5th International Symposium on Humidity and Moisture – ISHM 2006 Brazil May 02 – 05, 2006 – Rio de Janeiro, Brazil

Theory and Practice of Shear/Stress Strain Gage Hygrometry

Qamar A. Shams¹, <u>Ralph L. Fenner²</u>

¹NASA Langley Research Center, Hampton VA, USA ²Fenner Associates, Alpine, CA, USA

Abstract: Mechanical hygrometry has progressed during the last several decades from crude hygroscopes to state-of-the art strain-gage sensors. The strain-gage devices vary from different metallic beams to strain-gage sensors using cellulose crystallite elements, held in full shear restraint. This old technique is still in use but several companies are now actively pursuing development of MEMS miniaturized humidity sensors. These new sensors use polyimide thin film for water vapor adsorption and desorption. This paper will provide overview about modern humidity sensors.

Key words: Hygrometry, strain-gage, polyimide thin film, MEMS, desorption, humidity sensors

The rapid and accurate measurement of humidity has challenged the scientific community for a long time. During the last 15 years, an emerging Micro-Electro-Mechanical-System (MEMS) technology, coupled with the latest cutting edge technologies for smaller, faster, and inexpensive systems, has opened the way for development of capacitance type and cantilever stress/strainbased MEMS humidity sensors [1-8]. Though there is a lot of interest in these miniaturized size and low cost humidity sensors yet there is strong desire to improve accuracy and rapid response of these sensors. The authors believe that the improved response can be achieved if we understand the theory and basis of multimolecular condensation of moisture on natural polymers like cellulose, man-made polymers and other substrates. To increase our understanding, how these natural and man-made polymers absorb, desorb and transduce water vapors, we start with the basic structure of water and its different forms.

The water is a very reactive compound. Water molecules are bound by hydrogen bonds into

large and fluctuating aggregates. It is a weak acid and at the same time a weak alkali. The "OH" side reacts to make alkali and the positive side, "H", reacts to make acid. The polarity of a water molecule is depicted in Figure 1.

The water vapors are part of every human breath. The air we breathe - and its components (including water vapors) are critical to support our life. The measuring of pollution for the many chemical components that are in the air do not stand alone, and can't be separated from relative humidity. Any chemical reaction that takes place whether inside the body or outside is reliant on the water molecules. It is the destabilizing element – subject to change. Water is the only molecule that will condense within the temperature excursions of our environment, going freely between gas, liquid, and solid. Water is the only vapor that is different because it is condensable, and because it can change, physically separating from the other gases and physically transferring energy from one part of the earth's environment to another. The vapors from the oceans condense on the land and become rivers, returning as rain as a means of irrigating vegetation, to snow and ice as a method of storing energy in a single place, and in its time fed back to the energy system, flowing to the oceans.

The polarity of the molecule is centered around the oxygen atom. When water is condensed in an ice crystalline as shown in Figure 2, the molecules link in such a manner that it takes more space and have the least energy. In liquid form as shown in Figure 3, the water is amorphous and the molecules are linked closer together with moderate energy. Gas or vapor form of individual water molecule is called humidity. In humidity form, molecule as shown in Figure 4 are not linked together and have the



Figure 1 - Polarity of water molecule

highest energy.

 H_2O is a very reactive molecule at a high concentration. However, reactivity varies with temperature and becomes moderate at ambient temperature

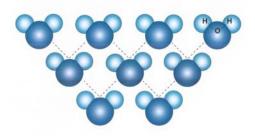


Figure 2: Ice Crystalline form of water having the least energy

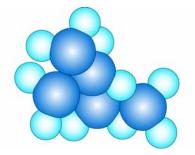


Figure 3: Water in liquid form has moderate energy

Water molecules affect our climate all the time. The water distribution in the atmosphere varies strongly with time, location, and altitude. It can transfer its energy from ice to water, and to gases. In gas form, vapors move with winds and can travel up to the stratosphere. It is here that water vapors absorb almost 70% of the known absorption of incoming sunlight which contribute to the warming of our earth planet.

