A novel Sol-Gel-based sensor for humidity detection

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Abstract-In the last years there were widespread uses and applications of humidity sensors in many different fields. In response to this situation, various kinds of humidity sensors, based on different materials and sensing principles, have been developed. The paper proposes a novel resistive humidity sensor based on cobalt doped silica thin film deposited on a quartz support by means of a sol-gel technology. This represents a first step in the realization of an integrated sensor able to measure both umidity and gas in environmental pollution applications.

I. Introduction

The widespread uses and applications of humidity sensors in many different fields is the reason of the growing attention of the scientific community toward research and develop of sensors device [1]-[11].
In recent years the use of humidity control systems has greatly increased in the quality control of production processes and products in a wide range of industries, such as the production of electronic devices, precision instruments, textiles and foodstuffs, and also in many domestic applications, such as intelligent control of the living environment in buildings, where humidity sensors are used to maintain a comfortable humidity level and for cooling. In addition, research labs, clean rooms and nuclear reactors are all environments that are highly affected by moisture levels and require constant monitoring [1]-[14].
Humidity sensors have to fulfil different requirements to satisfy a specific application: high sensitivity over a wide range of humidity and temperature, low hysteresis, linear response, suitable accuracy and fitness to integrated circuits. Other important parameters of the humidity sensors can be listed as long-term stability, response time, and power consumption.
In response to this situation, various kinds of humidity sensors, based on different materials and sensing principles, have been developed, such as resistive, mechanical, gravimetric, capacitive, thermal and so on.
Many efforts are also devoted to the development of smart sensors, intended as sensors that have logic functions, ability for self calibration and/or communication capability and for self-diagnostics. Integrated smart sensors are defined as chips that contain one or more sensors, signal conditioning, analog to digital (A/D) conversion, and a bus output. The final target is the development of intelligent systems, using all the aforesaid devices and technologies, which will be easy to operate and have microprocessor-compatible readouts for a simple integration in automatic monitoring systems. The preparation of the sensing element in the form of thin film is then highly desirable to respond to the micro- and nanotechnology demand.
Today, the most widespread sensors are based on polymeric materials, often accurate and cheap to realise. However, polymeric film sensors are too sensitive to water condensation and they cannot operate at high temperature.
Ceramic sensors exhibit better thermomechanical, chemical, and physical stability and hence the interest for the production of inorganic films, necessary for the fabrication of integrate sensors, is more and more increasing.
Among the preparation methods, the sol-gel process allows tailoring of the resulting compounds to the needs of the sensing application by the correct choice of the precursors and preparation conditions. Moreover, the sol-gel procedure provides a simple way to deposit on a proper substrate ceramic thin films by using spin or dip-coating.
The authors propose a novel resistive humidity sensor based on cobalt doped silica thin film deposited on a quartz support by means of a sol-gel technology.
The paper aims at the design and realization of a first sensor prototype that was made passing through an optimization phase regarding the planning of a suitable sensing material composition and the preparation of a uniform crack free film on the selected substrate.
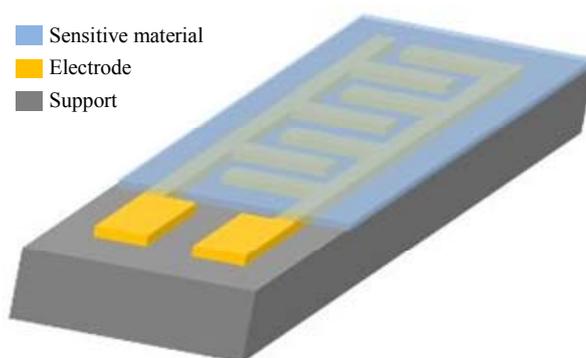
Sensitive material
Electrode
Support

Figure 1. The sensor configuration.

II. The proposed humidity sensor

As shown in Figure 1, the proposed humidity sensor can be divided in three main parts: support, microelectrode, and sensing material.

The support is constituted by a quartz slide characterized by high chemical affinity with the selected sensing material.

An interdigitated array type microelectrode allows the evaluation of the electrical response of sensing material to various relative humidity (rh) values. At this stage the microelectrode is manually realized by using silver paste.

