

Optical humidity-sensitive mechanism based on refractive index variation

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A novel composite model is put forward for humidity-sensitive material based on Maxwell-Garnett and effective medium theory. The analytical expression of the relation between effective refractive index and relative humidity is shown with different absorption factors and porosities. The larger the absorption factor is, the higher the refractive index is. The refractive index of humidity-sensitive SiO₂ film decreases with the increase of ceramic material porosity. The sensitivity of optical humidity sensor can reach the magnitude of 10⁻³. In comparison with the experimental humidity-sensing curve by the method of p-polarized reflectance and the analysis of mechanism, theoretical simulation is in agreement with experimental results. Therefore, this composite model is proved to be reasonable which lays new theoretical foundation in further research on optical humidity sensor.

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Relative humidity (RH) is the ratio of the actual partial vapor pressure of water to the saturation vapor pressure at the same temperature. Humidity sensing is important in various areas such as industrial process control in semiconductor facilities, pharmaceutical facilities, geotechnical and agricultural measurements^[1]. Recently, most of the commercial humidity sensors are electrical types which are dependent on the changes in electrical resistance or capacitance. Electrical humidity sensors are prone to electro-magnetic interference (EMI), so their readings would be influenced^[2]. The long-term stability of the sensors is also a problem because the lifetime of the sensor is susceptible to corrosion in high humidity environments. There is also the difficulty to perform remote sensing using electrical sensors. With the development of optical fibers and optical integration technology, the optical humidity sensors are studied and used widely. Optical humidity sensors make use of the change in the optical propagation property (such as light intensity, frequency or phase, etc.) to detect moisture in varying humidity environment. The advantages of optical humidity sensor include immunity to EMI, corrosion free, long lifetime, and remote sensing ability^[3].

At present, several kinds of theory for electrical humidity-sensing mechanism have been put forward, such as electron conductive mechanism, ion conductive mechanism, and electron-ion conductive mechanism^[4-6]. However, very few reports are available for optical humidity-sensing mechanism^[3].

In this letter, we present the optical humidity-sensing mechanism based on refractive index variation of humidity-sensing film material. At first, a composite model for humidity-sensitive ceramic material is set up. Next, based on Maxwell-Garnett and effective medium theory, the analytical expression of the relation between effective refractive index and RH is shown with differ-

ent absorption factors and porosities. The theoretical simulation is coincident with the experimental humidity-sensing curve by the method of p-polarized reflectance.

Owing to a certain volume fraction of pores in ceramic materials, the adsorption of water molecules on ceramic materials will induce an increase in thin film effective refractive index when RH of the environment increases^[7]. Humidity-sensitive ceramic material is composed of water layer, air, and material grain whose microstructure is close to an ellipsoid, as shown in Fig. 1. When varying humidity circumstance, the material ellipsoidal grain will adsorb the water in the air. Then, water molecules aggregate to form water layer around the grain. The crystalline grain and its ambient water layer are regarded as a complex. Further, the composite model is made up of the air medium and the complex of crystalline grain and water layer.

In dielectric physics^[8], there are various effective medium theories to describe the optical properties between metal-medium complexes. Among these, Maxwell-Garnett and Bruggeman approximation theories are suitable for our composite model which is composed of material crystalline grain, water layer, and pores. The crystalline grain and its ambient water layer are considered as a complex. According to Maxwell-Garnett theory, the dielectric constant of the complex can be expressed as^[9]

$$\varepsilon_3 = \varepsilon_2 \frac{1 + 2/3f_1a_1}{1 - 1/3f_1a_1}, \quad (1)$$

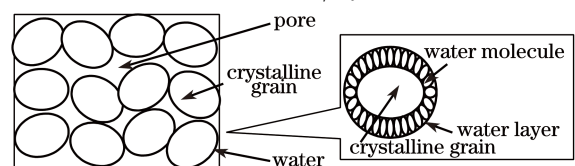


Fig. 1. Microstructure of humidity-sensitive ceramic material.

where footnotes 1, 2, and 3 represent crystalline grain, water layer, and the complex, respectively, ε_2 is the dielectric constants of water, f_1 is the ceramic material volume fraction, and a_1 is expressed as

$$a_1 = \frac{1}{3} \sum_{j=1}^3 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_2 + L_j (\varepsilon_1 - \varepsilon_2)},$$

where L_1 , L_2 , and L_3 are elliptic depolarization factors in a , b , and c axis, respectively, and $L_1 + L_2 + L_3 = 1$. Assuming that ellipsoid is ideal, which stands for $a = b$, $a/c = 2$, and $L_1 = L_2 = 0.4$, $L_3 = 0.2$.

