



EFFECT OF AIR HUMIDITY ON THE ANALYTICAL SIGNAL OF A SEMICONDUCTOR ETHANOL SENSOR

O. N. Kholboev — Senior Lecturer,
Askarov Suyunbek Tursunboy ugli,
Xudoyberdiyev Husan Xoldor ugli,
Fayzullayev Jaloliddin Salohiddin ugli

Jizzakh State Pedagogical University, Jizzakh, Republic of
Uzbekistan

Abstract: *The effect of ambient relative humidity on the analytical characteristics of a semiconductor ethanol sensor based on a nanostructured SnO₂–ZnO sensing layer was investigated. Particular attention was paid to changes in baseline resistance, chemiresistive response, response and recovery times, and reproducibility under controlled humidity conditions. The SnO₂–ZnO nanocomposite was prepared by a hydrothermal method followed by thermal treatment at 500 °C. Its phase composition, morphology, elemental composition, and surface characteristics were evaluated using X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and low-temperature nitrogen adsorption. The material contained tetragonal SnO₂ and hexagonal ZnO phases with an average crystallite size of approximately 19–26 nm and a specific surface area of 45.7 m² g^{–1}. Gas-sensing measurements were performed at 250 °C using 100 ppm ethanol in air at relative humidity levels ranging from 10 to 80% RH. The sensor response, expressed as Ra/Rg, decreased from 30.6 at 10% RH to 16.7 at 80% RH. Simultaneously, baseline resistance decreased because of competitive adsorption of water molecules and formation of surface hydroxyl groups.*

Keywords: *ethanol, semiconductor gas sensor, relative humidity, tin dioxide, zinc oxide, SnO₂–ZnO heterostructure, chemiresistive response.*

Introduction

Semiconductor metal-oxide gas sensors are widely investigated as compact analytical devices for the determination of volatile organic compounds in atmospheric air, industrial environments, biological samples, and technological

processes. Their practical advantages include relatively simple design, low manufacturing cost, compatibility with miniaturized electronic platforms, rapid electrical signal generation, and the possibility of continuous monitoring. Tin dioxide, zinc oxide, tungsten oxide, indium oxide, and their mixed or heterostructured systems are among the most intensively studied sensing materials because their electrical conductivity is strongly affected by surface adsorption processes [1, 2].

Ethanol is an important volatile organic compound whose quantitative determination is required in food and beverage production, pharmaceutical manufacturing, fermentation processes, occupational safety, breath analysis, and environmental monitoring. Semiconductor sensors based on SnO_2 and ZnO demonstrate high sensitivity toward ethanol due to the intensive interaction of ethanol molecules with chemisorbed oxygen species on oxide surfaces. However, their analytical response is determined not only by ethanol concentration but also by temperature, oxygen content, material morphology, crystallite size, catalytic additives, and environmental humidity [2, 3].

Humidity is one of the most important factors limiting the quantitative reliability of metal-oxide semiconductor sensors under practical operating conditions. Relative humidity in ambient air can vary over a wide range, while biological gas samples such as exhaled breath are normally characterized by particularly high water-vapor content. Water molecules readily interact with active metal-oxide surfaces, where they may undergo both molecular adsorption and dissociative chemisorption. As a result, surface hydroxyl groups are formed, the concentration of adsorbed oxygen species changes, and the electrical resistance of the sensing layer can shift even in the absence of the analyte [3–5].

Water vapor modifies this mechanism through several parallel processes. It may occupy adsorption sites otherwise available for oxygen or ethanol, interact with lattice oxygen, produce hydroxyl groups, alter oxygen-vacancy populations, and

provide proton-related surface conduction pathways. Consequently, humidity commonly decreases the response of metal-oxide sensors to reducing gases, although unusual enhancement effects have also been observed for particular compositions and morphologies [3, 4].

Materials and Methods

A nanostructured SnO₂–ZnO composite was used as the active semiconductor material. Tin(IV) chloride pentahydrate SnCl₄·5H₂O and zinc nitrate hexahydrate Zn(NO₃)₂·6H₂O of analytical grade were employed as precursors. Ammonium hydroxide was used to regulate the pH of the reaction medium, and deionized water was used for preparation of all solutions.