The sensing material is composed by a cobalt doped silica that is characterized by a humidity dependent changes in electrical resistance.

It is obtained using the sol-gel synthesis, a low cost technology that allows preparing ceramic materials with a homogeneous distribution of components on the atomic scale through a low temperature synthesis with a full control of the finite product microstructure. Such a methodology is based on reactions of hydrolysis and polycondensation of metal alkoxides in solution. The obtained wet gel is transformed in the final product by means of a suitable thermal treatment. One of most interesting aspects of the sol-gel technique is related to the possibility of employing the homogeneous solution obtained before the gelation in order to prepare thin films by means of the deposition techniques of spin and dip coating. In this research project, the dip-coating technique has been used.

In the following subsections some details on the preparation of the sensing material and the relative deposition are reported.

A. Sol preparation

The preparation of the sensitive solution follows the flow chart sketched in Figure 2a. Tetraethoxysilane (TEOS) was hydrolysed at 50°C without any alcoholic solvent using concentrate nitric acid as catalyst. The molar ratio employed was TEOS : H_2O : HNO_3 = 1 : 4 : 0.01. After an hour of stirring a clear sol was obtained and a suitable amount of $Co(NO_3)_2$ $6H_2O$ was added. The resulting homogeneous solution was further mixed at room temperature for 1 hour. As better described in the next section, in order to obtain the proper viscosity for the deposition of uniform cracks free film by dip-coating, the solution was 2-fold diluted with anhydrous ethanol. This method allows obtaining a stock solution in two days.

B. Thin film deposition

Carefully cleaned substrate was dipped into the solution and withdrawn, as shown in Figure 2b. Transparent pinkish film was obtained that was fully dried in air at 110 °C in an electric oven for one day.

The obtained thin film thickness was estimated to be equal to 0.8 μm ± 0.3 μm using an ALPHA-STEP 500 surface profilometer.

The dried film was finally subjected to various thermal treatments in a Lenton furnace, which ensured a stable temperature to within ± 2 °C. Thermal analysis techniques allowed the identification of the appropriate annealing temperature corresponding to the needs of a complete nitrate decomposition and elimination of organic residues. 400°C annealing temperature appeared to be the best response to such
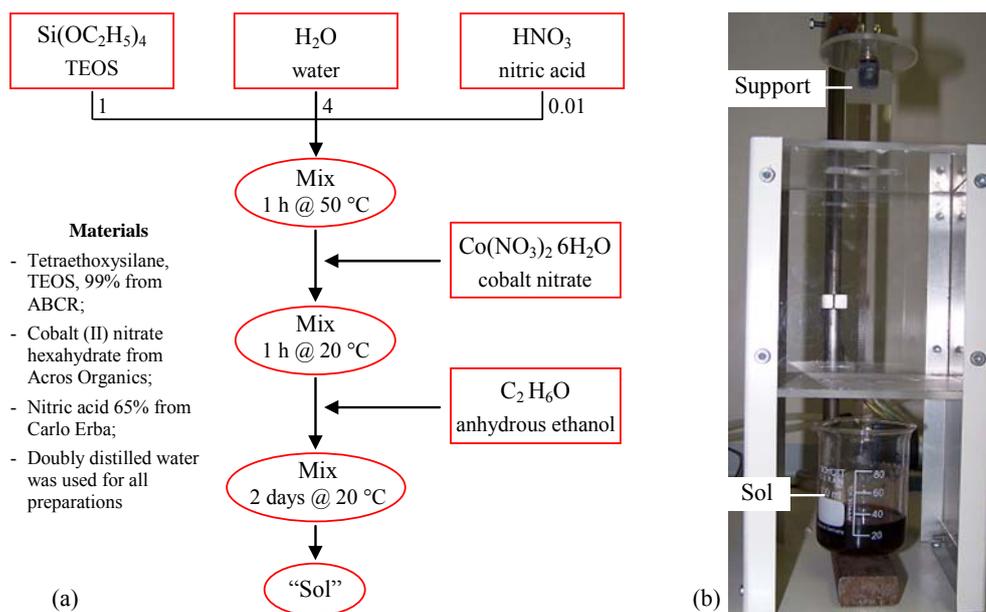
Figure 2. (a) Flow chart of sol preparation and (b) dip coat system for the film deposition.

requirements. Moreover, a fall of the specific surface area caused by structure collapse, generally observed at higher temperature, was thus avoided. In particular, the sample was heated at a rate of 10 °C min^{-1} up to 400 °C. The molar composition of the gel-derived samples can be expressed as 20Co·80SiO$_2$

III. Sensor optimization

The quality of sensors based on thin film deposition is essentially related to three parameters: the microelectrode geometry, the film composition, and the film uniformity.

