

A Polyimide-Based Capacitive Humidity Sensor

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Abstract—The design of a relative humidity sensor is studied in which the principle of operation is based on the change of dielectric constant of a thin film of polyimide. The design of the sensor is established in such a way that it would be suitable for an integrated-circuit type of fabrication. The studies have shown that the experimental data are described well by the use of the Looyenga equation for dielectric constant behavior coupled with the Dubinin equation to describe the absorption as a function of relative humidity.

I. INTRODUCTION

THE MEASUREMENT of relative humidity has always been a difficult and challenging one to make because of the interaction of other variables such as temperature and because of the lack of stable and reliable sensors. There are three major classifications of humidity sensors: those which measure mechanical property changes of a film or filament; those which respond to electrical property change such as resistance or capacitance, and psychrometric measurements which compare the latent heat of evaporation of a saturated environment to the environment in question. In this work we describe the design, construction, and testing of a humidity sensor based on the change in dielectric constant, and hence capacitance, of a thin film of polyimide. This includes consideration of the problems of hysteresis, which were minimal, as well as the relative speed of response and the sensitivity of the sensor.

A study was made of the mechanisms which describe absorption and dielectric constant change, and those mechanisms were correlated with the observed results.

The impetus for this work lies in developing the understanding of the mechanisms and limitations of the use of polymer thin films in humidity-sensing applications as well as developing a highly miniaturized sensor suitable for fabrication using integrated-circuit techniques, thereby greatly lowering the cost of such sensors.

II. THEORY OF OPERATION

Humidity is defined as the mass of vapor carried by a unit mass of vapor-free gas. If Dalton's law holds, the partial pressure of each species in the mixture is in direct proportion to its molar fraction. Then

$$H = (M_A p_A) / (M_B (1 - p_A))$$

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where M_A and M_B are the molecular weights of components A and B , respectively, and p_A is the partial pressure. For the humidity of water vapor in air, component A is the water vapor and component B is air.

Relative humidity (RH) is defined as the ratio of partial pressure of the vapor to the saturated vapor pressure (p_s) of the liquid at the gas temperature. For an ideal gas [1]

$$RH = 100p/p_s.$$

In order to be effective as a humidity sensor, the sensor must respond to the partial pressure of water, do so in a reasonably short period of time, and not be very sensitive to changes in temperature. The capacitive sensor, based on the dielectric properties of polyimide, seems to satisfy most of these desired characteristics. An alternative to the use of dielectric properties to measure RH was suggested by Yano and Wada [2]. Their results indicate that the relaxation frequency of a thin polyimide film changes linearly with RH. Although the linear relationship is an attractive one, the measurement itself is a more complicated one than that of measuring the capacitance.

The principle of measurement is based on the change in properties of a heterogeneous dielectric. Such a material is defined as a composite of two or more immiscible dielectrics in the same system. The system of concern here is that of water in the polymer polyimide. A plethora of theoretical and empirical formulas have been extensively reviewed and compared with experiments [3], [4], and compared with simple geometries where exact calculation of the composite dielectric is possible [5]. No mixture formula has been found which represents all or most of the experimental data. Theoretical formulas are often applicable to a specific geometry of one dielectric in another, and empirical formulas generally apply to a larger, but still limited, class of data.

There are a number of mixture formulas which could be used for cases such as this. Because the relative absorption of water in polyimide is quite low, all of the applicable equations are quite linear over the range of interest. The only significant difference among these formulas in the low mixture volume region is the slope. Therefore, the choice of a mixture formula is not critical.

We chose the semi-empirical relationship by Looyenga because the formula fits a wide range of data, and because when used in the equation by Dubinin [6] to describe the absorption of a vapor into a solid, very reasonable values of maximum absorption are produced, ones which agree very well with published data. Looyenga's equation for the dielectric constant of a mixture is given by

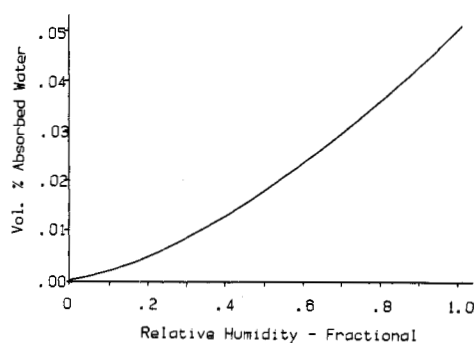


Fig. 1. Dubinin's equation for volumetric fraction of absorption v as a function of relative humidity.

$$\epsilon = (v_2(\epsilon_2^{1/3} - \epsilon_1^{1/3}) + \epsilon_1^{1/3})^3$$

where ϵ_1 and ϵ_2 are the dielectric constants of the polymer and water, respectively, and v_2 is the fractional volume of water absorbed.