Air medium and the complex of crystalline grain and water layer conform to the Bruggeman effective medium theory^[10]. With the polarization vector definition and the sum of the polarization vector being zero, the effective dielectric constant ε of the whole composite model has the expressions as

$$\sum_{i=3}^4 \vec{P}_i = 0, \quad (2)$$

$$\vec{P}_i = \frac{1}{3} f_i a_i \vec{E}_0 \quad (i = 3, 4), \quad (3)$$

$$a_i = \frac{1}{3} \sum_{j=1}^3 \frac{(\varepsilon_i - \varepsilon)}{\varepsilon + L_j (\varepsilon_i - \varepsilon)}, \quad (4)$$

where f_3 is the complex volume fraction of crystalline grain and water layer, f_4 is ceramic material pores volume fraction that is porosity, \vec{E}_0 is the electric field intensity of external electric field which leads to polarization.

From Eqs. (1)–(4), we can obtain

$$\sum_{j=1}^3 \frac{(\varepsilon_3 - \varepsilon) f_3}{\varepsilon + L_j (\varepsilon_3 - \varepsilon)} + \sum_{j=1}^3 \frac{(\varepsilon_4 - \varepsilon) f_4}{\varepsilon + L_j (\varepsilon_4 - \varepsilon)} = 0. \quad (5)$$

Obviously, $f_3 = 1 - f_4$.

Maxwell equations show that the square of refractive index n^2 equals the dielectric constant. Without considering any other factors, the effective refractive index n of the whole composite model is obtained by the Bruggeman approximation of a two-component material. The expression can be obtained from Eq. (5) as

$$f_3 \frac{n_3^2 - n^2}{n_3^2 + 2n^2} + f_4 \frac{n_4^2 - n^2}{n_4^2 + 2n^2} = 0, \quad (6)$$

where n_3 and n_4 are the refractive indices of the complex of crystalline grain and water layer and the pores, respectively. Equation (6) can be also written as,

$$b_2 n^4 + b_1 n^2 + b_0 = 0, \quad (7)$$

where

$$\begin{aligned} b_0 &= (f_4 + f_3) n_3^2 n_4^2, \\ b_1 &= n_3^2 (2f_3 - f_4) + n_4^2 (2f_4 - f_3), \\ b_2 &= -2(f_3 + f_4) n_3^2. \end{aligned} \quad (8)$$

Suppose that the number of adsorbed water molecules is in proportion with the environmental RH. In linear approximation^[11], there is,

$$f_2 = Q^x f_4, \quad (9)$$

where Q is the RH, x is the adsorption factor which represents the adsorption ability of humidity-sensitive materials.

In this work, we use sol-gel process to prepare SiO₂ film as humidity-sensitive material which has a high thermal stability and chemical stability. In numerical simulation, the refractive indices of SiO₂, water, and air are 1.453, 1.329, and 1, respectively.

According to the actual characteristics of sol-gel process and the experimental conditions, SiO₂ ceramic film porosity is chosen to be 30%^[12]. For various values of the adsorption factor x , we can get the humidity-sensing curves of the refractive index versus RH, as shown in Fig. 2.

From Fig. 2, it can be seen that at the points of RH=0 and 100%, all the curves with various adsorption factors have the same refractive index. When $x = 1$, the curve linearity at intermediate and higher RH levels is better than that at lower RH level; when $x = 2$, the curve shows good linearity and high sensitivity at all the RH levels; when $x = 3$, the curve linearity and sensitivity at lower RH level are both better than those at intermediate and higher RH levels.

The adsorption factor shows the distribution characteristics of material pore size. The bigger the adsorption factor x is, the more the thick pores are; the smaller x is, the less the thick pores are. Because water molecules are more adsorbable through thick pores, the bigger x is, the lower the concentration of capillary pores is, and the stronger the adsorption of water is. Therefore, under the same RH of the environment, the ceramic material's adsorbing capacity of water molecules enhances with the

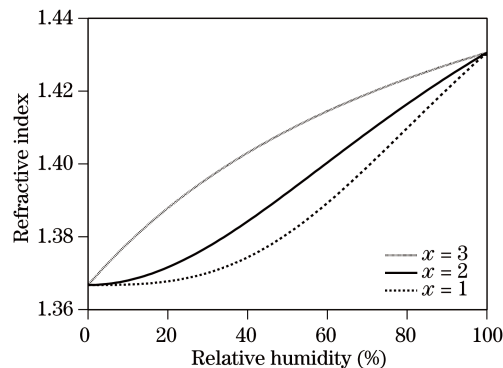


Fig. 2. Refractive index versus relative humidity with various values of adsorption factor x .