The humidity sensitive inorganic materials are generally not easy to prepare in thin film shape and they are not chemically stable while those materials suitable for thin film are not or only few sensitive to the humidity. These reasons made the choice of suitable materials very complicate. The preparation of silica film doped with a humidity sensitive oxide has been assessed.

As regard film uniformity, great effort has been done to deposit crack free films by varying not only the variables which affect the gel structure (solution chemistry and evaporation rate) but also those related to the deposition process (pull out rate and adherence to the substrate).

A number of tests were executed in order to choice these variables, changing them as reported.

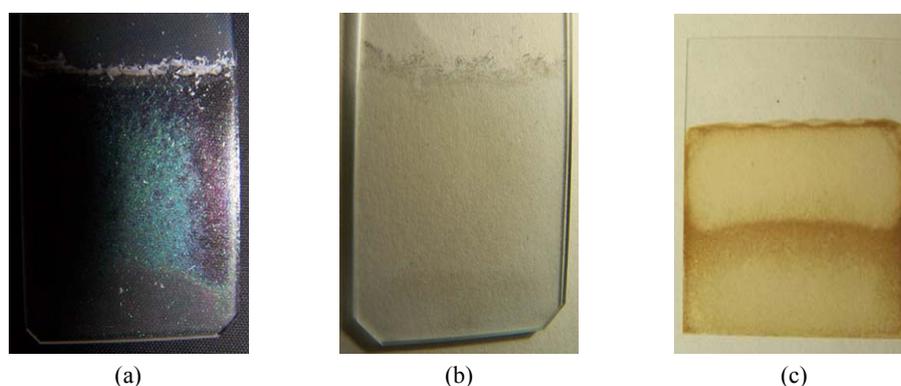Since the viscosity of the solution gradually increases with time and this in turn can affect the final film

Figure 3. The deposited films on the glass support for a 48 hours mixing time by using (a) 150 mm/min, (b) 100 mm/min, and (c) 60 mm/min withdrawing speed.
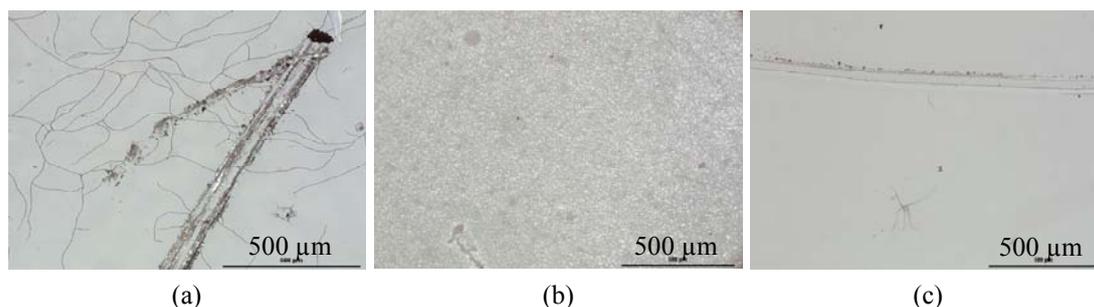
(a)　　　　　　　　　　　(b)　　　　　　　　　　　(c)

Figure 4. Optical microscope images of the deposited films on the (a) glass, (b) alumina, and (c) quartz support for a 48 hours aging time and 100 mm/min withdrawing speed.

properties [15], different aging times of the prepared solution (24 h, 36 h, 48 h, and 60 h) were considered. After a first set of tests, an aging time of 48 h has been selected because, in this condition, the solution showed the appropriate chemical-physical properties for film deposition.