Without these water vapors in the atmosphere, the earth temperature would be lowered by about 30 degrees K and will become uninhabitable. In other words, water vapors play a positive role in greenhouse effect. There is substantial water greenhouse effect in the troposphere, the lowest

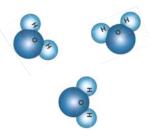


Figure 4: Free molecules in humidity form have the highest energy.

region of the atmosphere, as a result of the large water concentration. On the other hand, in the stratosphere region there is little greenhouse effect because of the small concentration of water.

The water and water vapors have played critical role in the formation of our planet. The climate of our planet is largely controlled by tropospheric phenomena, including the clouds, the global circulation of tropospheric air, and the exchange of energy between the oceans, surface, and troposphere as shown in Figure 5 [9]. The water vapors have also played a critical role in chemical evolution of organic molecules, leading ultimately to the appearance of life.

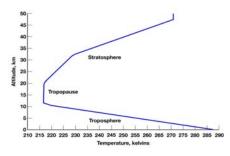


Figure 5: Atmosphere Temperature Profile

This evolution process can be divided into two processes.

1. The abiotic production of key precursor molecules, like H_2CO and HCN.

2. The reaction of these precursor molecules in the oceans to produce more complex organic molecules, like amino acids and carbohydrate (sub-components of nucleic acids, and proteins).

One possible scenario about the production of H_2CO is that it was a byproduct of sunlight and abundant N_2 , CO_2 , and H_2O gases present in the early atmosphere [10]. Once production of H_2CO is completed in the atmosphere, water (rain) transported these organic molecules to the oceans for polymerization which lead to more complex organic molecules.

Humidity in the Air and its Measurement:

The concept of humidity in air is simple. The temperature of the air determines the partial vapor pressure of the water that a given area can contain at saturation. The partial pressure of water vapors that exists at any time in a given air mass may be less than saturation. Relative humidity (RH), is the equilibrium moisture content of air and water activity (a_W) in the relative equilibrium moisture content of materials. Adsorb and desorb response can be transduced electrically by impedance or physically by stress /strain measurement.

Humidity divided by 100 become percent relative humidity. Because of the growth in the field of electronics, different types of humidity sensors like Dunmore sensor, the Pope cell the "dew cell" and the capacitive types were developed in the 1930s; the carbon type in the 1940s; the electrolyte; infrared; and Lyman-Alpha instruments in the 1950s; the automatic chilled mirror hygrometer; the aluminum oxide hygrometer; and Shear/Stress Strain Gage in the 1960s.

The authors believe that the improved response can be achieved if we understand the theory and the basis of multi-molecular condensation of moisture on polymers. To increase our understanding how these polymers absorb, desorb and transduce water vapors we will concentrate on four mechanisms;

- 1. To learn from Nature (How natural polymers like cellulose absorb water and balance water vapors in plants).
- 2. Langmuir's Theory of monomolecular adsorption.
- 3. BETs multilayer model of bound water in the polymer.

4. Van der Waal's condensation.

Cellulose (Natural Polymer) and its role for water adsorption in Plants:

Cellulose is a byproduct of photosynthesis which involve three elements namely, carbon, oxygen, and hydrogen. Water is a source of oxygen and hydrogen elements. Due to photosynthesis, these elements are combined in complex molecules and joined into different types of natural polymers. These polymers are cellulose, hemicellulose, and lignin. Cellulose polymer provides strength to the woods. Anhydrous glucose molecules polymerize into megamolecular-weight filaments of cellulose that bond to each other through cross linkages to form anhydrous crystals. Cells are bonded together with lignin in full shear restraint, creating a structure that is physically responsive to the stress induced by relative vapor pressure. Because of these characteristics, it has been used for humidity sensors [6].

In plants, cellulose is found in two forms, crystallite form and amorphous form. In crystallite form, there are no sites available for adsorbing water molecules. On the other hand, in amorphous form, there are sites available for water molecules as shown in Figure 6.

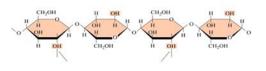


Figure 6: Hydrogen bonding to other cellulose molecules can occur at OH points.

The structure of a cellulose molecule has four units. Every second unit is inverted as compared to the first one. Also, the O site that connects two units is inverted at every second site. The cellulose molecule is developed in plants to store energy and provide structural support [3]. The cellulose crystallite structure is considered more effective than the hair hygrometer. The structure of wood results in the generation of an activating force in expansion and contraction. Cellulose selected for use as a humidity sensor is subjected to a processing and treatment program. The cellulose crystallites are the hygromechanical portion of the sensor. The paired elements are then coupled with a strain gage beam.

