Collagen as a Humidity Sensing Dielectric Material

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ABSTRACT

The motivating principle behind this research is the development of small, wearable devices that would use humidity and temperature measurements as metrics for health monitoring. If it is to be useful as a health monitoring tool, the device needs to respond quickly and predictably to changes in humidity. Collagen is shown to be a viable humidity sensing material for use in capacitive relative humidity (RH) sensors. As a natural by-product of meat and leather industries, collagen presents itself as an interesting and inexpensive alternative to polyimide dielectric sensing materials. We used gelatin, a partially hydrolyzed form of collagen, to allow for easier spin coating. We have successfully fabricated devices by depositing a collagen thin film (1.2 \(\mu\text{m}\)) via spin coating, followed by Au/Pd electrodes (60 nm) via sputter coating. A plastic mask made from a rapid prototyping machine was used during physical vapor deposition (PVD) to pattern electrodes. This simple method eliminates the need for the use of more complicated photolithography processes. Interdigitated electrodes (rather than parallel plate electrodes) form a 6 mm wide, planar capacitor structure that has little dependence on dielectric thickness and is not affected by dielectric swelling. Initial findings indicate that these devices very closely match the results of the commercial relative humidity sensor used for reference. The capacitance-humidity relationship is shown to be non-linear, with an average change of 3 fF for every 1\% change in RH around 60\% RH, and an average change of 7 fF for every 1\% change in RH around 80\% RH. In this work, we present the fabrication and characterization of these novel collagen-based relative humidity sensors.

INTRODUCTION

Humidity sensors are used for a wide variety of applications from automotive and appliance sensors to home comfort management. Different sensing methods are used based on the application, such as capacitive, mass sensitive, optical, and resistive \[1\]. This work focuses on capacitive relative humidity sensing. The main activity of this type of sensor lies in the difference of dielectric constant between water vapor and the dielectric material. Various materials such as metal oxides \[2, 3\], carbon nanotubes \[4\], and polyimides \[5-7\] have been used; each with benefits and drawbacks (e.g. oxides and nanotubes are more expensive than organic counterparts, but provide for a more durable device). The overarching goal of this research is the development of a sensor package; small enough to be incorporated into clothing...
for the monitoring of health indicators such as sweating (humidity), fever (temperature), and sudden drops (accelerations).

Some of the first advances in capacitive humidity sensing were to create sensors that became stable within two minutes [8]. Many humidity sensing technologies exist, but a large branch of humidity sensing deals with polymer-based capacitive humidity sensors [1]. By using a polymer that is selectively sensitive to a specific analyte, the swelling effects due to the absorption of the analyte can be measured [9]. These polymer-based sensors tend to be popular due to low cost and high sensitivity [10]. Recent research looks into using inkjet printers for polymer deposition. A narrow gap between parallel plates can draw in polymer solution from a reservoir via capillary forces, presenting a simple and novel option for fabrication [11]. A recent study presents paper as a low cost environmental sensor. These capacitive humidity sensors are created by printing silver nanoparticles onto a paper substrate with an inkjet printer [12].

The goal of this work is to assert the utility of collagen as an inexpensive alternative for more traditional dielectric materials. Coming from the bones, tendons, and skin of bovine and pigs, this by-product of the meat and leather industry presents itself as an appealing candidate. This work shows collagen to be a viable humidity sensing material.

THEORY

For this study, capacitive humidity sensors based on collagen are characterized and optimized. These sensors operate based on a difference in dielectric constant between water \((\varepsilon_w \approx 78)\) [11] and the dielectric material. The basic representation of a simple parallel-plate capacitor is represented as:

\[
C = \varepsilon \frac{A}{d}
\]  

(1)

where \(\varepsilon\) is the dielectric constant, \(A\) is the area of overlap between electrodes, and \(d\) is the distance between the electrodes. As water is absorbed into the dielectric material, a noticeable change in the dielectric constant of the capacitor occurs. This change can be represented as [1]:

\[
\varepsilon_{new} = [v(\varepsilon_w^{1/3} - \varepsilon_p^{1/3}) + \varepsilon_p^{1/3}]^3
\]  

(2)

where \(v\) is the fractional volume of water vapor in the dielectric material, \(\varepsilon_w\) is the dielectric constant of water, and \(\varepsilon_p\) is the dielectric constant of the humidity sensitive material. Equation (2) shows that the new dielectric constant will vary with respect to the cube of the fractional volume of moisture. Also a factor is the swelling of the dielectric material. Incorporating both of these into Equation (1), it becomes clear that an increase in dielectric constant would be directly opposed by an increase in the dielectric thickness. To combat this, interdigitated electrodes (IDEs) are used in combination with a thin dielectric layer.