Hydrothermal treatment was performed at 180 °C for 12 h. After cooling to room temperature, the precipitate was separated by centrifugation and washed repeatedly with deionized water and ethanol. The obtained precursor was dried at 80 °C and subsequently calcined at 500 °C for 3 h in air with a heating rate of approximately 5 °C min⁻¹.

The phase composition was studied by X-ray diffraction using CuKα radiation with a wavelength of 1.5406 Å. Diffraction patterns were collected over the 2θ range of 20–80°. Average coherent scattering domain sizes were estimated using the Scherrer relationship applied to the principal diffraction peaks.

Surface morphology was evaluated by scanning electron microscopy. The elemental composition was analyzed using energy-dispersive X-ray spectroscopy. The specific surface area was measured by low-temperature nitrogen adsorption using the Brunauer–Emmett–Teller method. Prior to adsorption analysis, the sample was degassed to remove physically adsorbed atmospheric species. For fabrication of the sensor, the SnO₂–ZnO powder was dispersed in a small amount of organic binder to obtain a homogeneous paste. The paste was deposited onto an alumina substrate containing interdigitated electrodes and an integrated heater. After drying, the sensing layer was stabilized by heat treatment at approximately 400 °C.

Gas-sensing measurements were performed in a controlled-flow chamber. The operating temperature of the sensing layer was maintained at 250 ± 2 °C. The total gas flow was kept constant during all experiments. Ethanol vapor was introduced into the carrier air to obtain a final concentration of 100 ppm.

Relative humidity was adjusted to approximately 10, 20, 30, 40, 50, 60, 70, and 80% RH. Humidified air was generated by passing a controlled fraction of the gas flow through a water-containing bubbler and mixing it with dry synthetic air. Humidity was measured immediately upstream of the sensing chamber using a calibrated digital humidity sensor. Since the SnO₂–ZnO material exhibits n-type semiconductor behavior, the sensor resistance decreased after introduction of ethanol. The response was expressed as $S = R_a/R_g$, where R_a is the stable resistance in humid air before ethanol introduction and R_g is the stable resistance in the presence of ethanol at the same relative humidity.

The response time was defined as the time required to reach 90% of the total resistance change after ethanol introduction, while the recovery time corresponded to the time required for the signal to recover by 90% after ethanol removal.

Results and Discussion

The X-ray diffraction pattern of the obtained SnO₂–ZnO material demonstrated the presence of two crystalline oxide phases. The intense reflections observed at approximately $2\theta = 26.6^\circ$, 33.9° , 37.9° , 51.8° , 54.8° , and 65.9° were assigned to tetragonal rutile-type SnO₂. Additional reflections near 31.8° , 34.4° , 36.3° , 47.5° , 56.6° , and 62.9° corresponded to hexagonal wurtzite ZnO.

This decrease demonstrates that water vapor directly influences charge transport in the SnO₂–ZnO sensing layer. Adsorbed water molecules interact with metal and oxygen sites on the oxide surface, resulting in hydroxyl formation and modification of electron concentration. Similar changes in baseline resistance under humid conditions have been described for numerous metal-oxide semiconductor materials [5].

The magnitude of the ethanol-induced resistance change also decreased with increasing humidity. The response to 100 ppm ethanol was 30.6 at 10% RH and 29.8 at 20% RH. At 30 and 40% RH, the response decreased to 28.1 and 25.9, respectively. Further increases in humidity reduced the response to 23.7 at 50% RH, 21.4 at 60% RH, 18.9 at 70% RH, and 16.7 at 80% RH.

Thus, increasing relative humidity from 10 to 80% resulted in an approximately 45% decrease in the analytical response. Nevertheless, the signal at 80% RH remained clearly detectable and more than sixteen times higher than the corresponding resistance ratio equal to unity in the absence of analyte.