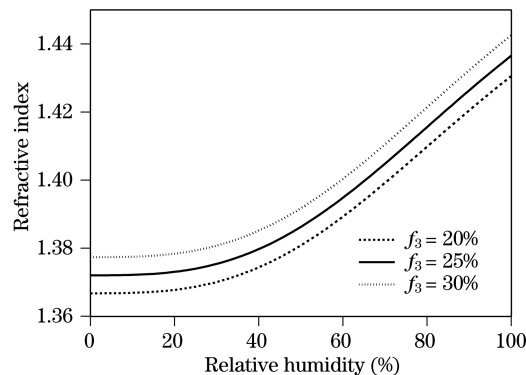


Fig. 3. Refractive index versus relative humidity with various porosities f_3 .

increase of x , which induces the increase of refractive index of the humidity-sensing material.

Porosity represents the compact degree of ceramic materials. In practice, the porosity of SiO_2 is probably from 20% to 35%^[8]. Figure 3 shows the humidity-sensing curves of refractive index versus RH with various porosities.

The curves shown in Fig. 3 present an obvious influence of ceramic material porosity on humidity-sensing. Throughout all the RH areas, the sensitivity at intermediate and higher RH levels is quite high with various porosities. The sensitivity varies linearly with RH in almost all regions except for the lower RH level. Besides, the value of porosity has a great impact on the refractive index. The bigger the porosity is, the smaller the refractive index is. It can be explained that the increase of porosity could enhance the water chemical absorption and physical capillary adsorption, improve the hydrophilicity of thin film, and then reduce the refractive index.

Sensitivity is one of the important characteristic parameters for humidity sensors. Humidity sensor sensitivity characterizes the changes of refractive index when the RH changes by 1%. In physical meaning, humidity sensor sensitivity should be the slope of the humidity-sensing curve. Figure 4 shows the curve of the refractive index change Δn versus the relative humidity.

From Fig. 4, we can get the following conclusions. With the increase of humidity, the sensitivity of humidity sensor increases and reaches the maximum at the point of 80% RH approximately. The maximum sensitivity above 10^{-3} is achieved, showing a very high resolution to the humidity. Therefore, the humidity-sensing material SiO_2 is more suitable for the detection at higher RH level than at lower and intermediate RH levels.

The schematic diagram of experimental arrangement is shown in Fig. 5. A 632.8-nm He-Ne laser with the power of 2 nW was used as the light source. The polarizer was a Gran-Taylor prism with an extinction ratio of 10^{-5} . Then, we put the sample on the optical turntable with an angle precision of $2'$. The two beams reflected separately from the two side surfaces of film glass were detected by a charge-coupled device light intensity distribution measuring instrument simultaneously. In this experiment, the laser divergence angle was 1.4 mrad. Statistical results show that the amendment would not affect the results of experiments and data fitting.

We used K9 optical glass to be the coated substrate with the diameter of 35 mm and thickness of 4 mm.

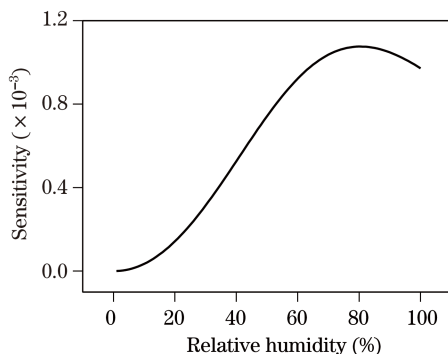


Fig. 4. Sensitivity versus relative humidity.

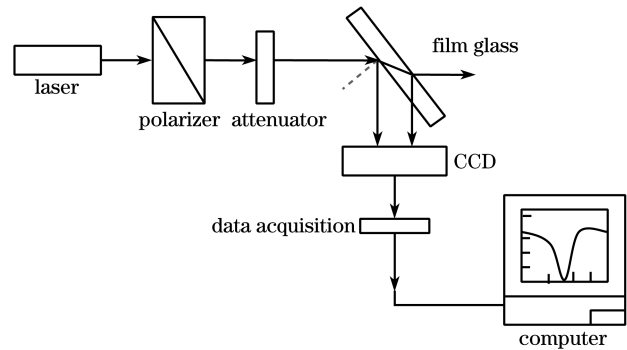


Fig. 5. Schematic diagram of experimental arrangement.

The surfaces of the optical glass were polished and the parallelity was better than $1'$.

At first, all the substrates were ultrasonically cleaned in acid and alkali. Then all the substrates were cleaned further in deionized water and ethanol. We used sol-gel method to prepare SiO_2 solution and adopted dip-coating to acquire film (L1FT, membrane machine). Firstly, we immersed the clean substrate vertically in the coating solution, and then lifted the substrate at a constant speed of 5 cm/min from the solution. Secondly, we placed the wet film in the loft drier (DHG-9036A type, electric thermostat loft drier) under the temperature of 60 °C for 10 min and then took out the glass and cooled it down for 10 min at room temperature. Then, we placed the thin film samples in tubular resistance furnace (SK2-6-12) under heat treatment in the heating rate of 3 °C/min at 450–550 °C to calcine them for 60 min. After the calcination, the samples were naturally cooled down to room temperature. Finally, we got the SiO_2 films after heat treatment.

In this experiment, we obtained the reflective index of thin films by double-sided p-polarized light reflectance method^[13,14]. The p-polarized light reflectance method was brought forward to measure the optical parameters of glass surface layer. It is simple in principle and convenient in measurement, especially for parameter measurement of multi-layer models. It is assumed that the two surfaces of thin film samples are symmetrical and the substrates are ideally transparent. If there is an incident light with the intensity of I_0 in the incident angle θ_i irradiating to the film, we only need to measure the two reflective beams I_a and I_b from the fore-and-aft surface of the sample after reflection and refraction in the incident light side. With a computer program based on optical thin-film theory and combined admittance theory, we only need to measure the angular modulation curves of the reflectance ratio γ of p-polarized reflectance and do numerical curve fitting to obtain the optical parameters of the sample.

In the humidity-sensitive experimental measurement, we controlled the humidity of sealed cell to be 20% RH by use of dehumidifiers and humidifiers at first, while using humidity sensor (TES-1360A, TES hygrometer) as a measuring mark. Then, we measured the reflectance ratio γ of p-polarized light intensity from the fore-and-aft surface of sample for incident angles θ_i from 50° to 70°. Thirdly, we made use of computer program and numerical approximation of experimental γ - θ_i curve to obtain the optical parameters of the sample. At last, we got the

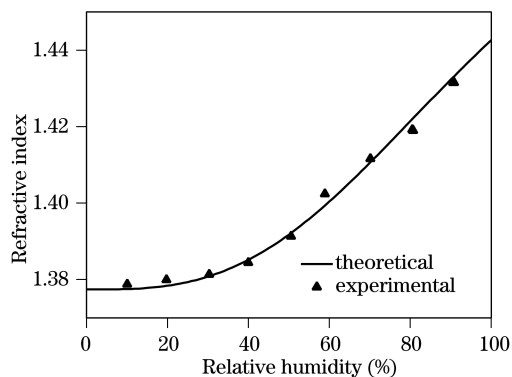


Fig. 6. Experimental and theoretical values of refractive index versus relative humidity.

film optical parameters at the RH values of 20%, 30%, 40%, 50%, 60%, 70%, 80%, and 90% by fitting in the same approach, respectively.

The comparison between the humidity-sensing curve based on composite model and our experimental results is shown in Fig. 6. The experimental parameter setting is the same as those in present composite model exactly, in which the refractive indices of SiO_2 , water, and air are 1.453, 1.329, and 1, respectively, and the porosities are both 30%. Figure 6 shows that when the RH changes from 0 to 100%, there is a corresponding increase from 1.379 to 1.430 in the film refractive index. The change in refractive index shows good humidity-sensing characteristics. Water adsorption on the humidity-sensitive film increases with the increase of RH. Therefore, it could promote the free movement of ions and enhance the conductivity. Accordingly, the effective dielectric constant of film increases which results in the refractive index changes. Through the comparison, it is found that the theoretical curve and the experimental curve coincide with each other and have the same trend in the whole RH range, Therefore, the rationality and correctness of the optical humidity-sensitive model is obvious.

In conclusion, the optical humidity-sensitive mechanism is discussed in different adsorption factors and porosities based on refractive index variation. The larger the adsorption factor is, the higher the refractive index is. The refractive index of humidity-sensitive SiO_2 film decreases with the increase of ceramic material porosity.

The variable value of refractive-index is as big as 0.05 between 0 and 100% RH. The sensitivity of optical humidity sensor can reach the magnitude of 10^{-3} . Therefore, this kind of materials with such high variations in refractive index could be used as a candidate for a transducer integrated in an optic-fiber sensor head.

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