.4. ZnO Deposits

In this study, we chose an ink with a 10 % concentration in weight of ZnO nanoparticles. These nanoparticles are put in suspension in the ethylene glycol; the ink so formed is shaken by hanging ultrasounds (30min) by means of the probe.

The stability of the ink is estimated by settling in a test tube. After several weeks we do not observe precipitate or transparent phase which would show sedimentation in time. This remarkable behavior allows having an ink which consists only of ZnO and ethylene glycol without any additive which could contaminate the sensing layer of the sensor. Other interest of the ethylene glycol is that it has a boiling point of 180°C , that allows, at 65°C , a slow and visible evaporation with the ink-jet camera. It is also possible to observe in real time the spreading of particles at the surface. At this evaporation temperature, the deposition process remains no sensitive to ambient agents (humidity, room temperature).

Our substrate contains circular and square designs for test. The maximal dimensions are $190 \mu\text{m}$ with a central circle of $145 \mu\text{m}$. With such dimensions and geometries, a direct writing is impossible considering the resolution of the line and that we wish to have a distribution localized only on the active zone of the device (above electrodes).

To avoid these phenomena and be able to write in this large surface, we chose to focus the writing in a surface exactly located by a hydrophobic treatment by Octadecyl trichlorosilane (OTS). This functionalization zone was given by photolithography. Then we deposit, as a filling, a certain quantity of drops by design, at low temperature (65°C to allow the ink to wet the hydrophilic surface (untreated OTS)). The evaporation of the ethylene glycol leaves a layer of ZnO which constitutes the sensing layer of the sensor (as it is shown in fig. 4).

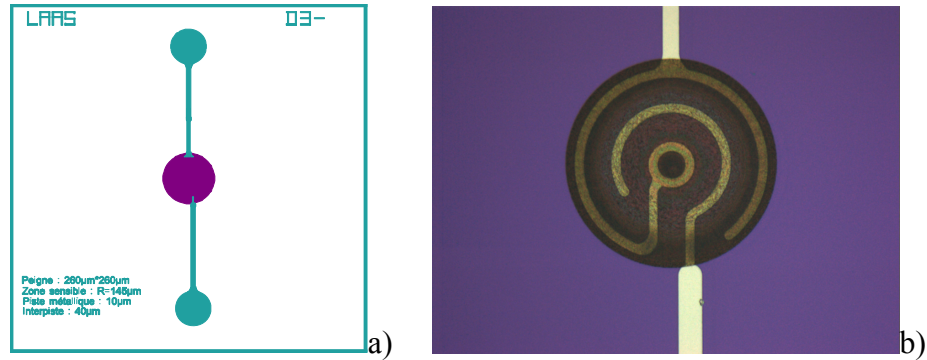


Figure 4. Design of used sensing cells : a) design of the device ; b) view of one sensing cell with ZnO layer

Some complementary studies show us that this kind of method allows reproducible deposits from one device to another for same parameters of the machine. Figure 5 is an example of the layer profile on the active area. This result presents, in the case of 30 drops on the functionalized zone, a good definition of this zone (no ZnO out of the zone) and relatively good homogeneity in thickness above the electrodes ($0.5\mu\text{m} \pm 0.15\mu\text{m}$ that corresponds to the thickness of metallization).

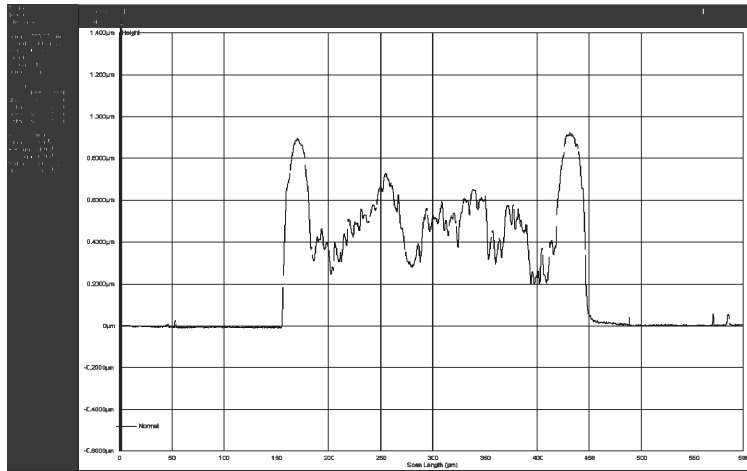


Figure 5. Example of ZnO profile obtained after annealing (30 drops)