This type of mechanical hyprometry has progressed during the last several decades from crude hygroscopes to state-of-the-art strain-gage sensors. The first strain-gage devices were built in 1960 using metallic beams instrumented with discrete silicon gages which were stressed by natural organic structures [3]. These physical adsorption sensors assembled from organic crystallite elements are very reliable but follow a type 2 adsorption curve of bound water, which produce non linearity and wide hysteresis. The next generation strain-gage sensor was developed in 1970 using cellulose crystallite elements, which were held in full shear restraint. This sensor produced a linear output from 0-100% RH with very low hysteresis [3]. These sensors are reliable, linear, accurate and capable of withstanding extremely hostile environments. They are relatively expensive to build and calibrate.

This old technique is still in use but some companies, and research and development institutions are actively pursuing state-of-the-art MEMS humidity sensors. The next generation humidity sensors evolved in the early 1980s and 1990s when shear/stress strain gage (S/SSG), resistance and capacitance type MEMS humidity sensors were developed [11,12,13]. Some of these sensors are shown in Figure 7.

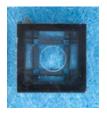


Figure 7(a): Cantilever-based MEMS S/SSG Humidity Sensor



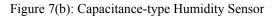




Figure 7(c): Capacitance-type Humidity Sensor

Evaluation criteria for different types of humidity sensors are; Quantity measured, Cost (including signal conditioner), Humidity range, Accuracy, Temperature range, Temperature effect, Long-term stability, Response time, Hysteresis, Linearity, Interchangeability, Lead effect, Resistance to contamination, Resistance to condensation, Cleanability, Calibration ease, Size/ Packaging, application and the chemicals to which these sensors will be exposed.

Copy of Natural Cellulose:

We have seen that natural (amorphous) cellulose can absorb and desorb water depending upon environment. Natural cellular structures do it because of their polymer properties. Researchers have started looking at similar types of lab-made polymers that can reflect properties of cellulose. Here is a brief description of polymers. Polyimides are polymers that contain an imide group as shown in Figure 8 (a). When polymers are polymerized, it takes either form of a linear structure or heterocyclic structure as shown in Figures 8(b) and 8(c) respectively.

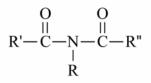


Figure 8(a): An Imide group

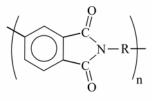


Figure 8(b): Heterocyclic Structure

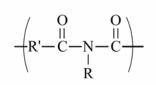


Figure 8(c): Linear Polyimide

After polymerization, the polymer can take one of the two structures. Heterocyclic polyimides are used in the electronics, automotive, and aerospace industry. The properties that originate from strong intermolecular forces between polymer chains can provide insight for water vapor absorption and desorption mechanism by the polyimides. Certain polyimides contain two different types of monomers, a donor and acceptor. The charge transfer does not only work between adjacent units but also between chains. Figure 9 shows how the carbonyls of the acceptor on one chain interact with the nitrogen of the donor on adjacent chains.

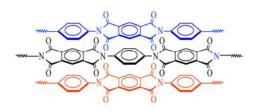


Figure 9: Polyimides stack in a manner that allow the carbonyls of the acceptor to interact with the nitrogen of the donor on adjacent chains.

Even though the water molecule is neutral as a whole, slight variation in charge distribution causes a dipole moment. This dipole characteristic of water can use acceptor and donor capability of polyimides to generate intermolecular forces between polyimide and water. This leads to a net attraction between polar molecules of water and thin polyimide films.

Afterwards, surface tension and van der Waals forces come into play. It is fair to say that van der Waals forces and surface tension are what holds water in place on polyimide thin film surfaces. When humidity level increases, other water molecules are attracted to the primary water layer because of polarity. The asymmetry of the water molecule leads to a dipole moment with a slightly more positive charge towards hydrogen atoms. This polar nature of water molecules causes dipolar interaction between water molecules as shown in Figure 10.