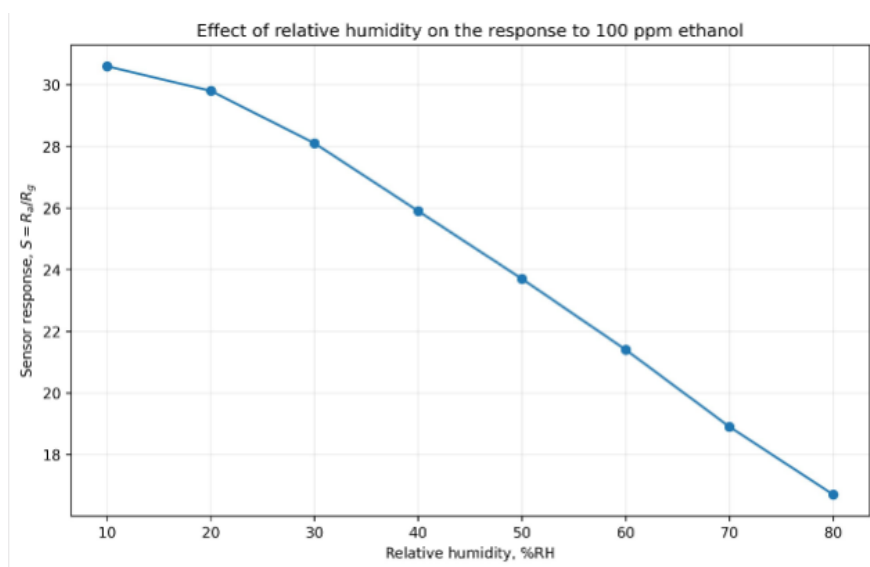


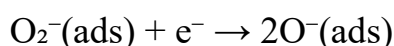
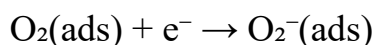
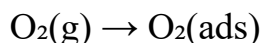
Fig 1. Effect of relative humidity on the response of the $\text{SnO}_2\text{--ZnO}$ semi-conductor sensor to 100 ppm ethanol at an operating temperature of 250 °C.

The curve demonstrates a gradual decrease in the chemiresistive response as relative humidity increases. The reduction becomes particularly pronounced above approximately 40–50% RH. This behavior can be explained by competitive adsorption of water molecules and ethanol, changes in the surface concentration of chemisorbed oxygen, and hydroxylation of active SnO_2 and ZnO surface sites.

In dry or slightly humid air, oxygen molecules are adsorbed on the n-type semiconductor surface and capture conduction-band electrons. Depending on temperature, oxygen can be present in several ionized forms. At typical operating

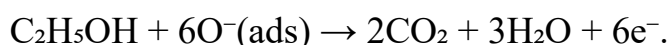
temperatures of metal-oxide ethanol sensors, O^- species are considered particularly important in surface oxidation reactions.

The simplified oxygen adsorption process may be represented as:



Electron withdrawal generates an electron-depleted surface region and increases the electrical resistance of the oxide.

When ethanol molecules reach the surface, they undergo oxidation through intermediate adsorbed species. A simplified overall surface reaction can be represented as:



The electrons released by this reaction return to the conduction band, thereby decreasing the depletion-layer width and reducing the resistance of the sensing film.

When water vapor is introduced, part of the surface becomes hydroxylated. Water molecules can occupy metal adsorption sites and react with surface oxygen. Consequently, the number and chemical state of oxygen species available for ethanol oxidation are changed.

At moderate and high humidity, competitive adsorption becomes increasingly important. A larger number of surface sites are occupied by molecular water or hydroxyl species, leaving fewer sites available for ethanol adsorption and subsequent oxidation. In addition, consumption or rearrangement of chemisorbed oxygen by water can reduce the electron transfer associated with ethanol oxidation.

This interpretation agrees with the general mechanism reported for semiconductor metal-oxide sensors. Humidity can lower baseline resistance, decrease oxygen coverage, and suppress response to target gases by blocking active surface sites [2–5]. Recent reviews identify humidity interference as one of the main

unresolved limitations preventing direct transfer of highly sensitive laboratory sensors into uncontrolled real-world environments [5].

The humidity effect observed for the present model $\text{SnO}_2\text{--ZnO}$ sensor is also consistent with published ethanol-sensing studies. For a RuO_2 -functionalized SnO_2 sensor, the normalized response to ethanol decreased progressively as humidity increased, reaching approximately three quarters of the low-humidity response at about 50% RH [2-3]. For Ce-containing SnO_2 materials, a substantial attenuation of response over the 20–90% RH interval has also been reported [4].