After optimization of the deposit parameters, the second objective of this study is to determine the correlation between the number of drops in the active zone and the sensitivity to target gases (CH_4 and $\text{C}_3\text{H}_7\text{OH}$). In that way, we studied different sensing layers with a number of drops from 30 to 80. That corresponds (with a non-linear relation) to average ZnO thicknesses from $0.5\mu\text{m}$ to $2.5\mu\text{m}$. Finally, wafers are annealed in a furnace at 400°C during 20 minutes to insure the layer cohesion.

3 ELECTRICAL MEASUREMENTS

3.1 Experimental Set up

After realization, complete wafer could be electrically characterized. In this work, we used a CASCADE semi automatic probe station with a chuck controlled in temperature (from ambient to 300°C). Moreover, as the test chamber is closed, it is possible to control the ambient atmosphere. A specific small pipe allowed us to inject gas vapors just above one sensing cell. Concerning electrical measurements, we used a source-measure unit (keithley 4200) to characterize our devices. Our objective is to obtain I(V) characteristics from which we can extract resistance value in air and during an injection of gas (methane and isopropyl alcohol).

3.2 Results

First work achieved is to evaluate the influence of ZnO film thickness on its electrical properties. Figure 6 illustrates variations of ZnO resistance for various drops from 30 to 80 at different temperatures. We can observe that the resistance decreased until 50 drops and seems to be stable for more drops. Above 50 drops, the number of drops has no more influence on the film response. Concerning the first behavior, that can easily be explained by the correlation (quasi proportionality) between thickness and resistance: when the number of drops increases, the film become thicker and the resistance decreased accordingly. Over 50 drops, ZnO particles are deposited in crown on the border of electrodes while the center stays unchanged. So we obtain an important thickness on the border and a constant thickness on electrodes and so a constant resistance. This effect is commonly encountered in ink-jet printing method. Concerning the thermal behavior of these deposits, the decreasing of the resistance is important at low temperature (100°C) and attenuated from 150°C to 300°C. We can also notice that the thermal sensitivity is higher for thin layers that also predicts their better sensitivity to gas.

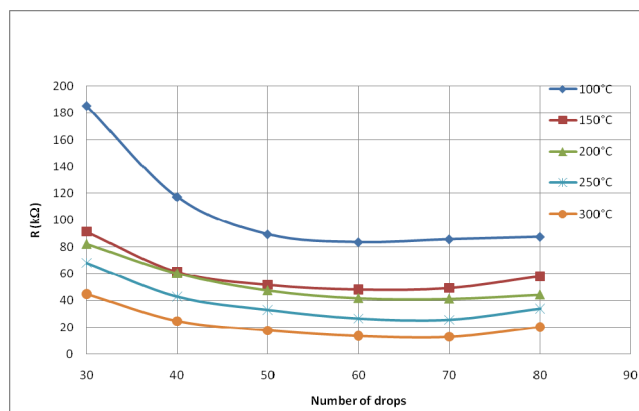


Figure 6. Resistance change of ZnO films for different number of drops and different temperature

The second part of this work concerns the behavior of ZnO films under gases according to temperature.

In a first hand, we determine how the ZnO films react under gases. The curve presented in figure.7 gives an example of transient response under CH₄ for one of the thinnest layer. It shows the conductivity (current) variations during gas atmosphere changing from air to CH₄ alternatively. When the gas is injected, the current increased rapidly and reached a stable value (400mA for this kind of device with 30 drops). Then, the current returns to the reference value after stopping injection. That demonstrates a stability of the film responses.