Figure 10: Dipole Interaction between water molecules

Another force responsible for keeping moisture attracted to the surface is cohesive force between liquid molecules called surface tension. If there is enough water, the cohesive forces are shared by molecules in all directions, but on the surface there are no atoms on the upper side, hence only attractive forces are between neighboring molecules. This attractive force is called surface tension. At the surface, discontinuities in densities produce two-dimensional "surface tension". The magnitude of surface tension depends upon cohesive forces. Interfacial tension (γ_{12}) can be calculated using tension in both regions (say γ_1 and γ_2) minus the work of adhesion (W₁₂). In our case, γ_1 and γ_2 are surface tension of water and polyimide respectively, while W₁₂ is the adhesion force of attraction between water vapor and polyimide thin film. Where there is liquid and solid interface, we can ignore pressure difference across a curved interface (which is the case of interfacial tension in liquids). Examples of three liquid tensions are capillary height, drop, and bubble-shape.

The spin-coating process to deposit thin polymer coatings and the shrinkage caused by subsequent thermal processing results in an anisotropic expansion of the films when exposed to humidity. As seen in Figure 11, the plot of relative humidity (%RH) vs. output (m-V) is non-linear. This is because of anisotropic expansion and three different sorption processes in a polymer film when exposed to humidity [14]. A) At low humidity levels, water is absorbed in micro-voids. B) At humidity levels above 50% RH, absorption is dominated by cluster formation. C) The third absorption, also

known as Henry dissolution occurs over the whole humidity range. This process is described by equation, $C_K = C_H + C_L + C_C$ where C_H is Henry sorption; C_L is Langmuir sorption; and C_C is clustering sorption. The first two sorption processes are nonlinear while the third one responds in a linear fashion. At low humidity levels as shown in Figure 11 the sorption of water can be modeled by means of Langmuir isotherms and causes a convex appearance. This process changes at humidity levels above 50% and absorption is dominated by a cluster formation and causes the concave shape.

There are some other capacitance-type humidity sensors that use similar types of polymer coating. In operation, water vapor in the active capacitor's dielectric layer of these devices, equilibrate with the surrounding gas and the change in capacitive reactance is measured. Figure 11(b) shows typical response of capacitance type humidity sensor.

Mechanism of Water Sorption in Polyimide films: (Basis of small-scale Humidity sensors)

Thin polymer films have found widespread applications in silicon-based microelectronic devices due to their unique material properties. Polyimides, polymers that contain recurring amide groups as integral parts of the main polymer chains, have been extensively used in the aerospace and electronics fields because they are thermally stable, mechanically strong, and electrically insulating [15-17]. Interest in these materials is particularly high where large-scale integration, and miniaturization. high-speed signal processing in semiconductorbased components are important factors. Such demands require varied properties of polyimide materials. Accordingly, polyimides of different structures are used for different chain applications [16, 17]. In case of small-scale humidity MEMS sensors, commercially available polyimide is spin coated on cantilever beams and on dielectric film between the capacitance plates. As a result of the spin-coating process and subsequent thermal processing, polymer layers show in-plane orientation [16]. When exposed to a humid environment, these polymer thin films tend to expand due to the sorption of water molecules [16, 17]. In some of the previous studies, the swelling of thin polyimide films have been found to be anisotropic [16].

Polyimides have relatively high uptakes of water. Water sorption has a significant effect on the dielectric constant of polyimides. It causes increased conductivity of the dielectric insulator and promotes corrosion of the conducting metal leading to potential device failure [18-20]. Properties of these films can be changed by different methods like ion implantation and incorporation of fluorine during deposition. Both, the dielectric constant and the water uptake of polyimides, can be reduced by incorporating fluorine into the polymer [21-23].

Decreasing the imide content of the polymer is another way for changing film characteristics [24]. Because of high permeability, polyimide films can also be used as membranes for water vapor separation [25-27]. The water vapor sorption and diffusion properties of polyimides are very important for their use in humidity sensors. Investigations of water vapor sorption and diffusion properties of polyimides have been widely reported [28-43].

