Research Article

Water Vapor Sensors Based on the Swelling of Relief Gelatin Gratings

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We report on a novel device to measure relative humidity. The sensor is based on surface diffraction gratings made of gelatin. This material swells and shrinks according to the content of water vapor in air. By sending a light beam to the grating, diffracted orders appear. Due to the gelatin swelling or shrinking, first order intensity changes according to the relative humidity. Calibration curves relating intensity versus relative humidity have been found. The fabrication process of diffraction gratings and the testing of the prototype sensing devices are described.

1. Introduction

Devices like sensors and transducers devoted to collect the data from the physical world have developed slowly. Thus, new and better sensors should be made. These new sensors should be sufficiently accurate or suitable for most industrial applications. The content of water in air (or water vapor) is important [1] in various industries like medical and health industry (humidity controlled hospital operation rooms, incubators, and air conditioning), automotive industry (window defogger), food processing industry (food dehydration), meteorological industry, semiconductor industry (clean rooms), building and construction industry, and more. Ideal humidity sensors should fulfill requirements like (a) good reproducibility over a wide range, (b) short response time, (c) small hysteresis, (d) good durability and long life, (e) resistance against contaminants, (f) low cost, (g) sensitivity to the measured property only, (h) not influencing the measured property, and more. However, it is difficult to find a humidity sensor that fulfills the mentioned characteristics. For this reason many different measurement methods and sensors have been developed, each having certain advantages and limitations and each suitable for some but not all applications.

Among the conventional techniques for humidity detection [2] is the mechanical hygrometer where materials expand and contract in proportion to humidity change. Common materials include synthetic fibers and the human hair. The method is inexpensive but slow and presents nonlinearity and hysteresis. Other techniques are, for example, the chilled mirror hygrometer [2] based on a temperature-controlled reflective condensation mirror, infrared [2], and Lyman-alpha instruments and those based on optical [2] fibers and MEMS technology [3, 4]. These MEMS-based sensors use electronic devices that cannot be used in flammable environments because they introduce a spark risk. Every type of humidity sensors has found a niche market where its performance characteristics apply. But new requirements for humidity measurements are coming up.

Here we present the use of a spark-free optical method that uses diffraction gratings as sensors. It is an alternative method to measure relative humidity (RH). In Section 2 we present the material used to fabricate the grating sensor. Section 3 describes the diffraction gratings fabrication method. Section 4 presents the gelatin grating behavior as a function of relative humidity. Section 5 describes the principles of the measuring method and calibration plots and in Section 6 we conclude the paper.

2. Gelatin

Materials used in the measurement of relative humidity are of different kinds. Some commercial humidity sensors work on the basis of transduction of water vapor concentration into an electrical measurement by a sensing film [1, 3, 4]. Among the materials used to fabricate these films are porous ceramics, polymers, and polyelectrolytes. We have used a material that is highly hygroscopic, gelatin. This characteristic is due to the high number of polar groups [5] in its molecular structure. Water molecules are absorbed and adsorbed by the gelatin films surface where there are physical and chemical interactions. Also there are modifications in the bulk of the film due to water accumulation on and diffusion into the film. When gelatin absorbs water molecules it swells and under desorption it shrinks.

Another characteristic of gelatin is that it can be hardened by chemical or optical methods. Among the last methods is the one that uses dichromates. The next steps are followed to harden the gelatin [6]. A gelatin thin film is made by pouring a small amount of a solution of gelatin and water onto a glass substrate. After drying, plates are sensitized in an ammonium dichromate water solution. Then plates are left overnight in a light-tight box to dry the film. Hardening occurs when film is exposed to actinic radiation (UV or visible) and the hexavalent chromium ion Cr^{6+} is either directly or indirectly photo induced to trivalent Cr^{3+}. This compound forms a cross-link bond between neighboring gelatin molecules hardening the gelatin. This creates a hardness differential between highly light-exposed regions and underexposed regions. Besides the hardening, Cr^{3+} forms several intermediate chromium compounds. During the development process with water, residual compounds are removed and the gelatin swells. Light-exposed regions absorb less water than unexposed regions because they are more hardened. After drying, unexposed regions are thicker than exposed ones showing a relief that is a copy of the spatial distribution of the recording light.

From the optical point of view gelatin shows a refractive index of about 1.5. Thin gelatin films show high transmission and low scattering.