We have also studied the reproducibility of ZnO films responses. We have followed two times this process achieved at 300°C for the same device: First, we measure current of the film for different values of voltage without any gas. Then, we achieve an injection of CH₄ and process the same IV measurement.

The results are presented in Figure.8. “SansGaz” means without gas.

The IV-curves “300°C_SansGas_1” and “300°C_Methane_1” are the first process and “300°C_SansGas_2” and “300°C_Methane_2”, the repetition. We can see that curves of the second process are exactly similar to those of the first process. Those results are interesting for our future gas sensor performances.

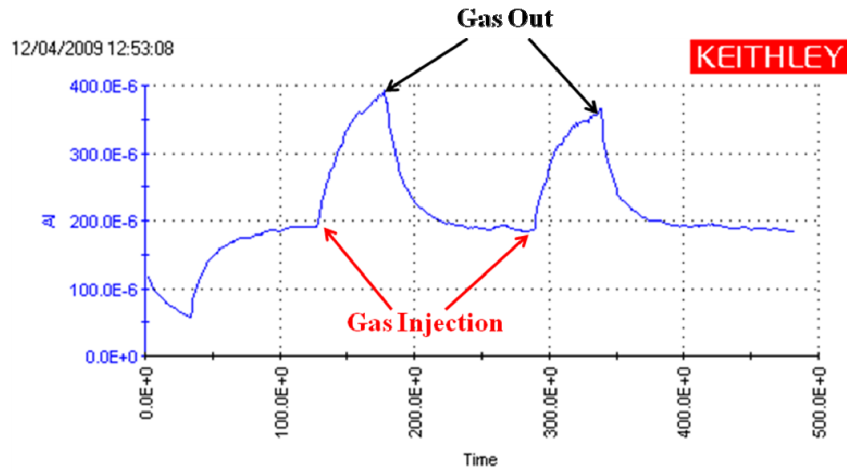


Figure 7. A transient response of a deposit under air and CH₄

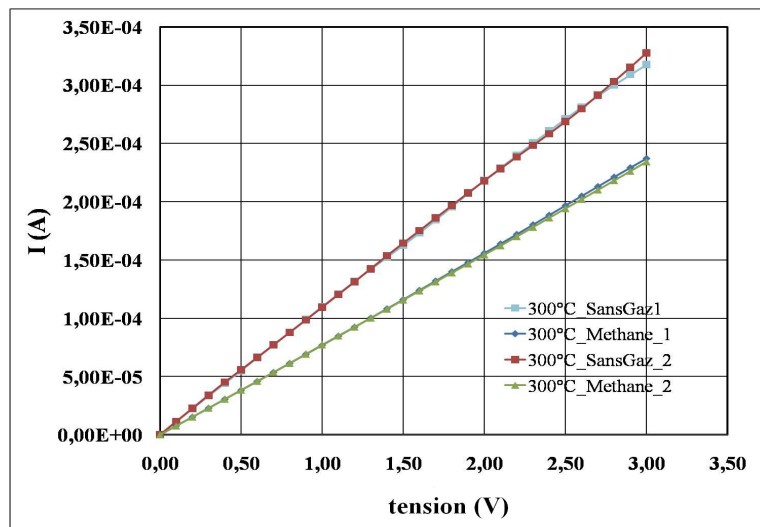


Figure 8. Reproducibility of electrical behavior: IV measurement under air and CH₄

In the second part, we studied the behavior under gas through the relative sensitivity of the different sensing cells at different temperatures from 200°C to 300°C. The relative sensitivity is defined by the relation 2. where R_{gas} and R_{air} represent the resistance values under gas and under air respectively.