Figure 3 shows the films obtained on glass supports for three values of withdrawing speed, 150 mm/min, 100 mm/min, and 60 mm/min. The best result was obtained for the speed of 100 mm/min. An higher pull out rate, 150 mm/min, leads to an extensive crack surface that is likely to be induced by the thickness effect [15]. The pull out speed of 60 mm/min appears to be two low in the sense that causes film gelation in different extent through film surface.

Glass slides, alumina, and quartz support were used to find the best adhesion with the selected sensing materials.

The uniformity of the prepared films was evaluated by means of a Nikon EPIPHOT 300 optical microscope. For an aging time of 48 hours and a withdrawing speed of 100 mm/min, Figure 4 shows, on a microscopic scale, the deposited film on the three supports under analysis.

A scratch on the surface can be noted on the Figures 4a and 4c. These were voluntary made in order to show the presence of the film deposited on the support. The quartz support (Figure 4c) showed the best performance in terms of uniformity of the film deposition.

Finally, in compliance to the results obtained in this optimization stage, the sensor was made following the procedure described in the section II by using a quartz support (Herasil silica glass slides, Haereus), with a viscosity of the solution related to a 48 hours of the aging time and a pull out rate of 100 mm/min

IV. Preliminary experimental results

Once the prototypal sensor was realized, its performance in the rh detection was investigated. A suitable measurement station, sketched in Figure 5, has been set-up. It includes: a Weiss technik300-ABTD-20JU climatic chamber; an Optica General Eastern dew point analyzer equipped with a SIM-

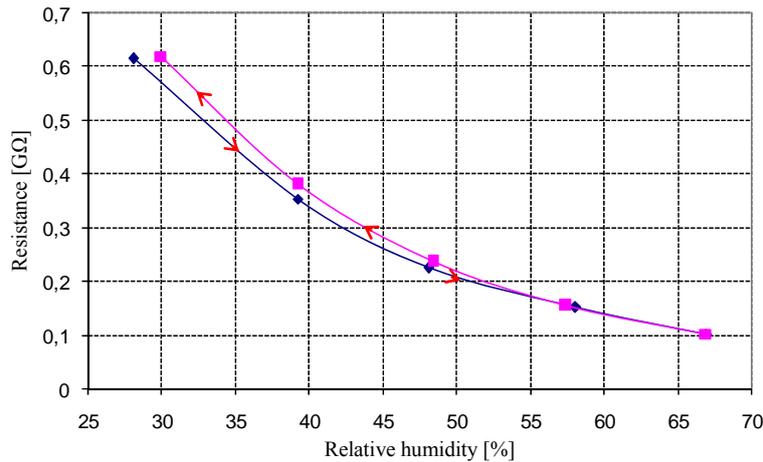Figure 5. The developed measurement station.

Figure 6. Output characteristic of the realized prototypal sensor.

12H digital hygrometer; an Agilent Technologies 3458A digital multimeter (DMM); the realized prototypal sensor.
Both the digital hygrometer and the realized sensor were placed inside the climatic chamber that allows both the regulation and control of temperature and relative humidity to the desired values (in the range of (-10 ÷ 80) °C and (0 ÷ 100) % respectively). The resistance output of the realized sensor was measured by a DMM and compared with the relative humidity measured by the digital hygrometer.
Different working conditions were analyzed changing for different values of rh and temperature.
Figure 6 shows the output characteristic of the sensor at a temperature of 30 °C.
Looking at Figure 6 it is possible to highlight a resistance variation of about 500 MΩ for a change of rh from 30 % to 70 %. The sensor shows an hysteresis of 12 % and a non linear behavior with a good sensitivity that change from 5 MΩ/% to 30 MΩ/%.

V. Conclusions

A first prototype of a resistive humidity sensor based on thin film deposited by means of sol-gel technology was designed and realized. An optimization stage was required to define some of the key parameters for the realization of an uniform crack free film. In particular, the support, the solution viscosity and the pull out rate have been analyzed and properly chosen. The first prototype of the humidity sensor has shown a good sensitivity with an hysteresis of 12%.
Improvements in the performance of the proposed sensor can be obtained realizing the interdigitated electrode by means of lithography technology. This will allow a great reduction of the resistance response of the sensor with a consequence of an easy interfacing with a conditioning system and a reduction of problem related to the parasitic components in the measure of the sensor response.

Acknowledgments

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