TiO$_2$-TiO$_2$ composite resistive humidity sensor: ethanol cross-sensitivity

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Abstract. The fabrication method and characterization results of a TiO$_2$-TiO$_2$ composite bead used for humidity sensing along with its negative cross-sensitivity to ethanol vapor are reported. The bead shaped resistive sample sensors are fabricated by the drop-casting of a TiO$_2$ slurry on two Pt wire segments. The dried bead is pre-fired at 750°C and subsequently impregnated with a Ti-based sol. The sample is ready for characterization after a thermal annealing at 600°C in air. Structurally, the bead is a composite of the micron-sized TiO$_2$ crystallites embedded in a matrix of nanometric TiO$_2$ particle aggregates. The performance of the beads as resistive humidity sensors is recorded at room temperature in standard humidity level chambers. Results evince the wide dynamic range of the sensors fabricated in the low relative humidity range. While the sensor conductance is not sensitive to ethanol vapor in dry air, in humid air, sensor’s responses are negatively affected by the contaminant.

Keywords: TiO$_2$, Sol-gel impregnation, Composite, Humidity sensor, Dynamic range, Cross-sensitivity.

1. Introduction:
Next to temperature, humidity is the most frequently measured environmental parameter. In addition to monitoring relative humidity (RH) levels in our living spaces, humidity sensors help keep RH levels optimal for industrial production. Particularly, humidity measurement and control in low RH range is of technical significance in many advanced technologies [1-5]. Humidity-sensitive materials, i.e. materials whose electrical properties, mainly conductivity [6, 7] and/or dielectric constant [8, 9], are affected by humidity, are classified into three main categories of electrolytic [10], ceramic [11], and polymeric [12]. Ceramic humidity sensors are typically considered superior because of their thermal, mechanical, and chemical stability, as well as their longevity and recyclability [11, 13]. Among ceramic type humidity sensors, the thin film metal oxide capacitive sensors operates based on the change in the dielectric constant of the oxide material with respect to the change in the atmospheric conditions [14]. Porous ceramics are usually used in production of humidity sensors [2]. Some of the common ceramics are ZnCr$_2$O$_4$, MgAl$_2$O$_4$, SnO$_2$ [15] and TiO$_2$ [2], Al$_2$O$_3$ [16]. Making humidity sensors from other materials, such as TiO$_2$, BaTiO$_3$ and α-hematite, has also been reported in the literature [17, 18]. Conductance measurement on the sensing elements of these sensors requires forming at least two metal-metal oxide contacts [19-21] stable during the normal lifetime of the device. Considering the harsh environmental conditions and the electrochemical processes taking place, such contacts are made utilizing noble metals [19]. Forming of metal contacts to polycrystalline semiconductors is an important and intricate part of the gas and humidity sensor fabrication [22]. Making metallic connections to polycrystalline TiO$_2$ has been the subject of many investigations [23, 24]. Environmentally hazardous gaseous components, particularly volatile organic compounds, have
negative effects on the performance and accuracy of the humidity sensors [25]. Similarly, humidity changes in the atmosphere affect the responses of gas sensors [26]. Ethanol vapor, for instance, affects the responses of both capacitive and resistive humidity sensors, and the ideal device is the one whose responses to humidity change is not influenced by such contaminants in the surrounding atmosphere. Here, we investigate the significance of the pore size distribution in the TiO$_2$-TiO$_2$ composite resistive humidity sensors, and investigate their dynamic range and cross-sensitivity to ethanol vapor.

2. Experimental:
Ti Rutile TiO$_2$ powder is mixed with distilled water for slurry preparation; 12 mg of the produced viscous slip is dropped onto the junction of two d= 60 µm pure platinum wire segments. After drying, the sample is sintered at 750°C for 30 minutes. Ten similar samples are prepared. Five samples, after cooling in air down to room temperature are impregnated with titanium alcoxide solution in ethanol. The impregnated samples are dried at room temperature and subsequently annealed at 600°C which converts the injected sol to titanium dioxide. The fabricated sample is shown in Figure 1. In this sensor structure need for metal deposition on the oxide ceramic is removed and the suspension wires, i.e. the Pt wire segments, operate as the electrical contacts. Further information regarding the fabrication process is given in references [19].