3. Diffraction Gratings Fabrication Method

Among the materials best suited to make holograms is dichromated gelatin (DCG). This material was proposed by Shankoff in 1968 [7]. It is possible to make phase (bulk or relief) holograms that can reach high diffraction efficiency. In our experiments we made sinusoidal relief gratings with dichromated gelatin plates. They consisted of a glass plate and a gelatin thin film (about $20\,\mu m$ thick) [8]. To make relief sinusoidal gratings we recorded the interference pattern given by two beams (Figure 1).

A laser emitting light at a wavelength of 532 nm was used. Interbeam angle was such that the distance between peaks in the interference pattern was about $70\,\mu m$. Sensitive DCG plates were placed in the optical recording configuration. After exposure time plates suffered a water-alcohol development. The resultant grating showed a sinusoidal relief
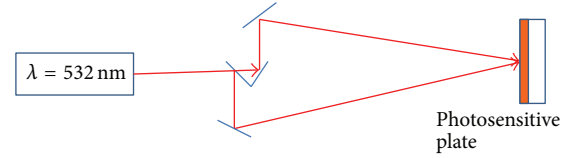

FIGURE 1: Diagram of the interferometric optical configuration used to fabricate gelatin relief gratings with dichromated gelatin.

profile. Gratings with modulations depth between $0.5\,\mu m$ and 4 microns were obtained. They were studied with an Atomic Force Microscope (AFM). Figure 2(a) shows an image of a grating surface. Figure 2(b) shows the profile of the grating. This grating had a modulation depth of $2.27\,\mu m$ and a pitch, or distance between crests, of $70\,\mu m$. A photograph of one of such gratings is shown in Figure 3.

These gratings are considered thin elements because their Q-factor [9] is about 0.01. The Q-factor is defined as $Q = 2\pi\lambda T/nd$, where $\lambda = 632$ nm, $d =$ distance between crests, $70\,\mu m$, $n =$ gelatin refractive index, 1.5, and $T =$ gelatin film thickness, $20\,\mu m$. For a grating to be considered thick its Q-factor should have a value greater than 10.

4. Gelatin Grating Behavior as a Function of Relative Humidity

In this section we comment on the bulk modifications that suffer the gelatin gratings with changes in RH. As we have mentioned gratings were made by recording in a DCG plate a sinusoidal interference pattern. After development and drying the result was a grating with a surface modulation $h_1(x)$ (Figure 4).

If this grating is illuminated with a wave $C(x)$, then the transmitted wave will have a phase variation imposed on it by the surface relief and the change in refractive index in the gelatin bulk due to water molecules absorption. Surface relief will give a phase variation of the form [10]:

$$\psi(x) = \gamma k n h(x) = \gamma k n \left[h_0 + \frac{h_1}{2} \cos(\psi_0 - \beta x) \right], \quad (1)$$

where h_1 is the peak to peak variation of the modulation, h_0 is the average thickness, γ is a proportionality constant, and $\beta = k \sin \alpha_r$. α_r is the angle that the illuminating beam makes with the z axis and $k = 2\pi/\lambda$. In a first approximation we could say that this relation (1) could describe the behavior of the gelatin surface relief gratings. However, we should consider the absorption of water vapor by the gelatin. Surface of gelatin will absorb more water molecules than the bulk. Thus a gradient of moisture will be present from the surface of the film to the bulk of the gelatin. The absorption of water molecules will give a change in refractive index. Besides these phenomena, crests will absorb more water molecules than valleys because they are less hardened. These gradients of moisture in the z and x directions will give as a result a spatial distribution of refractive index because water presents a refractive index of 1.33 and gelatin presents a refractive index of about 1.5. Thus, in formula (1) the variation of height

Digital instruments nanoscope
Scan size   100.0 μm
Scan rate   1.001 Hz
Number of samples   256
Image data   Height
Data scale   1.900 μm
Engage X position
Engage Y position

X: 20.000 μm/div
(μm) Z: 1900.000 nm/div
Placab-1
Unhardgel .001

0°

□ View angle
☀ Light angle

(a)

Section analysis

L	34.766 μm
RMS	813.45 nm
l_c	DC
$R_a(l_c)$	119.30 nm
R_{max}	608.94 nm
R_z	322.44 nm
R_z cnt	6
Radius	187.58 μm
Sigma	203.81 nm

Spectrum

Surface distance	34.893 μm
Horizontal distance	34.766 μm
Vertical distance	2.239 μm
Angle	3.685°
Surface distance	
Horizontal distance	
Vertical distance	
Angle	
Surface distance	
Horizontal distance	
Vertical distance	
Angle	
Spectral period	
Spectral frequency	
Spectral RMS amplitude	