The two last figures (figures 9 and 10) present curves of relative sensitivity of ZnO films to CH₄ and vapor of isopropyl alcohol at different temperatures. A maximum response is obtained at 225°C for CH₄ detection and at 300°C for Isopropyl Alcohol detection for all the deposit (free from thickness influence). We also observe that a deposit of 30 drops give the best sensitivities.

$$S_R (\%) = 100 \times \frac{R_{gas} - R_{air}}{R_{air}} \quad (2)$$

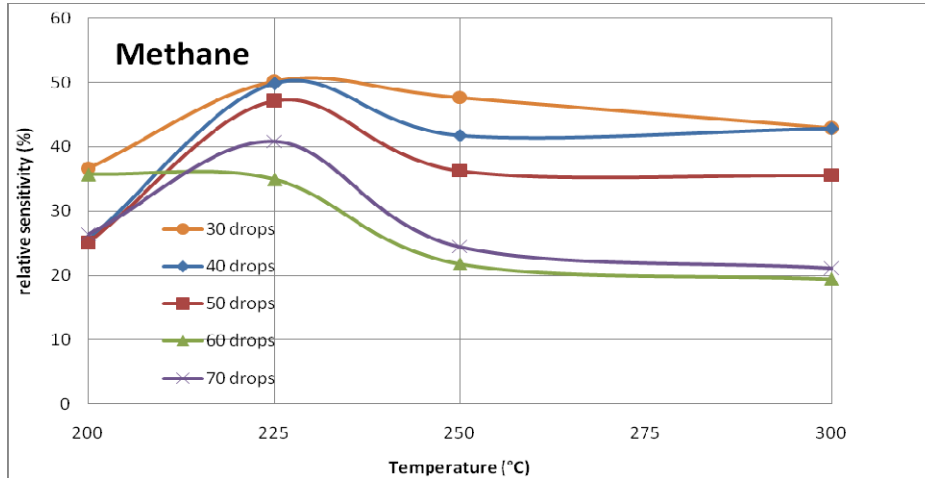


Figure 9 . Relative sensitivity to CH₄ at different temperature and for different deposits

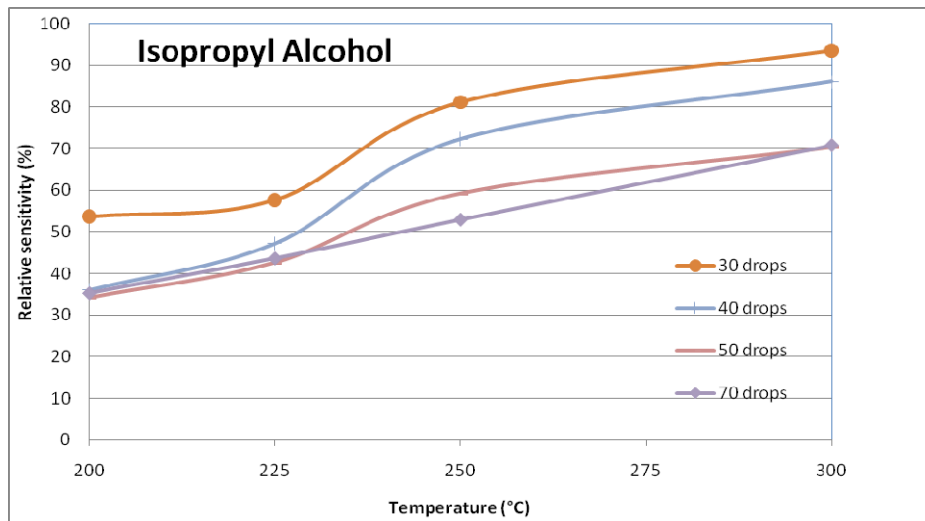


Figure 10. Relative sensitivity to isopropyl alcohol at different temperature and for different deposits

4 CONCLUSION

This paper presents a new way of manufacturing efficient low cost gas sensors based on metal oxide deposited by ink-jet printing method. In our case, we presented the ink jet process, the material used (ZnO in ethylene glycol) and the parameters that give the best homogeneity and reproducibility. Concerning the gas detection, first results show, that the thinner layer of ZnO (0.5 μ m) gives the highest resistance but also the best sensitivity to methane and isopropyl alcohol vapors (at 225°C and 300°C respectively). This work indicated that the ink-jet printing method is promising for the preparation of sensing layers for gas sensors, especially to integrate different materials on a multi sensor array, in accordance with literature [14].

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