![Figure 1](image.png)

**Figure 1.** The TiO2-TiO2 composite bead formed on two crossed platinum wires.
Standard salts (see Table 1) are used for providing test chambers of calibrated relative humidity. Philips XL30 scanning electron microscope (SEM) is used for imaging; a micrograph of the sample sintered at 750°C is shown in Figure 2.

| Standard salt       | Humidity level at 25°C |
|---------------------|------------------------|
| Silica gel          | 4%                     |
| Magnesium chloride  | 25%                    |
| Sodium chloride     | 75%                    |
| Potassium chloride  | 85%                    |

The pore size distribution is determined by line averaging method on the obtained SEM micrographs. The population of the different size range pores is graphically presented in Figure 3.

Figure 2. SEM image of the TiO2 ceramic body produced.

Figure 3. Pore size distribution in the TiO2 bead
The experimental layout utilized for cross-sensitivity examinations between atmospheric humidity and ethanol contamination is schematically shown in Figure 4. The temperature at the outer chamber is controlled using a system comprising a PT100 temperature sensor and a PID controller connected to a distributed fine wire heating element on the chamber, which stabilizes the temperature in the chamber at 298±0.2 K.

To minimize the electrode-ceramic connection deterioration due to the electrochemical corrosion, conductance measurements are carried out at 17 Hz. At this frequency, the capacitive admittance of the sample and parasitic parallel to the sample are insignificant compared to its conductance. Closed chambers of different RH levels, in the range of 2-95%, are obtained by injecting predetermined volumes of distilled water into the dry air (RH=2%) chamber using a micro-sampler. The injected water is evaporated to obtain the specified humidity level inside the chamber. The produced stable RH levels are monitored by a commercial humidity sensor (HIH 4000) prior to and during each measurement. The output of the reference sensor is calibrated in closed chambers of standard RH levels obtained using different saturated salt solutions (see Table-1). To examine the effect of ethanol on the humidity sensing process, ethanol is introduced to the chamber air at predetermined conditions; the temporal changes in resistivity are continuously recorded.
3. Results and discussion:
The variations of sample conductance vs. the ambient relative humidity are given in Figure 5. It is clear from this diagram that the examined sample is more appropriate for the lower relative humidity range as the slope of the characteristic diagram is higher at RH<25%. At this humidity range, water vapor condensation mainly occurs in the smaller pores of the bead [2]. This is consistent with the result showing over 80% of the pore volume to be less than 70 nm in diameter (see Figure 3). Further increase in the humidity level saturates the nano sized pores, while it still can condense in the micron sized pores leading to a considerable decrease in slope of the characteristic curve of the sensor.

![Figure 5. Variations of bead conductance with the relative humidity in the surrounding atmosphere.](image)

![Figure 6. Temporal variation of the bead conductance; the sensor is exposed to dry air (RH<2%) at t=10; significant level of ethanol](image)
At room temperature, no chemical reaction occurs between the effective surface of the sensor and the adsorbed ethanol molecules, neither do the surface adsorbed ethanol molecules promote surface conductivity. This is clear from the experimental results illustrated in Figure 6, demonstrating that the sensor does not respond to the addition of substantial level of ethanol vapor to the atmosphere. The simultaneous effect of humidity and ethanol is investigated by repeating similar experiment in humid air chamber. Based on the results shown in Figure 7, the conductance of the sample at equilibrium in RH=50% air drops significantly when the atmosphere is contaminated with ethanol vapor. Since ethanol does not influence the resistivity of the device (see Figure 6), the decrease in the bead conductance is attributed to the effective competition of the ethanol molecules with water molecules in the process of surface adsorption. The results of this experiment clarify the immensity of the errors caused by the presence of organic vapor contaminants in humidity sensing.

4. Conclusion
The fabrication of a TiO2-TiO2 composite resistive humidity sensor was reported. The sensor performs best in the RH< 25%. The nanoporous structure necessary for low level humidity detection was created by sol impregnation followed by thermal annealing in air. The sensor is insensitive to the presence of ethanol in dry air, but it was shown that ethanol contamination decreases conductance of the sensor in a humid atmosphere. A model was proposed for this negative cross sensitivity.

5. References
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