DC   Min
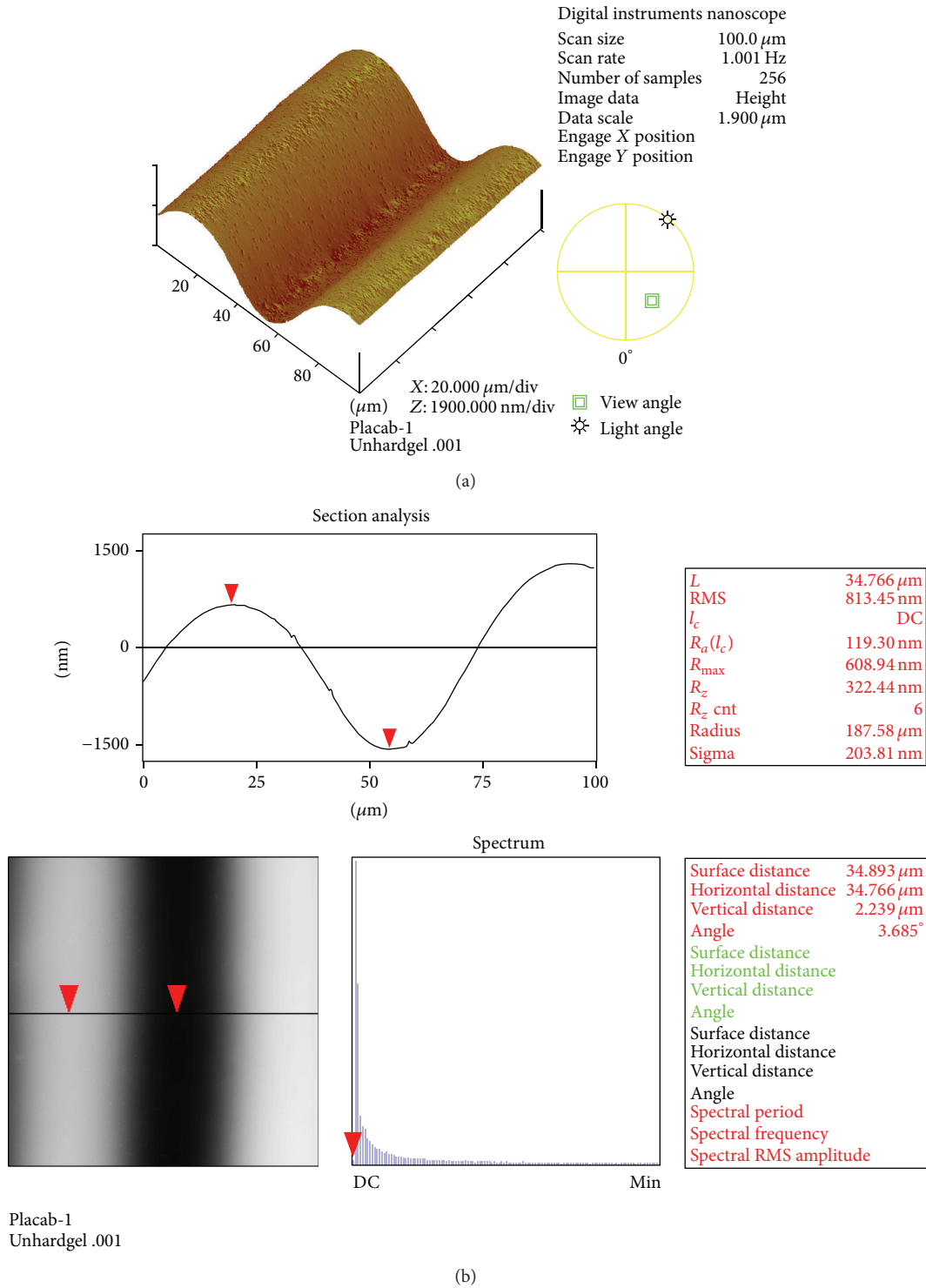
Placab-1
Unhardgel .001

(b)

FIGURE 2: (a) Grating surface given by an AFM. (b) Profile of a grating surface also given by an AFM.

$h(x)$ due to water absorption is not the only parameter that affects the phase of the incoming light but also the variation of the refractive index n that depends on the depth of the film z and on the coordinate x, that is, $n(z, x)$. This parameter is difficult to characterize due to the fact that binding of water molecules to gelatin chains is a function of the polar groups [11].

5. Principle of the RH Sensing Method

Experiments reported here were developed at room temperature.