Solubility(S) and diffusion coefficients (D) are determined with the transient sorption and desorption experiments using a gravimetric method of measuring water vapor uptake on freestanding polymer films. The process by which gases, vapors or liquids are transmitted depends on the structure of the polymer membrane or film. For a polymer film with gross pores, mass transport occurs primarily by viscous processes when there exists a pressure difference across the pores, and by ordinary or Fickian diffusion in the presence of a concentration difference across the pores [44].

It is, of course, desirable to fabricate polymer thin films without pores. However there is an activated-diffusion- type penetrant transport in such films; a process in which the gas dissolves in the film at higher concentration surface, then migrates through the film under a gradient and finally desorbs or evaporates from the surface at the lower concentration. The absorbed water vapor mass depends on the mass of the polymer itself, so it is useful to relate the mass of the absorbed water to the mass of the dry polymer. The mass of the absorbed water, and consequently the saturation concentration, depend on the temperature, so it is important that all measurements be performed at a constant, specified temperature. It has been reported that the maximum values of water uptake and expansion as well as the degree of non-linearity

for humidity measurement is influenced by the annealing conditions [45].

The amount of sorbed water depends on the chemical structure and the morphology of the polymer chains as well. Also, it is dependent on the film thickness. Furthermore, higher anneal temperature results in higher film densities that lead to reduced mass uptake.

Adsorption isotherms:

When free gas come in contact with polymer, the surface shows affinity towards vapors. The molecules either enter the surface or remain attached to the surface, called adsorption. The free vapors (which are not in direct contact with the surface) and the adsorbed vapors finally will establish equilibrium. In such a case, the fractional coverage of the surface is dependent on the overlying vapor pressure. The variation of this fractional coverage with pressure at a given temperature is called adsorption isotherm. Several researchers worked on different models for adsorption isotherm establishment. Here we will briefly discuss two isotherms. The first one is Langmuir isotherm and the second one is the BET isotherm. The Langmuir isotherm depends upon a number of factors.

- 1. The temperature of the system (which remains the same during experiment).
- 2. The pressure of the gas surrounding the polymer surface.
- 3. Kinetic equilibrium between adsorbed and surrounding gas/vapors.
- 4..Adsorption is restricted to monolayer coverage.
- 5. Each surface site can accommodate, at most, one molecule/vapor.
- 6. The ability for adsorbtion at a given site is independent of the state of the neighboring site.

It is concluded that there is no net change of surface coverage (θ). The change of θ due to adsorption is equal to the rate of change of θ due to desorption. In equation form it can be written as follows:

 $\theta = N/S = bP/1+bP$

Where N is the number of adsorbed molecules and S is the available polymer surface sites and b is the ratio of adsorbed rate constant to rate of desorption constant, $b = b_a/b_d$ So surface coverage can be calculated if we know pressure (P) of the gas (including water vapors) and ratio of adsorption rate constant to desorption rate constant. In Langmuir model, assumption is that adsorption could occur only on the unoccupied sites. This restriction was ignored by Stephen Brunaur, Paul Emmet, and Edward Teller and they devised another isotherm equation called BET isotherm. The assumptions made for BET isotherm are:

- 1. The molecules are adsorbed on a flat, uniform surface of the solid due to van der Waals forces between the gas and the solid.
- 2. Once molecules are adsorbed on the solid surface, additional molecules can adsorb either on the remaining free surface or additional layers built on the first layer of adsorbed molecules.
- 3. There is no lateral interaction between the molecules of the adsorbed layers.

Under the BET model, surface coverage θ will be

$$\theta = bz / (1-z) \{1-(1-b)z$$

where
$$b = b_a/b_d$$
 and $z = P/P^*$

b is analogous to parameter for Langmuir. The BET simplifies to the Langmuir when relative pressure z < 0.01 and b > 100 [46]

The Use of Polymer thin films in Humidity sensors:

Capacitance-type polymer sensors use polyamide or cellulose acetate polymer thin films deposited between conductive electrodes. The thin film acts as a capacitive dielectric medium that changes its dielectric constant as the moisture is adsorbed.. In MEMS humidity sensors, cantilever beams are coated with polyimide thin films. These thin films adsorb and desorb water vapors depending upon environment.

Characterization Matrix:

A series of tests to characterize MEMS humidity sensors were performed as follows:

1. Characterization of polymer coated cantilever-

beam based MEMS sensors without signal conditioning unit.