FABRICATION

Initially, collagen dissolved in acetic acid was spun onto glass and silicon surfaces with no success. The collagen solution does not adhere to the surface. This led to the decision to use
partially hydrolyzed collagen (gelatin). The gelatin dissolved in water (0.75g in 20mL) will produce a gel at near room temperatures. When heated to around 55°C, it becomes a sticky, viscous fluid that adheres well to the glass surface. The solution is spun onto the glass slide at 1500 rpm for 50 seconds. Once the gelatin touches the cold substrate, it begins to gel again, causing an uneven coating. Therefore, it is important to drop the warm solution on after the substrate is already spinning. After coating, the glass slide is heated on a hot plate at 55°C to drive off excess moisture and the gelatin film is left behind. This results in a film that is 1.2 µm thick, as measured with a stylus surface profilometer (DekTak II A).

Figure 1: Masks used for PVD. These masks were manufactured with a rapid prototyping machine.

Electrodes were deposited onto the paper via PVD. Figure 1 shows the plastic masks (35 mm x 45 mm) that were created with a rapid prototyping machine and used for the deposition of gold/palladium alloy. The Au/Pd electrodes were deposited with a Denton Desk II sputter coater. This method provides a very thin coating, giving 50 nm thick electrodes. The finished devices are 6 mm wide, with 3 fingers (0.55 mm wide, 5 mm long) from each electrode. The devices are created with extra metal on either end as contacts to allow for easier measurement. An example device can be seen in Figure 2a. While it may not offer much utility, an interesting characteristic of collagen is its transparency.

CHARACTERIZATION

Steady state measurements were taken in order to evaluate the base values of capacitance for various humidity levels. The measurement setup can be seen in Figure 2b. The devices were cycled through four steps of relative humidity: 50%, 70%, 90%, and 50%. Each of these steps lasts 5 minutes, and the cycle is repeated 3 times. This method also provides information about the repeatability. Capacitance measurements were taken using a GLK 3000 capacitance meter [13] controlled by LabView. An Omega OM-73 temperature/humidity data logger [14] was used for a reference humidity level. Humidity levels were controlled with a Blue M Model VP-100RAT-1 Vapor-Temp controlled relative humidity test chamber. The dry bulb (which controls
temperature of the atmosphere within the test area) was set to 36 °C to create a body temperature environment. The humidity level is controlled by the wet bulb temperature which heats the water, changing the dew point of the chamber. This temperature combination creates a specific relative humidity level.

![Image](image1)

**Figure 2:** (a) Gold/Palladium electrodes on collagen coated on a 25 mm x 75 mm glass slide. The wire under the slide illustrates the semi-transparent nature of the devices. (b) The experimental setup; the devices are connected to a capacitance meter controlled by a nearby computer.

**RESULTS**

Steady-state tests show a good agreement between the collagen device and commercial reference sensor (Figure 3a). The darker line shows information from the commercial humidity sensor (in % RH), and the light line shows data from the fabricated devices (in picofarads). The ripples seen in the data are a result of the wet bulb and dry bulb switching on and off in order to maintain the desired environmental conditions. The relationship between capacitance and humidity is clearly non-linear, but the transitions between humidity levels do line up. This is shown even with transitions due to the chamber varying wet bulb temperature to maintain a nearly constant environment. The trend seen in Figure 3a indicates accurate, but inconsistent results from the collagen devices. When changing humidity levels, the collagen devices have a very quick initial response, followed by a gradually increasing capacitance during an adjustment period. This causes hysteresis that can be seen in Figure 3b, where the device may have multiple
values of capacitance for a given humidity level. The device is said to be accurate because its response to changes in humidity line up very well with the reference sensor’s response.

Figure 3: (a) shows sensor data (capacitance) and commercial reference data (humidity). The two are responding similarly to changes in humidity within the chamber. The fluctuations are from the chamber working to maintain a constant humidity level. Data points have been replaced by continuous lines to better illustrate the response of the device. (b) shows a plot of the capacitance with respect to the relative humidity. There is obviously some hysteresis present.

CONCLUSION

Collagen has been shown to be a promising novel humidity sensitive material. Used in its hydrolyzed form, it adheres well to silicon and glass surfaces, and its properties make it suitable for thin film deposition techniques such as spin coating. Unfortunately, the characteristics of the collagen gel that make it easy to work with and sensitive to humidity also cause it to be easily damaged by the accumulation of liquid water which dissolves the gel. Adding a crosslinking agent to the gel and crosslinking after spinning could enhance the structural properties, but the effects on sensitivity will have to be evaluated. Future work will also involve fabrication and characterization of devices at the micro-scale.

Another device characteristic that will need to be optimized is response time. To evaluate response time, the environment around the device must be rapidly changed. The chamber used for the accuracy tests can change input levels in around 15 seconds according to the commercial reference sensor. To get an accurate measurement of the sensor response, a box was fabricated to seal the device in the appropriate initial conditions while the chamber set to new parameters. The box then opens rapidly to expose the sensor to the new environment. This input is assumed to be instantaneous, and will be used in future testing to determine a more exact response time.

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REFERENCES