When light impinges on a relief grating it is diffracted by each slit and in the far field the diffracted orders appear. Position of the diffracted orders is a function of the grating
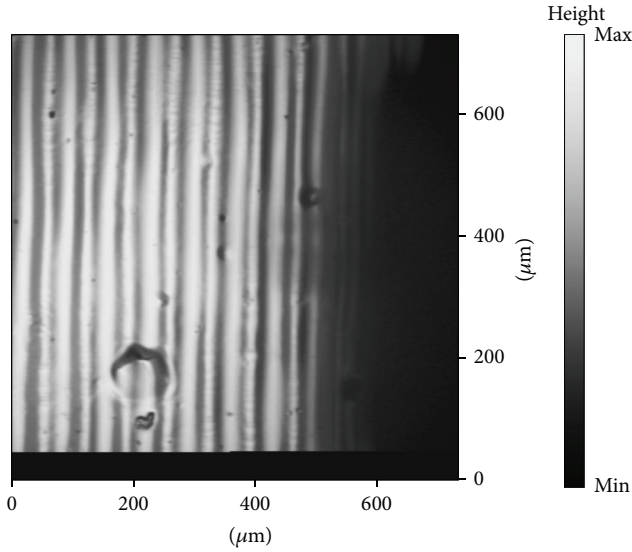
FIGURE 3: Photographic image of a surface grating given by an optical microscope.
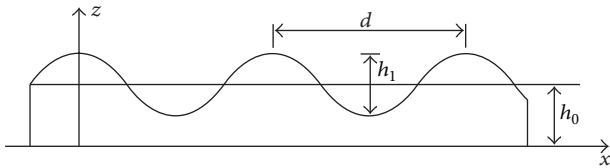

FIGURE 4: Diagram of a sinusoidal surface grating where d is the distance between crests, h_0 is the mean thickness, and h_1 is the modulation.

pitch. However, its intensity is a function of the depth of surface modulation h_1 and the change in refractive index. This modulation depends on RH as exposed in Section 4. To test the response of gelatin relief gratings to RH a simple climatic chamber was built. A diagram of the chamber is shown in Figure 5.

A He-Ne laser was used to illuminate the grating. Laser intensity was stabilized within ±0.2%. However, it was left working about half an hour before the experiment began to assure a constant intensity. After light was diffracted by the grating first order intensity was sampled by the detector. An air pump was used to circulate air through a plastic cylinder filled with silica gel that absorbed water vapor from the air. An electronic hygrometer was used for calibration. In Figure 6(a) we can see the behavior of first order intensity as a function of relative humidity. We can notice a span range of about 25%. In Figure 6(b) the behavior of another diffraction grating is shown. We can notice that plot in Figure 6(a) shows a minimum value at 25% RH while plot in Figure 6(b) shows the opposite.

We can explain this behavior in the following way. Intensity in a given order is a function of the delay between waves arriving from each slit. This delay is caused by the depth of modulation and the water molecules absorbed in the gelatin. Thus if optical path is such that waves from the slits
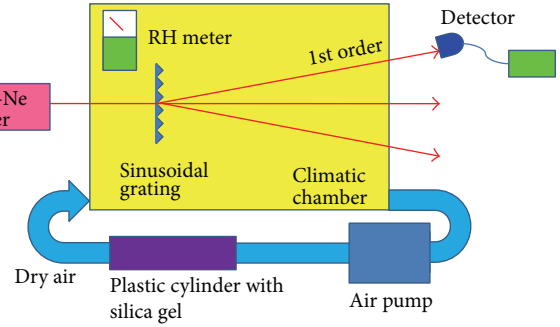

FIGURE 5: Schematic plain view of a climatic chamber showing a system used to evacuate the moisture. A He-Ne laser was used as a light source to illuminate the grating. First order intensity was monitored when relative humidity changed.

arrive in phase at the given order its intensity will be high. However, if waves arrive out of phase intensity will be low. Thus, first order intensity is a function of the optical path (i.e., depth of modulation and refractive index) which in turn depends on the RH.

We have mentioned in Section 4 that the phase modulation that a sinusoidal surface grating imposes on a transmitted light beam is given by formula (1) ($\psi(x) = \gamma k n h(x) = \gamma k n[h_0 + h_1/2 \cos(\psi_0 - \beta x)]$). Let us suppose that water vapor molecules absorbed by the gelatin do not change the gelatin refractive index but just affect the grating profile h_1. By scalar diffraction theory [12] we know that the behavior of first order intensity of a sinusoidal surface grating is given by the Bessel function $J_1^2(h_1/2)$. Figure 7 shows the behavior of first diffracted order as a function of modulation h_1. We can notice a maximum diffraction efficiency of about 33%. However, if we would like to make a relation of this plot with the ones given in Figure 6 it will not be possible because we need to consider in the formula the layer thickness h_0 which imposes a phase delay. Besides that, we have mentioned in Section 4 that the gradients of moisture in the gelatin bulk (z direction (Figure 4)) and in the x direction also will affect the refractive index, that is, $n(z, x)$. This refractive index modulation should be known to make possible the comparison of plots given by experiment and theory.

