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Fe_2O_3–silicone adhesive composite based humidity sensors

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This study presents the electrical properties of Fe_2O_3 based humidity sensors fabricated by the use of Fe_2O_3 powder and silicone liquid adhesive. For the fabrication of Cu/Fe_2O_3-Adhesive/Cu sensors, Fe_2O_3 powder was mixed in a 50 wt. % silicon liquid adhesive and then deposited between copper electrodes. These preliminary deposited Cu electrodes having 40 µm gap between them were deposited on glass substrates by vacuum thermal evaporation. The capacitance and dissipation of the sensors were measured under the effect of relative humidity (RH) and the resistance was calculated. It was found that with increase in humidity from 54%-94%, the resistance of the sensors decreases by 6375 times and capacitance increases by 5714 times respectively. The resistance and the capacitance-humidity relationships show significant change in the range of 54%-80% RH and 80%-94% RH respectively. The humidity dependent properties of the sensor make it attractive to be use in capacitive and resistive type humidity sensors. Thus it can be used in the humidity meters for environmental monitoring and assessment purposes.

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1. Introduction

Humidity sensors play very important role in the number of applications such as meteorology, building air-conditioning, nuclear reactors, automotives environmental monitoring, diagnostic and health caring, pharmaceutical, medical and food industry [1-8] etc.

Depending upon the basic sensing principles, humidity sensors are classified as resistive, capacitive, thermo-elemental [9], oscillating and mechanical [6]. Each type of sensors has specific application based on its unique advantages. Required parameters for efficient and commercially acceptable humidity sensor are wide range sensitivity, high accuracy, linear response [3, 5] short response and recovery time, small hysteresis [9], long term physical and chemical stability, low power consumption and low cost [10]. For fabrication of humidity sensors, organic and inorganic materials are used in the form of ceramics, composites and conducting polymers [3, 11].

Sensors are investigated in two designs; one is surface type and other is sandwich type configuration. It has been found that the sandwich type devices carry some demerits like complex technology, expensive processes and short circuiting, while the surface type devices provide the best alternative due to their simplicity and lower cost [12].

For humidity sensing polymers are used in their original form, polymers blend, doped polymers, copolymers or polymer composites with organic and inorganic semiconducting materials [12-16]. The working principles of humidity sensing polymers are different. Ionic polymers are based on variation of electrical conductivity or resistance with adsorption of water molecule [15]. The adsorption or desorption of water molecule causes a change in the dielectric constant of the polymer thin film lying between two electrodes and accordingly in the capacitance of the sensor.

In resistive type humidity sensors, the adsorption of water molecules causes to produce conductive ions due to ionization of polymer electrolyte [10] or changes due to doping. Generally with the increase in humidity and by dissociation of mobile carriers the conductivity of a polymer electrolyte increases [17].

Out of inorganic materials, iron oxide is widely used for the fabrication of humidity sensors [18]. Being an n-type semiconductor iron oxide (Fe_2O_3) has band gap of 2.1 eV. In addition to humidity sensing, Fe_2O_3 has potential applications in photoelectrodes, pigments, catalysis and sensors [19]. The humidity sensing mechanism is based on chemical and physical adsorption of water molecules [20], which results in change in electrical conductivity or capacitance [21]. Condensation of adsorbed water molecules takes place on the surface of materials and conduction in the condensed aquatic layers is carried out by the proton due to Grotthuss mechanism. Chen and Lu discussed in detail about this mechanism [1].

The study of humidity sensing properties of Fe_2O_3 has been presented in [22-25]. Polino et al. particularly reported the humidity sensitivity of silica-coated αhematite sintered pellets, which were investigated by volt-amperometric and impedance spectroscopy techniques [25]. Khalil et al. investigated humidity sensing properties of Fe_2O_3/SiO_2 composite (1:10 atomic ratio) [20]. The impedance spectroscopy and DC electrical conductivity of large area sample (1mm thick and 13 mm dia. pellets) was measured. It is concluded that after the formation of first chemisorbed layer of water, there is no more effect of increase in humidity on the conductivity, while the observed increase in conductivity with increase in humidity is credited to percolation conduction. In this conduction hopping of ions takes place in a percolating network, which is produced by physisorbed layers of water. Neri et al. studied the humidity sensing properties of Li and Au doped Fe_2O_3 thin films fabricated by liquid-phase deposition (LPD) technique and concluded that Li increases the sensitivity by providing preferential adsorption sites for hydrogen, while the Au reduces the resistance baseline drift by stabilizing the phases of amorphous iron oxide [18]. In another study Neri et al. also investigated the humidity sensors based on thin films of iron oxide doped with Li^+, Zn^{+2} and Au^{+3} [26]. On the base of experimental results they concluded that humidity sensing properties are correlated with charge density and concentration of dopants on the surface.

In continuance of our efforts for the development of a variety of sensors [27-28], we are presenting the properties of the humidity sensors based on the Fe_2O_3 and silicone adhesive composite.

2. Experimental

For the fabrication of Cu/Fe_2O_3-Adhesive/Cu humidity sensors, commercially available Fe_2O_3 powder was used, which was produced by Riedel-de Haen (Germany). The average particle size of powder was 0.78 µm, which was analyzed by Shimadzu SACP-3 particles size distribution analyzer. To make the composite, the Fe_2O_3 powder and silicone liquid adhesive (50 wt. %) were mixed, while the composite was deposited between copper electrodes by drop-casting. The 100 nm thick and 10 mm long Cu electrodes having 40 µm gaps between them were preliminary deposited on glass substrates by vacuum thermal evaporation. The average thickness of the composite's layers was equal to 100 µm. The composite layers showed good adhesion to the substrate, and stability of properties. The Fig. 1 shows schematic diagram of the Cu/Fe_2O_3-Adhesive/Cu humidity sensor.

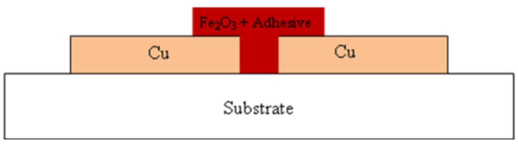

Fig. 1. Cross-sectional view of the Cu/Fe_2O_3-Adhesive/Cu humidity sensor.

The fabricated devices were dried at room temperature for three days. The change in capacitance (*C*) and dissipation (*D*) were measured with respect to change in relative humidity by using indigenously made humidity chamber (which was fabricated in our laboratory) and ESCORT ELC–3133A digital display LCR meter. Humidity and temperature inside the humidity chamber were measured by the digital hygrometer, made by Fisher Scientific. The results of measurements were recorded and used for the calculation of resistance. The resistance (*R*) of the samples was determined from the values of capacitance and dissipation by using following expression [29].

$$R = 1/(2\pi f C D) \quad (1)$$

where *f* is frequency.

3. Results and discussion

The resistance-humidity relationship for the Cu/ Fe_2O_3 adhesive/Cu sensor at a frequency of 100 Hz is shown in Fig. 2. The relative resistance-humidity relationship is shown in Fig. 3, where it can be seen that the resistance decreases by 6375 times as humidity increases from 54 % to 94 %, while change in resistance is more significant in the humidity range of 54 to 80 %.

The capacitance-humidity and relative capacitance-humidity relationships of the sensor are shown in Fig. 4 and Fig. 5 respectively. It can be seen that capacitance increases by 5714 times due to 50% increase in humidity. The abrupt change in capacitance is observed in the humidity range of 80% to 94% RH. The presented results show that from the sensitivity point of view, the resistance and the capacitance measurements are complementary for the measurement of humidity in a wide range, particularly, from 54% to 94% RH.

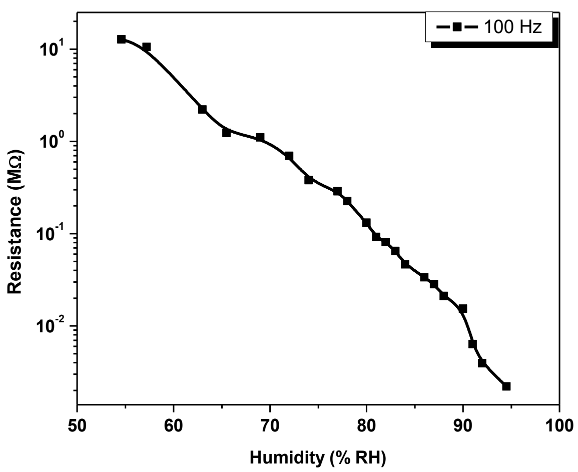

Fig. 2. Resistance-humidity relationship for the Cu/ Fe_2O_3-Adhesive/Cu sensor at a frequency of 100 Hz.

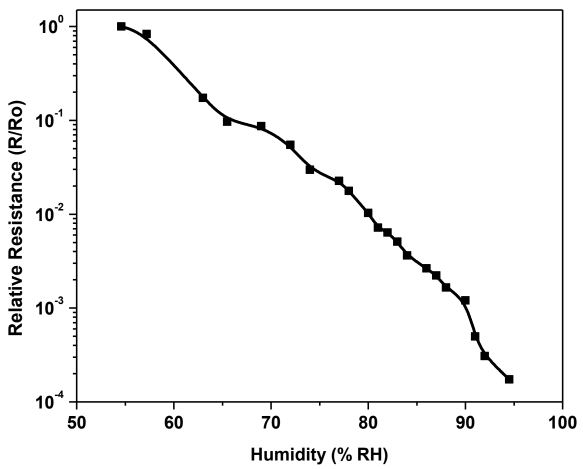

Fig. 3. Relative resistance (R/R_o) humidity relationship for the Cu/ Fe_2O_3-Adhesive/Cu sensor at a frequency of 100 Hz. R_o is initial resistance at RH=54%.

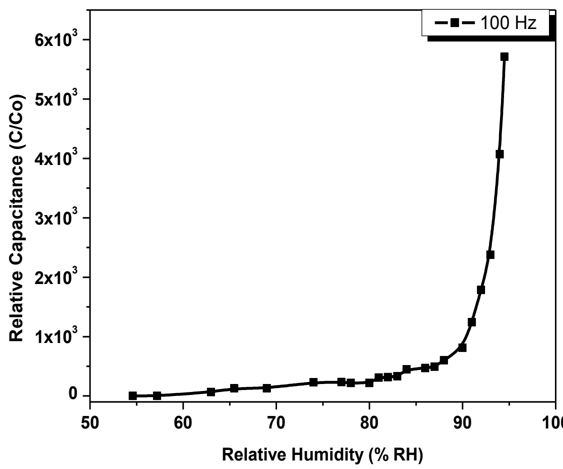

Fig. 5. Relative capacitance (C/C_o) humidity relationship for the Cu/ Fe_2O_3-Adhesive/Cu sensor at a frequency of 100 Hz. C_o is initial capacitance at RH=54%.

This large decrease in resistance in lower humidity range may be due to the following reasons

i) Donation of electrons to the metal oxide by chemisorptions

ii) Occurrence of ionic conductivity due to little absorption of water

While the decrease in resistance is small in the upper range of humidity and H^+ is responsible for conduction in this range [20, 30]. In the lower humidity range increase in capacitance is small and it increases abruptly in higher humidity range. On the exposure of sensor to the humid atmosphere, initially at the lower humidity, water vapors adsorb (chemisorbed) on the surface and physisorption starts as the humidity increases. Due to high dielectric constant of water these physisorbed aquatic layers are one of the reasons for increase in capacitance in this range of humidity.

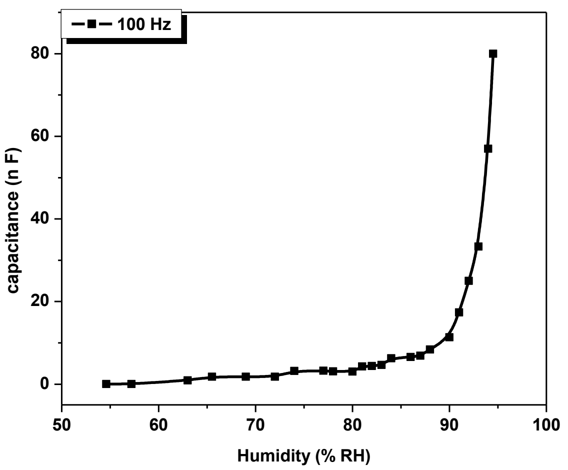

Fig. 4. Capacitance-humidity relationship for Cu/Fe_2O_3-Adhesive/Cu sensor at a frequency of 100 Hz.

Moreover, other reasons behind the decrease in resistance and increase in capacitance with increase in humidity may be the following [31-35]: absorption of water molecule in the composite layer, which increases the dielectric constant and decreases the resistance due to displacement current, doping of the composite and formation of charge transfer complexes. There are number of factors, which affect the capacitance of the sensor. They are relative dielectric constant of the thin film material, area of electrodes, and gap between electrodes. Capacitance relies upon material's polarizability, sources of which are electronic (α_e), dipolar (α_{dip}) and ionic (α_i) [36]. Another form of polarizability due to transfer of charge carriers (electrons and holes) at normal conditions is also reported [35, 37-38]. In general due to relative displacement of orbital electrons, electronic polarizability occurs, which possibly at higher frequencies (>1000 Hz) affect the capacitance measurements. On the basis of sensor response, it is assumed that by the absorption of water molecules in the composite layer the dipolar polarizability of the sensor increases.

The simulation of capacitance-humidity and resistance-humidity relationships is done by the following exponential function [36].

$$f(x) = e^x \quad (2)$$

In case of capacitance-humidity relationship the above function has been modified as given in Eq.3.

$$C/C_o = e^{k_1 \Delta H (H/H_m)} \quad (3)$$

Where ΔH is the change in humidity, H and H_m are the initial and maximum relative humidity respectively. The k_1 is the constant having value of 0.2168/% RH and it is also called humidity capacitive factor. Fig. 6 shows the comparison of experimental and simulated capacitance with respect to relative humidity. It can be seen that there is a reasonable matching in the experimental and simulated curves.

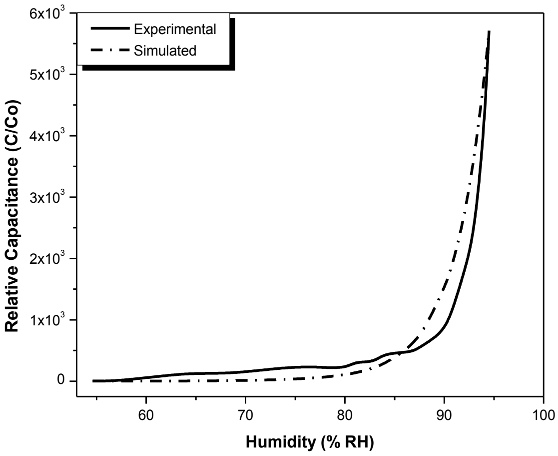

Fig. 6. Comparison of experimental and simulated capacitance of the sensor with respect to relative humidity.

For the simulation of resistance-humidity relationship exponential function given in Eq.2 is modified in the following way

$$R/R_o = e^{k_2 \Delta H(H/H_m)} \quad (4)$$

Where ΔH is the change in humidity, H and H_m are the initial and maximum relative humidity respectively. The k_2 is the constant having value of -0.217/% RH and it is also called humidity resistive factor. The comparison of experimental and simulated results is shown in Fig. 7 and it is evident that the simulated and experimental results are in good agreement with each other.

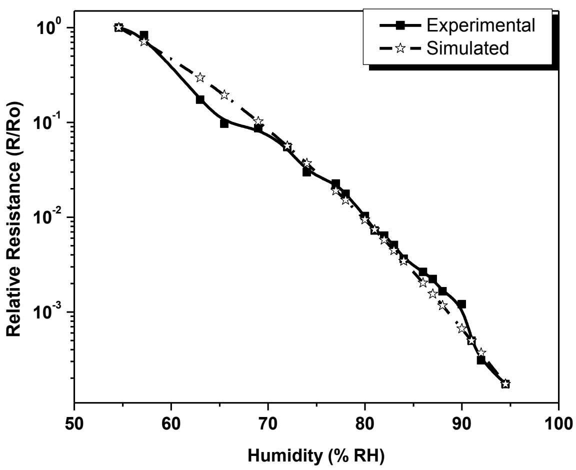

Fig. 7. Comparison of experimental and simulated resistance-humidity relationship of the sensor.

The future work will be devoted to optimization of simulation approximation in order to make simulation results more close to experimental data.

4. Conclusion

Surface type humidity sensors based on Fe_2O_3 and silicone adhesive composite layers have been fabricated. The composite layers show good adhesion to the substrate and stability of the properties. The effect of relative humidity on resistance and capacitance of the sensor has been studied in the humidity range of 54 % to 94 %. Results reveal that with increase in humidity resistance decreases and capacitance increases. The resistive and the capacitive sensitivity allow to measure humidity at wide range of values. Due to their wide sensing range, these sensors are suitable for designing a cheaper, simpler and efficient meter for the measurement of humidity for the purpose of environmental monitoring.

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