 Characterization of polymer coated Capacitance type humidity sensor with built-in signal conditioning.

The sensors were exposed to different humidity conditions (10, 20, 30, 50, 70, & 90%) at different temperatures (10, 20, 30, & 50° C). Variation of the sensor output (m-Volts) as a function of relative humidity (%RH) at a constant tempera-ture is shown in Figure 11(a). As expected, the output increases with increase in humidity. Similarly the sensor output increases with temperature for a constant RH%. Properties of the final processed polyimide film are dependent upon the post-deposition temperature [40]. If cured at 350° C for 60 minutes, these polyimids films show virtually no degradation even after 1000 hours of testing.

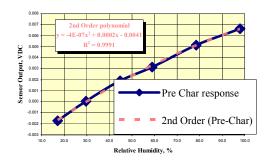


Figure 11(a): Cantilever-beam based MEMS humidity sensor (without signal conditioning)

As seen in the Figure, plot of relative humidity (%RH) vs. output (m-V) is non-linear. This is because of anisotropic expansion and three different sorption processes in a polymer film when exposed to humidity [41]. A) At low humidity levels, water is absorbed in microvoids. B) At humidity levels above 50% RH, absorption is dominated by cluster formation. C) The third absorption, also known as Henry dissolution occurs over the whole humidity range. This process is described by equation, C_K $= C_{H} + C_{L} + C_{C}$ where C_{H} is Henry sorption; C_{L} is Langmuir sorption; and C_C is clustering sorption. The first two sorption processes are nonlinear while the third one responds in linear fashion. At low humidity levels, as shown in Figure 11, the sorption of water can be modeled by means of Langmuir isotherms and causes convex appearance. This process changes at humidity levels above 50% and absorption is dominated by cluster formation and causes the concave shape.

The capacitance-type humidity sensors use similar type of polymer coating. In operation, water vapor in the active capacitor's dielectric layer of these devices, equilibrate with the surrounding gas and the change in capacitance is measured. Figure 11(b) shows typical response of the capacitance type humidity sensor.

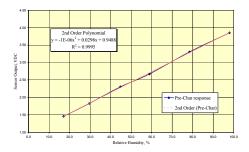


Figure 11(b). Capacitance type humidity sensors characterization (with signal conditioning)

In this plot, again all three processes; Langmuir isotherm, cluster formation, and dissolution of water are apparent but on a smaller scale as linearity is improved because of built-in signal conditioning.

The principle upon which all these small size humidity sensors (cantilever-beam based and capacitance type) work depends upon coating of polymer thin films. Measurement of RH% directly depends upon absorption of water vapors by polymer films. The water vapor mass absorbed depends on the mass of the polymer itself, so it will be useful to relate the mass of the absorbed water to the mass of the dry polymer. Mass of the absorbed water, and consequently the saturation concentration, depends on the temperature, so it is important that all measurements be performed at a constant temperature. It has been reported that the maximum value of water uptake and expansion as well as the degree of nonlinearity for humidity measurement is influenced by the anneal conditions [39].

Structural effects influence the sorption behavior also. The performance and reliability of the polyimide films can be improved by changing the chemical and physical structures [42]. High degrees of molecular ordering and in-place orientation of the polymer reduce moisture uptake but increase the humidity-induced stress in the film.

Polymer Surface Characterization:

A large number of techniques are available today for characterizing polymer surfaces and unique information on the chemistry and surface morphology is now available. The most commonly used technique is optical microscopy that can resolve ~ 1 micron. Higher resolution imaging (<1 micron) is accomplished with Scanning Electron Microscope (SEM). The SEM can resolve surface features up to a few nanometers. However, SEM does not provide high contrast images on flat films, but requires vacuum and often requires a conducting coating on the surface of the test film. Atomic Force Microscope (AFM) has the advantage that no special sample preparation is required. Images are usually obtained by raster scanning the tip over the surface while a feedback system adjusts the tip-sample spacing to maintain the force constant. Hence, the image is a constant force contour map whose features often reflect the physical structure of the surface. In the present study, AFM was used to analyze polymer-coated films.