6. Comments

We have reported a simple sensing concept suitable for the measurement of RH. The sensing principle is based on the dependence of the swelling and shrinking of gelatin films on RH variations. The grating fabrication process is simple and the testing of prototype sensing devices has been done.

In the future we will build a more elaborate climatic chamber to find the response time of gelatin gratings. In a first attempt we could say that response time is about a minute but measurements should be done.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.
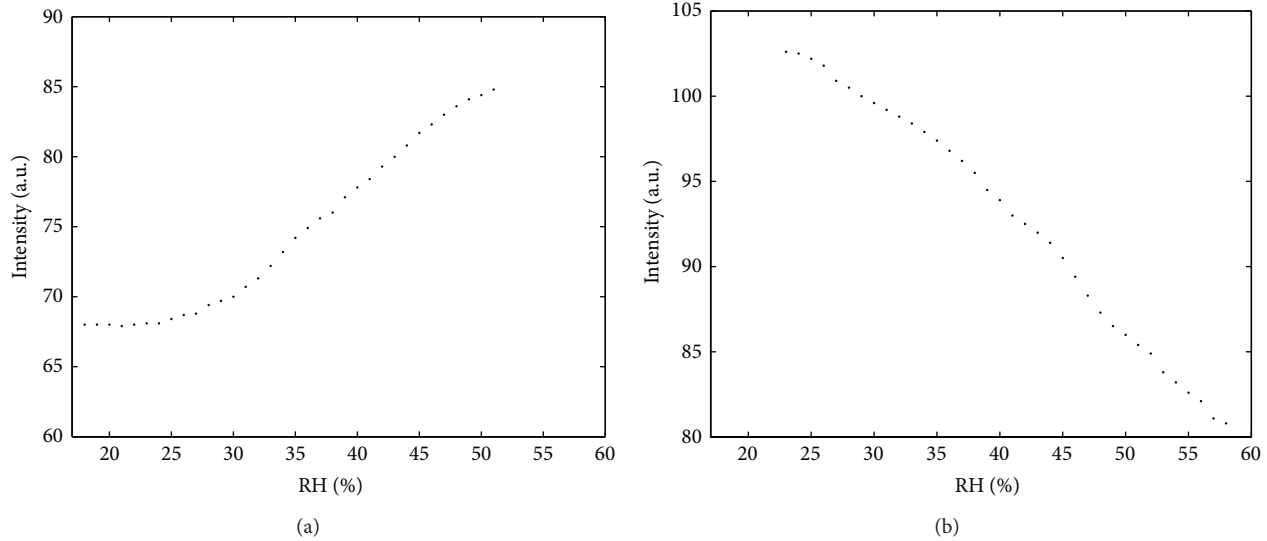
(a)

(b)

FIGURE 6: (a) and (b) show the behavior of first order intensity as a function of relative humidity (%) for two different gratings. In one of them optical delay in the grating was such that at about 25% RH first order intensity was a minimum (a). The opposite was true for the other grating (b).
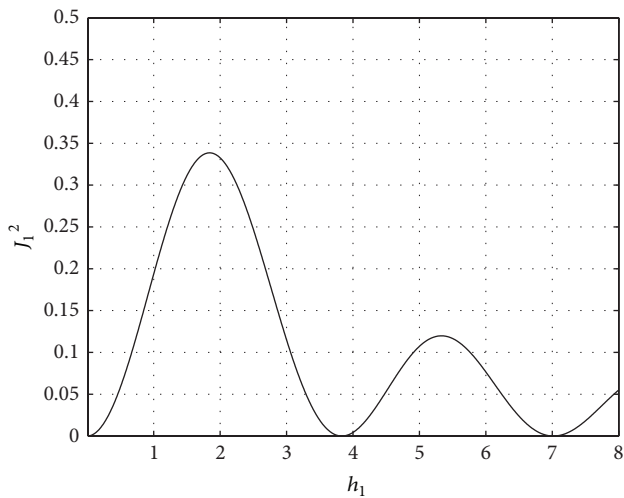

FIGURE 7: Behavior of the first order diffraction efficiency of a sinusoidal surface grating. h_1 is the depth of modulation.

Acknowledgments

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