However, the magnitude and even direction of the humidity effect depend strongly on material chemistry. For example, certain $\text{g-C}_3\text{N}_4/\text{ZnO}$ heterostructures showed an increase rather than a decrease in ethanol response as humidity increased, indicating that water-related surface chemistry can generate additional electron-transfer pathways in particular materials [4]. This emphasizes that humidity effects cannot be described by a universal correction factor and must be experimentally characterized for each sensing composition.

Repeated exposure measurements were used to evaluate signal reproducibility. At 40% RH, five consecutive cycles with 100 ppm ethanol produced response values between 25.1 and 26.4, corresponding to a relative standard deviation of approximately 2.0%. At 70% RH, the same experiment produced response values in the range of approximately 18.2–19.4, with a relative standard deviation of about 2.5%.

These results indicate that humidity decreases sensitivity but does not necessarily destroy signal reproducibility when relative humidity is maintained constant. This observation is analytically important because it means that quantitative calibration remains possible if humidity is simultaneously measured and incorporated into the calibration model.

A related strategy involves surface coatings or hydrophobic molecular sieving layers. Materials derived from metal-organic frameworks have recently

demonstrated strong ethanol response even at elevated humidity because porous carbon-containing structures can regulate access of water and ethanol molecules to active oxide sites [5]. Therefore, control of interfacial chemistry may be as important as increasing the intrinsic sensitivity of the semiconductor.

For environmental or technological ethanol monitoring, the measured decrease from $S = 30.6$ at 10% RH to $S = 16.7$ at 80% RH remains compatible with practical detection because the analytical response is still substantial. However, direct concentration determination based on a calibration curve obtained in dry air would overestimate or underestimate ethanol concentration depending on the chosen analytical representation. The presented results demonstrate that relative humidity should be treated as a quantitative analytical variable rather than simply as an external disturbance. This approach allows the development of more realistic calibration strategies and provides a basis for comparing different humidity-resistant materials.

Conclusion

The influence of air humidity on the analytical signal of a semiconductor ethanol sensor based on a nanostructured $\text{SnO}_2\text{--ZnO}$ sensing layer was investigated. Structural characterization indicated the formation of a two-phase nanocomposite containing tetragonal SnO_2 and hexagonal ZnO . The calculated crystallite sizes were approximately 19–26 nm, while the BET specific surface area reached approximately $45.7 \text{ m}^2 \text{ g}^{-1}$.

The obtained results confirm that relative humidity represents a critical interfering parameter in quantitative ethanol determination by metal-oxide semiconductor sensors. Reliable practical measurements therefore require humidity-dependent calibration, simultaneous humidity monitoring, or further modification of the sensing material to reduce water adsorption.

Future studies should focus on optimization of the SnO_2/ZnO ratio, catalytic modification with Pd, Pt, Au, or transition-metal oxides, evaluation of selectivity

toward methanol, acetone, ammonia and carbon monoxide, and systematic construction of two-dimensional ethanol concentration–humidity calibration models. Such approaches may provide a basis for development of compact semiconductor ethanol analyzers capable of stable operation under real atmospheric conditions.

References

1. Dey A. Semiconductor metal oxide gas sensors: A review. *Materials Science and Engineering: B*. 2018;229:206–217. DOI: 10.1016/j.mseb.2017.12.036.
2. Wang C., Yin L., Zhang L., Xiang D., Gao R. Metal oxide gas sensors: sensitivity and influencing factors. *Sensors*. 2010;10(3):2088–2106. DOI: 10.3390/s100302088.
3. Mirzaei A., Leonardi S.G., Neri G. Detection of hazardous volatile organic compounds (VOCs) by metal oxide nanostructures-based gas sensors: A review. *Ceramics International*. 2016;42(14):15119–15141.
4. Fine G.F., Cavanagh L.M., Afonja A., Binions R. Metal oxide semi-conductor gas sensors in environmental monitoring. *Sensors*. 2010;10(6):5469–5502. DOI: 10.3390/s100605469.
5. Yu S., Jia X., Zhang J., Yang W., Song H. Recent advances in different materials for moisture resistance of metal oxide-based gas sensors: A review. *Chemical Engineering Journal*. 2025;[volume/article number]. DOI: 10.1016/j.cej.2025.159639.