A large number of models exist to describe the absorption of a gas into a solid. Of particular interest here is a rather recent theory by Dubinin [6] which describes the absorption of a vapor into micropores. This formula is semi-empirical in nature, requiring three empirical fitting parameters, but derives from a specific physical model and includes standard thermodynamic functions.

Dubinin's equation is as follows:

$$v = v_m^0 \exp [-(RT \ln x/E)^n - \alpha(T - T_0)]$$

where v_m^0 is the maximum fractional volume of absorption at the temperature T_0 , R is the universal gas constant, T is absolute temperature, and α is the thermal coefficient of limiting absorption. The variable E is the free energy of absorption and n is an empirical factor determined by trial and error. A graph of Dubinin's equation is shown in Fig. 1. The use of this equation fit our experimental data quite well as will be shown in the discussion of experimental results.

III. SENSOR CONSTRUCTION

A photograph of the RH transducer developed in this work is shown in Fig. 2. The electrode which is exposed to the environment (top electrode) is a series of concentric circles connected electrically to a large bonding pad. The bottom electrode is a planar metal film deposited on a silicon wafer. The polyimide dielectric, DuPont 2566, is a film which we varied in thickness from 0.5 to 1.8 μm and has a through-hole patterned into it to facilitate electrical contact to the bottom electrode.

There are several reasons for the choice of this particular electrode geometry: 1) The thin metal lines (10–15 μm wide) permit rapid absorption and desorption of water vapor in the bulk of the film, 2) the circular geometry has uniform absorption for each region of the sensor surface, and 3) the avoidance of sharp corners gives a uniform electric field. Because the geometry is determined by photolithographic techniques, it is quite reproducible.

Because the absorption is a bulk phenomenon, the value of the maximum percent absorption will be independent of film

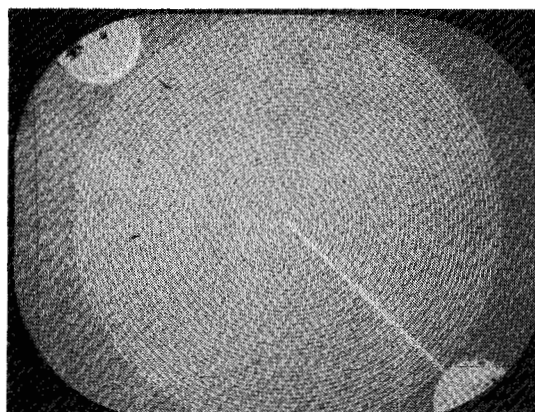


Fig. 2. Photomicrograph of the RH transducer. The top electrode has 15- μm -wide lines with 10- μm spacings.

thickness. Hence for thinner films, and thus larger capacitances, the absolute change in capacitance with relative humidity will be larger and thus easier to calibrate.

The polyimide was spun onto the wafer and cured using a three-stage cure with the "A" stage being 30 min at 150°C, the "B" stage being for 60 min at 250°C, and the final stage being for 20 min at 425°C. The polyimide was patterned in an O_2/CF_4 plasma similar to that described in [7].

IV. EXPERIMENTAL RESULTS

The transducers were 100 mil in diameter and were mounted in flat packs for testing. The testing at RH values from 30 to 95 percent was done in an environmental chamber capable of humidity control. The reference hygrometer had an absolute accuracy of 3 percent. For lower RH values the sensor was placed in a desiccator. The RH dropped from around 30 percent when the desiccator was opened to close to 0 percent after a period of time.

The capacitance of the sensor was measured using a GR 716-C capacitance bridge over a range of frequencies of from 200 Hz to 100 kHz. For response time measurements, a Boonton 72B capacitance meter was used with the output connected to a strip chart recorder. The temperature of the ambient was measured using a thermocouple connected to a Keithley 870 digital thermometer.

One source of experimental error was the package itself. It was noted that the stray capacitance of the package varied with humidity, and that variation was removed from the final data presented on the capacitance as a function of RH. A representative graph of capacitance versus RH for a typical device is shown in Fig. 3. This device has a polyimide film thickness of 1.38 μm as determined by interferometry. The top electrode has 15- μm -wide metal lines with 10- μm spacings. The temperature was 30°C and the measurement frequency was 1 kHz. The three points which lie on the RH = 100 percent line illustrate the effect of condensed water on the device at saturation. The bridge readings in this region are unstable, and the dissipation factor was extraordinarily high so that these readings are not reliable.

Since the shape of the curve just below saturation does not indicate a great slope, it is natural to extrapolate the RH = 100 percent value from the region just prior to that. This extrap-

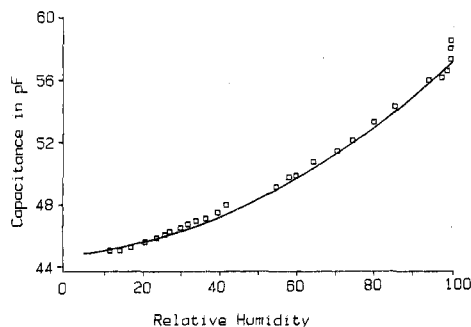


Fig. 3. Typical graph of capacitance as a function of relative humidity. The top electrode has 15- μm lines with 10- μm spacings. The polyimide was DuPont 2566 and was 1.38- μm thick. The squares are measured data points and the solid line is the theoretical curve.

olated value may then be used to estimate the maximum volumetric percent of absorbed water. We determined that value to be 0.043 by this method. For a similar DuPont product (Kapton[®]), the maximum weight percent of absorbed water has been found to be 0.044. The Pyralin[®] 2566 has a density of 1.055 gm/cm³, and thus the corresponding volume percents will be slightly higher. This excellent agreement with the accepted values for maximum absorption provides firm support for the choice of Looyenga's equation.

Using the general form of the Looyenga equation and interpreting the appropriate empirical constants, the general expression for capacitance as a function of relative humidity is given by

$$C = (0.287X^{1.725} + 3.553)^3$$

where $X = \text{RH}/100$. We used a value of 2.93 for the dielectric constant of polyimide and 80.0 for the dielectric constant of water in deriving this equation. This equation is plotted as the solid line in Fig. 3. The excellent agreement with experimental data points is clear.

Fig. 4 shows the effect of film thickness of the C -RH curves. As would be expected, the only noticeable effect is that of a change in the capacitance with virtually no change in either the ν (emp) value or in the free energy of absorption E . Of course the absolute change in capacitance is greater for the thinner films, something which was previously discussed, and this naturally is desirable from the point of view of sensitivity of the sensor.

Extensive studies of the temperature dependence of the sensor were not made in this work; however, some observations can be made based on studies by others. For example, Sacher and Susko have reported in two separate papers that the concentration of absorbed water for various polyimides is independent of both temperature and thickness [8], [9]. In this work, we have observed that the value of the dielectric constant of polyimide is independent of temperature over the range from 50° to 180°C. So we tentatively conclude that the sensor is not likely to exhibit a substantial temperature dependence, but further work needs to be done in this area.

The frequency dependence of the measured capacitance is

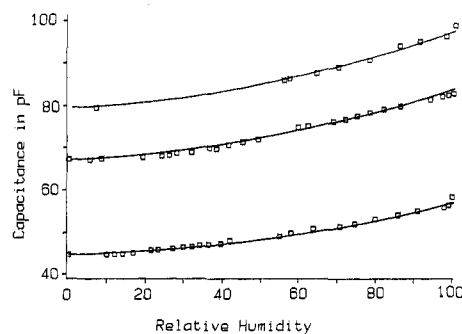


Fig. 4. Capacitance-RH curves showing the effect of film thickness. For the top curve, the thickness was 0.993 μm , the ν (emp) was 0.0359, and the E was 1516 kJ/mol; for the middle curve, the thickness was 1.157 μm , ν (emp) was 0.039, and E was 1635; for the bottom curve, the thickness was 1.375 μm , ν (emp) was 0.0427, and E was 1461.

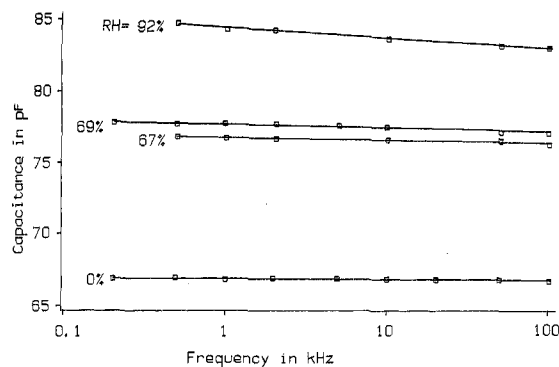


Fig. 5. Measured capacitance as a function of frequency for several values of RH.

plotted in Fig. 5 in which it is seen that the variations with frequency are not substantial and this simply eases the problem of detecting the RH by techniques such as using a balanced bridge method.

Hysteresis was not observed for these sensors, although the reference hygrometer may not have been sufficiently sensitive to delineate minor variations. It should be noted that it has been observed that the absorbed water content of polyimide is essentially constant at any given RH [9]. This means that the equilibrium value of absorbed water does not depend on the direction from which that particular value of RH was approached. Thus we would expect that the hysteresis would not be a very large effect, even if it were observed.

The typical response times for the sensor were in the range of 30 s in still air at room temperature. Desorption times were much longer than absorption times, 30 s compared to 6 s. Response time is divided into two parts, a delay time and a fall time. The delay time corresponds probably to the removal of residual surface moisture. Table I gives values for desorption for samples with different thicknesses and linewidths. Samples with thinner linewidths exhibited faster desorption times which is to be expected considering that the desorption is limited by diffusion from under the electrode regions.

The absence of a clearly defined dependence of response time on thickness of the film suggests that the desorption is

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TABLE I
RESPONSE TIME OF THE SENSORS FOR VARIOUS POLYIMIDE THICKNESSES AND
TWO DIFFERENT LINEWIDTHS EXPRESSED AS LINEWIDTH/SPACING

DEVICE	THICKNESS (microns)	LINEWIDTH (microns)	t_d (sec.)	t_f (sec.)	$t_R = t_f - t_d$	STANDARD DEVIATION
25 B	1.375	15/10	10.0	24.0	34.0	3.0
35 A	1.25	15/10	13.3	25.0	38.3	11.9
40 B	1.157	15/10	10.0	14.3	24.3	2.1
45 A	0.993	15/10	11.8	21.8	33.6	3.1
b#1	0.50	10/7.5	8.25	12.4	20.7	5.5
A9-6	1.157	10/7.5	6.27	15.6	21.9	6.0
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Average (for 15/10)	(1.19)	15/10	11.15	19.8	30.8	6.4
Average (for 10/7.5)	(0.83)	10/7.5	7.26	13.2	21.3	0.8

limited by the surface properties of the polyimide. This has been observed to be the case for a wide variety of materials where desorption takes place at or near the surface of a solid [10].

Some long-term tests were performed on sensors to study the effects of aging. One transducer was desiccated to initially determine the capacitance at 0-percent RH, then a number of C versus RH tests were performed. The sensor was again desiccated to determine any change in the initial capacitance. The initial and final desiccations were 52 days apart and three C versus RH tests were performed in between them. The sensor was stored under room ambient conditions (average 55-percent RH, 22°C) between tests. The values of C were 213.48 and 214.2 pF, respectively. This is a drift of 0.34 percent in capacitance. Even this small of a change, however, can cause an error of 4 percent in the zero reading of relative humidity. Thus this type of a sensor would benefit from a differential technique for readout such that a second sensor structure, not exposed to humidity, would be used on the same die.

Additional work on moisture diffusion in polyimide and its use in capacitive humidity sensing may be found in [11] and [12], respectively.

V. CONCLUSIONS

A relative humidity sensor has been described in which the diffusion of water through polyimide is used to change the

average dielectric constant of a capacitor structure. A theoretical description of the C versus RH variations is afforded by combining the Looyenga expression for dielectric constant of a mixture with the absorption description of Dubinin's equation. Excellent agreement was noted between theory and experiment.

A particular design of the sensor was implemented which is suitable for integrated-circuit type of fabrication, being potentially capable of fabrication on the same die as the detector and readout circuitry. The sensor was stable over extended time periods, although in some applications, zero drift might have to be adjusted for.

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