Here are 2-D and 3-D scans of typical polymer coating on humidity sensors. The scans in Figures 12(a) and 12(b) provide visual and qualitative information on many physical properties including size, morphology, surface texture and roughness. These poly-type surface structures show average roughness of 18 nm.



Figure 12(a): 2-D AFM scan of typical polymercoated surface section of humidity Sensor. This scan has a dimension of 1.66 um x 36.7 nm.

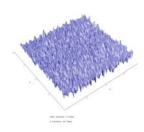


Figure 12(b): 3-D AFM scan of typical polymercoated surface section of humidity Sensor. This scan has a dimension of 1.66 um x 1.66 um x 36.7 nm.

Roughness of polymer films on the surface of humidity sensor:

Quantitative measurement of the nanometer scale roughness provides surface texture and helps in the measurement of adhesive properties of polymers. On one typical polymer coating, shown in Figure 13, three different spots were used to determine surface roughness.

		1HI	
tai yan	18.00	tean 1	194
	144	104	100
	144	100 ()	
	1022	174442 C	-

Figure 13: Average surface roughness for typical polymer coated humidity sensor (1 um).

Total length Rt, roughness average Ra, rootmean square Rq, and ten points height Rz were calculated as follows.

The average roughness is the integral of the absolute value of the roughness profile height over the evaluation length.

Ra = 1/L Integral abs. R(x) dx

The root-mean-square (rms) average roughness of a surface is calculated from another integral of the roughness profile:

Rq = 1/L r2(x) dx

Rz is the sum of the height of the highest peak plus the lowest valley depth within a sampling length. The calculated roughness values of a typical polymer coated film are:

Rt = 11.65 nm, Ra = 3.37 nm, Rq = 4.25 nm, and Rz = 20.84 nm.

Measuring the surface texture is critical. For example, surface texture can alter the optical properties of materials, control adhesive properties of polymers, and control the density of absorption. The relationship between surface roughness and absorption of water vapors will be reported in other paper.

2D and 3-D images of polymer coated films after isopropyl alcohol wash:

Surface roughness of polymer coated films improved after isopropyl alcohol wash as shown in Figures 14(a) and 14(b). The linearity improves only for cantilever-beam based humidity sensors and it deteriorates for capacitance type sensors. The reason could be that contamination on all four polymer coated cantilever beams are cleaned by the isopropyl alcohol wash and that they are completely dried up in twenty-four hours. Hence, polymer film responds to water vapors in an improved way while this is not the case with capacitance type humidity sensors. The protective polymer layer on capacitance type humidity sensors provide mechanical protection for the porous platinum layer as well as from contaminants such as dirt, dust and oils. When this sensor is washed with isopropyl alcohol, it cleans the first polymer layer and filters into second polymer layer. This filtered isopropyl alcohol does not dry up in twenty four hours (after which time the sensor again). Hence the sensor was tested characteristics deteriorate. The results reported in this paper are preliminary and not conclusive.



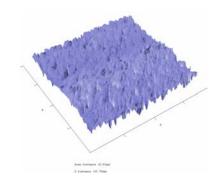


Figure 14(b): 3-D AFM scan of cantilever-beam based sensor after soaking in isopropyl alcohol.

Conclusion:

During the last 15 years, an emerging Micro-Electro-Mechancial Systems (MEMS) technology, coupled with the latest cutting edge technologies for smaller, faster, and inexpensive systems, has opened the way for development of capacitance type and cantilever stress/strainbased MEMS humidity sensors. These sensors use industrially proven thermoset polymer thin films. These sensors were thoroughly characterized and polymer thin films analyzed before and after exposure to extreme humidity. An attempt was made to increase our understanding, how natural (like cellulose) and lab-made polyimide absorb, desorb, and transduce water vapors. In addition, the application of Langmuir theory of monomolecular adsorption, BETs multilayer model of bound water in the polymer and Van der Waals' condensation in cantilever-based MEMS sensors and capacitance type sensors were investigated.

Acknowledgement:

The authors gratefully acknowledge support of Ms. Wendy Padilla (Fenner Associates) and Cecil G. Burkett (NASA Langley Research Center) to accomplish tasks reported in this paper.

Figure 14(a): 2-D AFM scan of cantilever-beam based sensor after soaking in isopropyl alcohol.

REFERENCES:

- "Proceedings of the Workshop on Microtechnologies and Applications to Space Systems" May 27-28, 1992 JPL Publications 93-8.
- [2]. H. Helvajian, "Microengineering Technology for Space Systems" The Aerospace Press, Monograph 97-02.
- [3]. Fenner, Ralph L., "Cellulose Crystallite/ Strain Gauge Hygrometry", Sensors, May 1995.
- [4]. Chatzandroulis S., "Fabrication of single Si cantilevers using a dry release process and application in a capacitive-type humidity sensor" Microelectronics Engineering 61-62 pp. 995-961, 2002.
- [5]. Chin-Yen Lee and Gwo-Bin Lee., et al., "Micromachine-Based Humidity Sensors with Integrated Temperature Sensors for Signal Drift Compensation", Journal of Micromechanics And Microengineering, 13 pp. 620-627, 2003.
- [6]. Mehmet Dokmeci and Khalil Najafi., "A High-Sensitivity Polyimide Capacitive Relative Humidity Sensors for Monitoring Anodically Bonded Hermetic Packages", IEEE Journal of Micro-ElectroMechanical Systems, June 2001.
- [7]. Celin Laville and Claude Pellet., et al., "Comparison of Three Humdidity Sensors for a Pulmonary Function Diagnosis Microsystems", IEEE Sensors Journal, April 2002.
- [8]. K. Govardhan and Z. C. Alex, Proceedings of International Conference on Smart Materials Structures and Systems, July 28-30, 2005, Banglore, India.
- [9]. Levine, Joel S., "The Photochemistry of Atmospheres" Academic Press, Inc. 1985, Page 9.
- [10]. Pinto, J.P., G.R. Gladstone, and Y.L. Yung 1980. "Photochemical production of formaldehyde in primitive atmosphere. Science 210, 183-185.
- [11]. Fenner, R and Zdankiewicz, E. "Micromachined Water Vapor Sensors: A Review of Sensing Technologies", IEEE Sensors Journal, Volume 1, No 4, Dec. 2001.
- [12]. Fenner, R., Kleefstra, M. Zdankiewicz, E. "New Micromachined Water Vapor Sensor for Home Appliances", Sensors Magzine, May 2002.
- [13]. Honeywell, "Humidity sensor in a single in-line package" Electronics Times, September 25, 2000.
- [14]. Wolf R. Vieth, "Diffusion In and Through Polymers, Carl Hanser Verlag, Munchen, 1991.
- [15]. Fager, M. M. Khojastech, and J. E. McGrath (eds.), Polyimides: Materials, Chemistry and Characterization, Elsevier, Amsterdam, 1989.
- [16]. D. Wilson, H. D. Stenzenberger, P. M. Hergenrother (eds.) Polyimides, Chapman and Hall, New York, 1990.
- [17]. M. J. M. Abadie and Sillion (eds.), polyimides and

Other High Temperature Polymers, Elsevier, Amsterdam, 1991.

- [18]. H. Ikeno, A. Oh-saki, N. Ozaki, M. Nitt, K. Nakaya, and S. Kobayashi, SID Digest 45 (1988).
- [19]. R. S. Mulliken, Molecular Complexes, John Wiley & Sons, New York, 1969.
- [20]. S. Nagakura, J. Chem. Phys. 23(8); 1441 (1955).
- [21]. R Haight, R. C. White, B. D. Silverman, and P. S. Ho, J. Vac. Sci. Technol. A. 6(4):2188 (1988).
- [22]. C. J. Lee, J. Macromol. Sci. Rev. Macromol Chem. Phys. C29(4): 431 (1989).
- [23]. J. M. Salley and C. W. Frank, Polym. Preprints. (Am. Chem. Soc. Div. Polym. Chem.) 33:855 (1992).
- [24]. A. Nakamura and H. Makino, Maku(Membrane) 12: 289, 293 (1987).
- [25]. K. Nakagawa, Y. Asakura, S. Nakanishi, H. Hoshino, H. Kouda, and Y. Kusuki, Koubunshi Ronbunshu 46: 40 (1989).
- [26]. N. Tanihara, K. Tanaka, H. Kita, K. Okamoto, A. Nakamura, Y. Kusuki, and K. Nakagawa, J. Chem. