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Fabrication and Characterization of Organic-Inorganic (Orange Dye-Vanadium Oxide) Composite Based Humidity Sensors

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The orange dye-vanadium oxide (OD-V_2O_5) composite films were deposited from their aqueous suspension at various gravity conditions: at normal (positive) gravity (+1g) and negative gravity (-1g) by drop casting on to the surface type substrates having silver electrodes which were deposited by vacuum thermal evaporation. The aqueous suspension was prepared by dissolving and mixing OD and V_2O_5 in a distilled water with 2:1 wt%, respectively. The area of each silver electrode was 5x5 mm^2 and the gap between two electrodes was 30 µm, while the thickness of composite films was 10 µm. The effect of humidity on electrical parameters (capacitance and impedance) of the films were studied and it was observed that with rising humidity the impedance of all the samples decreased up to 30333 times while the capacitance increased up to 2000 times. The samples deposited at +1g showed more sensitivity (-2.6 MΩ/%RH) towards humidity as compared to samples deposited at -1g (-1.89 MΩ/%RH). These results are explained by influence of positive and negative gravity, surface tension forces and composition of the solution on the film formation.

Keywords: Organic semiconductor; Orange dye-vanadium oxide composite; drop-casting; gravity method; humidity sensing.

1. INTRODUCTION

Study of the effect of humidity on the characteristics of the semiconductors is important from the point of technology and applications. Humidity sensors play an important role in assessing the environmental conditions [1-3] and are often used in industrial applications. Based on their measuring principles, they have several categories; such as resistive, capacitive, gravimetric, hydrometric, integrated and optical types [4-8]. The nature of sensors fabricating hygroscopic materials and the design of sensors mainly control their performance [9].

To fabricate a humidity sensor, various sensing materials and techniques are reported in literature. The capacitive type humidity sensors based on porous silicon have been fabricated by bulk micromachining and surface micromachining techniques [10, 11]. For the manufacturing of humidity and temperature sensors a technique known as thin-film surface-micromachining was suggested in 2001 [12]. Among the capacitive type sensing materials the polyimide [13, 14] and cellulose acetate butyrate [15, 16] are extensively used for the fabrication of capacitive type humidity sensors. Karimov *et al*. in 2008 reported a plainer construction of capacitive humidity sensors using copper phthalocyanine (CuPc) films [17]. They reported up to 200 times increase in the capacitance value by increasing ambient humidity.

The humidity effects on the conductivity (electrical) of single-walled carbon nanotubes (SWNTs) were studied by many researchers and it was described that H_2O molecules play a role of donor and alter their electrical characteristics [18-21]. Whereas, in double-walled carbon nanotubes (DWNTs) the water molecules act as an acceptor [22]. Furthermore, it was also observed that in the presence of humidity the DWNTs also act as electric dipole by transferring outer tubes electron to inter-wall region [22]. On exposing MWNTs (multi-walled carbon nanotubes) to humidity, variation in impedance was noted by Ref. [23] and it was credited to *p*-type conduction of nanotubes (MWNTs). Moreover, it is reported that ambient humidity causes to change the Schottky barrier's height that arises between metallic electrode and *p*-type MWNTs [23]. Analysis of the above mentioned papers show that response to effect of humidity of CNTs depends of : (i) technology of fabrication , (ii) kind of CNT, (iii) structure of sample and (iiii) range of humidity. Usually the resistances of the samples was changed at the effect of humidity from 1.2 [21] to 5 [19] times.
Moreover, the graphene and graphene oxide due to their hydrophilic nature and admirable electronic, mechanical and thermal properties are also being investigated for humidity sensing. Their sensing mechanism is based on change in resistance in response to humidity [24-26].

In Ref. [27] the OD-PANI composite based humidity sensors were fabricated by drop-casting and tested in the range of 30%-90% RH. It was observed that with increase in humidity the capacitance increased and the impedance exponentially. On humidification and dehumidification hysteresis was observed in the impedance-humidity and capacitance-humidity relationships of the sensors having large thickness that may be the result of the differences in the diffusion rates of water molecules in these processes.

An organic/inorganic nanocomposites based interdigitated thin film humidity sensor was investigated [28]. The composite was comprised of MPTMS (3-mercaptopropyltrimethoxysilane), PSDA(poly diphenylamine sulfonic acid) and nano-ZnO. Investigation of the effect of humidity on organic semiconductors is important from practical point of view. At the same time these researches may deepen knowledge about the basic properties of materials fabricated in different conditions. This article is the continuation of our work for the investigation of the properties of organic and composite materials and devices [7, 8, 27, 29-33]. Here, we present fabrication of orange dye-V_2O_5 composite based samples in different gravity conditions (positive (+1g) and negative (-1g) gravity) and the results of investigations of their properties under the effect of humidity.

2. EXPERIMENTAL

The commercially available (from Sigma Aldrich) V_2O_5 powder and orange dye (OD) were used for the deposition of films. The molecular structure of the orange dye is shown in Fig.1 and its IUPAC name is 3-(ethyl{4-[(4-nitrophenyl)diazenyl]phenyl}amino)propanenitrile. The aqueous suspension was prepared by dissolving 10wt.% of OD in a distilled water followed by mixing of 5wt.% of V_2O_5. The OD shows good water solubility while V_2O_5 makes suspension. The composite films were deposited in to the gap between two silver electrodes. These electrodes on glass substrates had a gap of 30µm were preliminary deposited by vacuum thermal evaporation. The width and the thickness of electrodes were 5 mm and 100 nm, respectively. The thickness of composite film was 10 µm. The schematic illustration of samples with surface-type silver electrodes and OD-V_2O_5 film is shown in Fig.2.

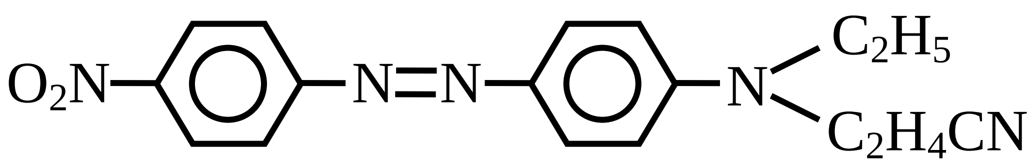

Figure 1. The orange dye's Molecular structure

Figure 2. Schematic illustration of sample with surface-type silver electrodes and OD-V_2O_5 film

The films were deposited simply by solution deposition of OD-V_2O_5 composite at +1g and -1g by the following way: the substrates were fixed in horizontal position, for +1g deposition the drop of solution was put on the top of the substrate (as shown in Fig.2) where silver electrodes were faced up. For -1g deposition the drop was put to the substrate from below (opposite to the position which shown in Fig.2) where silver electrodes were faced down. In +1g deposition the resultant force which affects the drop and deposition of the thin film was sum of the gravity and surface tension forces. In -1g deposition the resultant force which affects the drop and deposition of the film as well was difference of gravity force and surface tension force, i.e. small force. So, during positive gravity deposition the gravity force exerts pressure on the drop, while during negative gravity deposition the gravity force pulls down the drop in vertical direction. As the conditions of film deposition at +1g and -1g were different, then different properties of the films could be expected. The details of the films deposition will be described elsewhere. For the measurement of humidity and temperature TECPEL 322 meter was used. Impedance and capacitance at 1kHz were measured by use of LCR meter MT 4090. The AFM images were made by use of FlexAFM (Nanosurf). All the experiments were carried out at room temperature in a conventional humidity chamber.

3. RESULTS AND DISCUSSION

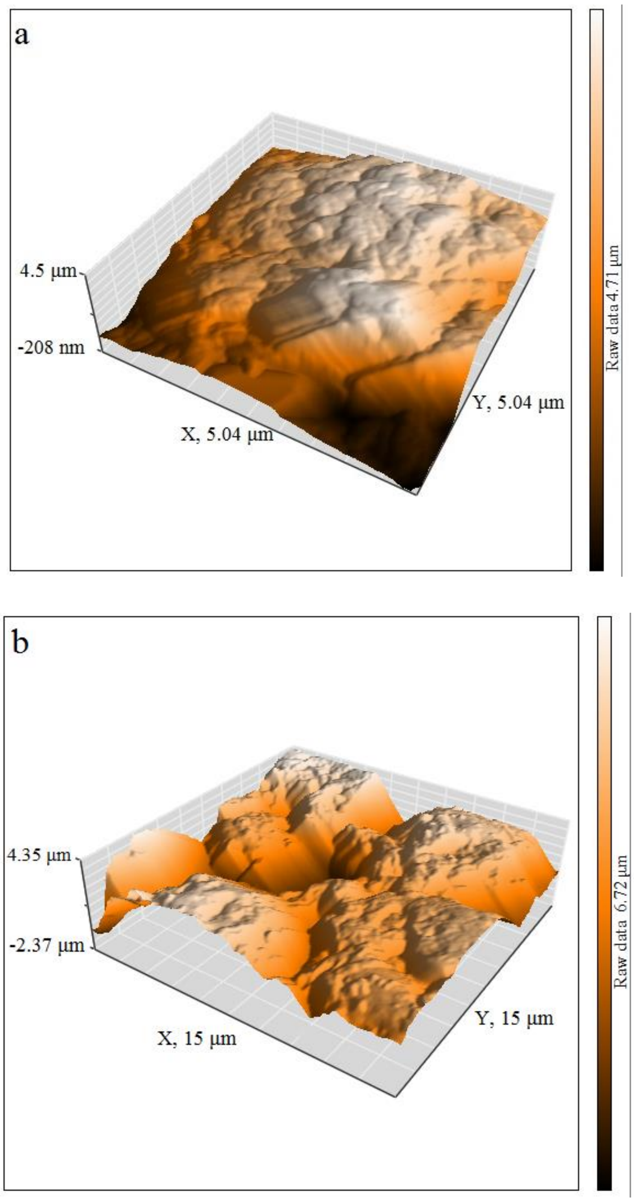

Figure 3. AFM images of the OD-V_2O_5 composite films deposited at (a) +1g and (b) -1g

Figure 3a and 3b show AFM images of OD-V_2O_5 films deposited at +1g and -1g, respectively. The highly developed surfaces show that these films are very suitable for humidity sensing. The higher surface area increases the sensitivity of the film.

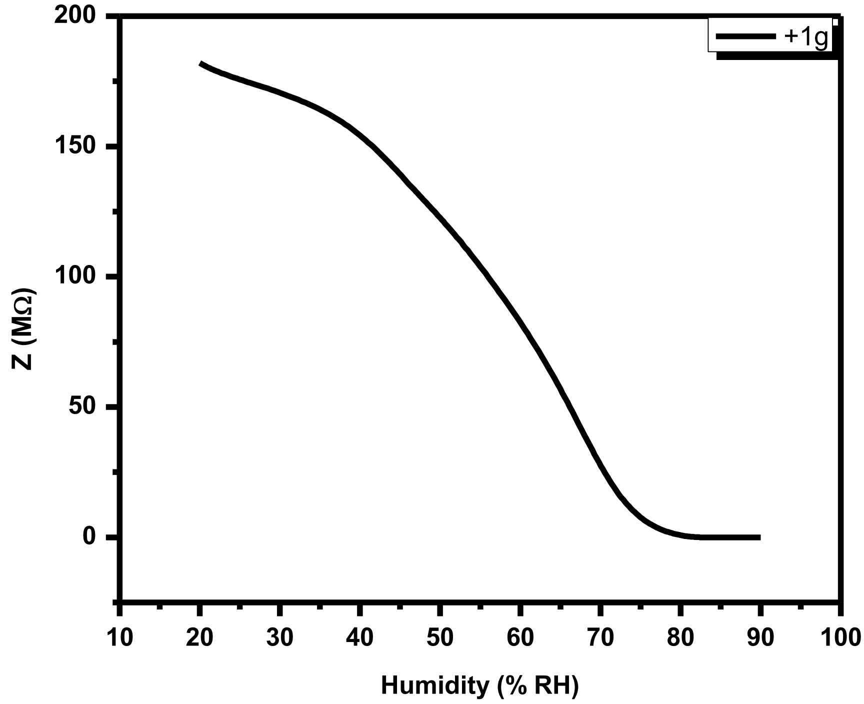

Figure 4. Effect of humidity on the impedance of sample having OD-V_2O_5 composite film deposited at gravity of +1g

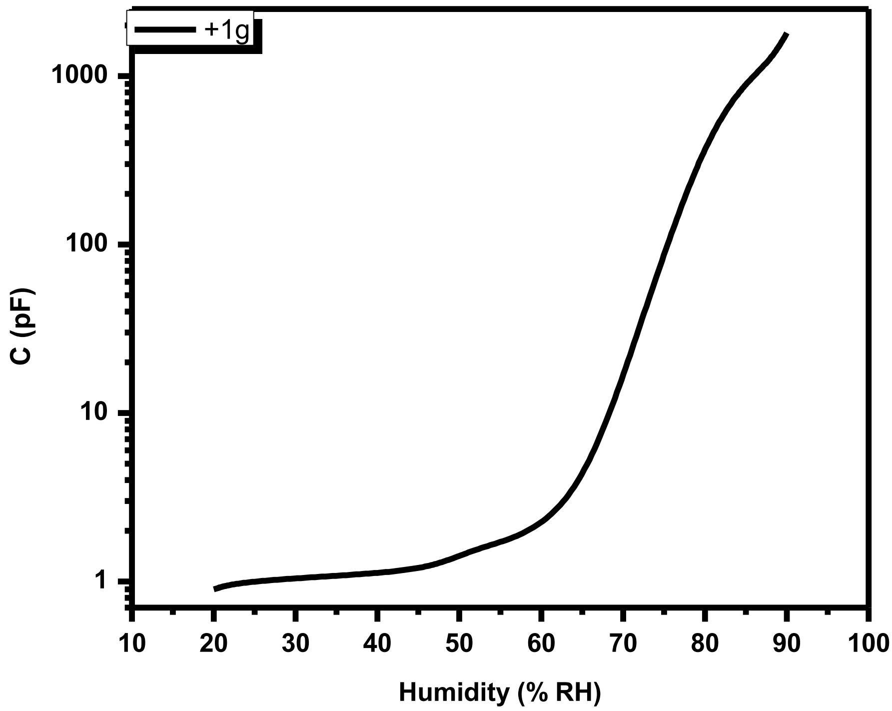

Figure 5. Effect of humidity on the capacitance of sample having OD-V_2O_5 composite film deposited at gravity of +1g

The effect of humidity on the impedance and capacitance of the sample having OD-V_2O_5 composite film deposited at gravity of +1g is shown in Fig.4 and Fig.5, respectively. It can be seen that with increase in humidity the impedance decreases and the capacitance rises.

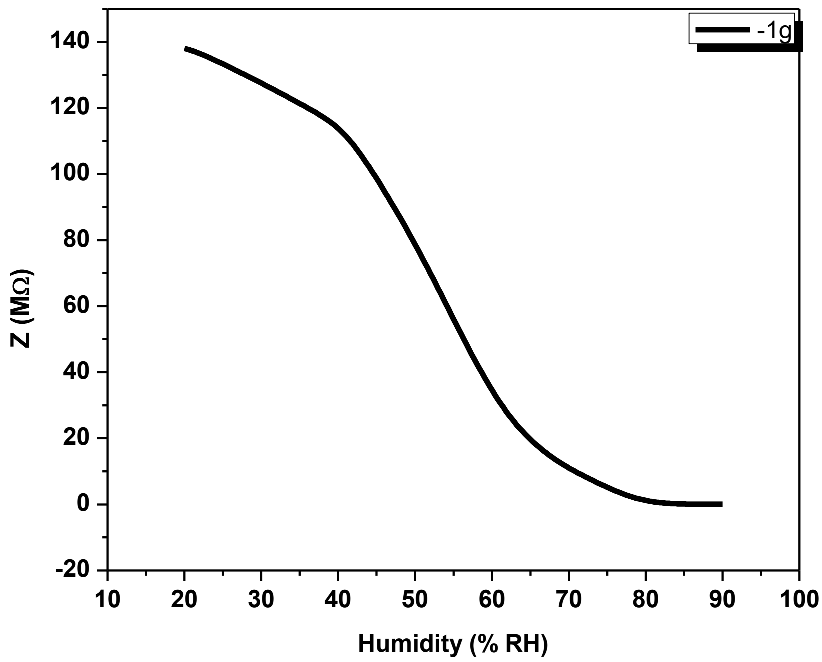

Figure 6. Effect of humidity on the impedance of sample having OD-V_2O_5 composite film deposited at gravity of -1g

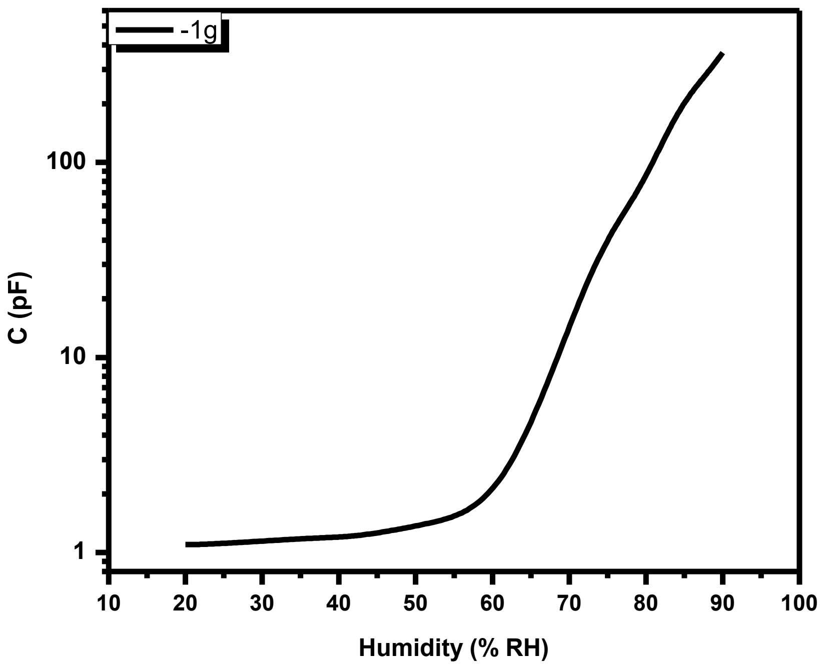

Figure 7. Effect of humidity on the capacitance of sample having OD-V_2O_5 composite film deposited at gravity of -1g

The effect of humidity on the impedance and capacitance of the sample having OD-V_2O_5 composite film deposited at gravity of -1g is shown in Fig.6 and Fig.7, respectively. It can be seen that the result, in principle, are similar to the relationships shown in Fig.4 and Fig.5.

On the investigation of adsorption-desorption behavior the hysteresis was observed between 70% RH and 30% RH. The maximum value of hysteresis was up to 7% for impedance-humidity relationship and up to 6% for capacitance-humidity relationship. The adsorption-desorption behavior of sample prepared at +1g is shown in Fig.8. Moreover, the response recovery times of the sensors were also measured and it was found that the response time was in the range of 13s to 16s, while the recovery time was in the range of 40s to 46s.

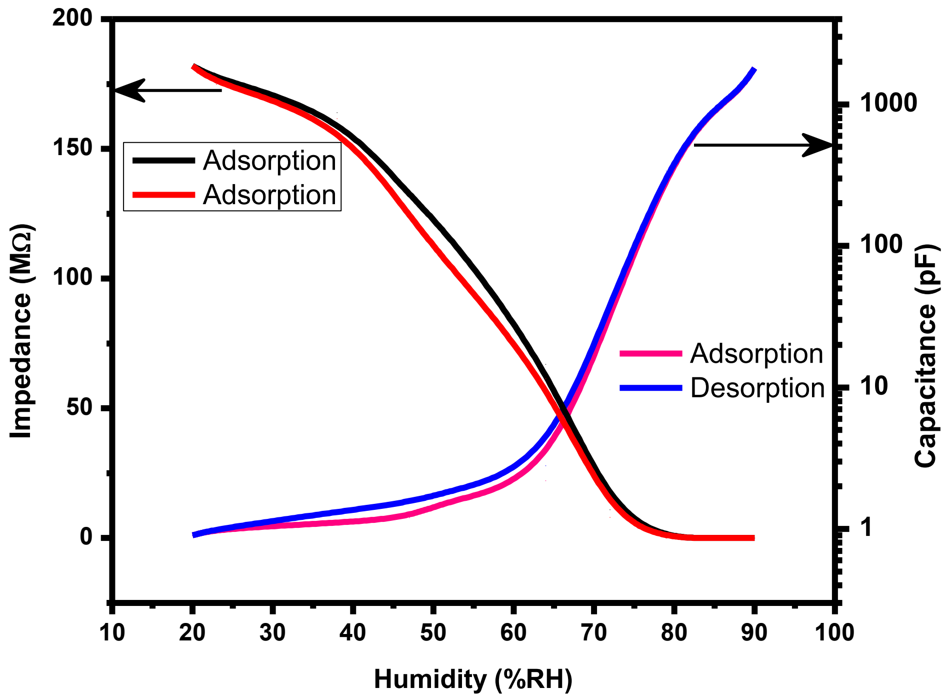

Figure 8. Adsorption-desorption behavior of the sample prepared at +1g

In Table 1 the data of the humidity effect on the capacitance and impedance of the OD-V_2O_5 composite fabricated at acceleration of +1g and -1g are presented.

Table 1. The humidity effect on the capacitance (C) and impedance (Z) of OD-V_2O_5 composite samples at 1kHz.

Sr. No	Sample composition	Film deposited at acceleration	Humidity Range (%RH)	Z(MΩ) (RH=20%)	C(pF) (RH=20%)	Z_H/Z_L	C_H/C_L
1	OD-V_2O_5	+1g	20-90	182	0.9	30,333	2000
2	OD-V_2O_5	-1g	20-90	132	1.1	6,900	333

Z_H and C_H are highest values of impedance and capacitance, Z_L and C_L are the lowest values of impedance and capacitance.

Table 1 shows that OD+V2O5 samples have higher values of initial impedance and lower value of initial capacitance for the sample deposited at +1g. The Z_H/Z_L and C_H/C_L ratios are higher in the case of OD+V2O5 samples deposited at +1g with respect to the samples deposited at -1g. It may be due to the films deposition conditions, i.e. deposition of the films at +1g and -1g. In particular, in the case of film deposition at +1g the resultant gravity and surface tension forces are larger than in the case of deposition at -1g. It means at -1g film deposition from solution take place at lower gravity force. As it is known that gravity conditions crucially effect the properties of the samples [34]. From theoretical and practical points it would be very interesting that films may be deposited at resultant force equal to or around of ~0, i.e. at weightless or quasi-weightless conditions. By changing the composition of solution such conditions can be achieved where the resultant force would be equal or close to zero.

A resistance-capacitance parallel connection can be used to represent the sample's impedance (Fig.9).

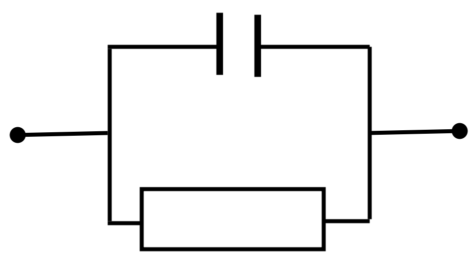

Figure 9. Sample's equivalent electric-circuit

Electronically the relationship among the impedance (Z), capacitance (C) and resistance (R) is the following [35]:

$$Z = R/(1 + j\omega RC) \quad (1)$$

It is well-known that the capacitance is dependent on the material's polarizability, there are many basic sources of polarizability such as ionic (α_i), electronic (α_e) and dipolar (α_{dip}) polarizability [36]. In current situation important role is played by dipolar (α_{dip}) polarizability because of the existence of absorbed H_2O (dipoles) in the OD and/or composite. Electronic polarizability which exist because of relative displacement of orbital electrons is universal. The charge-transfer complexes are also formed because of H_2O molecules in OD and/or composite; it is also considered that the ionic polarization occurs in organic materials as well.

The increase in sample's capacitance with rising humidity may be elucidated as follows; The absorption and adsorption of H_2O molecules causes to increase sample's dielectric permittivity because of their higher dielectric permittivity. This takes place on diffusion of water molecules from surface to bulk of humidity sensitive film. In this process it may considered that water molecules play a role of filler that first of all contribute to humidity properties, while the orange dye-V_2O_5 composite plays a role of matrix. This matrix also contribute to the parameters of the humidity sensor mostly through initial values of the impedance and capacitance at low concentration of the water molecules in the samples. The role of only orange dye in humidity sensing was investigated earlier by our group [37]. Furthermore, such behavior of the sensor (rising capacitance and lowering impedance) may be regarded to existence of displacement current (firstly) and occurrence of possible doping of sensing material (secondly) because H_2O molecules. In addition to above rising concentration of charges and increase in polarizability are also considered responsible for this type of behavior. The detailed description of above mechanisms concerning to some solids is given in Ref. [36].

Simulation of capacitance-humidity and impedance-humidity relationships can be done by use of Clausius-Mosotti equation [36] which was used in a number of papers by us [38, 39].

The humidity sensitivity (S) of OD-V_2O_5 composites samples with regards to impedance and capacitance can be estimated as [40]:

$$s(Z) = {}^{\Delta Z}/_{\Delta RH} \quad (2)$$

$$S(C) = {}^{\Delta C}/_{\Delta RH} \quad (3)$$

where *ΔZ*, *ΔRH* and *ΔC* represent the change in impedance, relative humidity and capacitance, respectively. By use of the experimental results presented in the Fig.4 to Fig.7 it can be shown that *S(Z)* and *S(C)* values of the OD-V_2O_5 samples deposited at +1g, and -1g are equal to -2.6MΩ/% and 26 pF/%, and -1.89 MΩ/% and 5pF/% on average. The comparison of obtained results with previously reported results is given below in Table-2

Table 2. comparison of obtained results with previously reported results

Sr.#	Sensing Material	Range (%RH)	Sensitivity (MΩ/%RH)	Ref.
1	OD	25-98	-2.29	[41]
2	OD-CNT	25-98	-0.16	[41]
3	OD-PANI	30-90	-1.66	[27]
4	V_2O_5	11-97	0.0035	[42]
5	V_2O_5-Doped TiO2:WO3	10-100	-0.77	[43]
6	OD-V_2O_5	20-90	-2.6	Current study

4. CONCLUSION

1. By the use of energy saving technologies such as solution deposition, the OD-V_2O_5 composite films were deposited. The humidity sensors were fabricated from the aqueous solution at different gravity conditions: at positive (normal) gravity (+1g) and negative gravity (-1g) by drop-casting on the surface-type substrates having silver electrodes, which were deposited by vacuum thermal evaporation.

2. For the OD-V_2O_5 composite samples, it was found that under the humidity effect the capacitance and impedance of the samples deposited at +1g changed more with respect to the samples deposited at -1g.

3. The technology of films deposition at different gravity conditions (+1g and -1g) was used to fabricate humidity sensors that can be applied for environmental assessment and monitoring and also as a teaching aid.

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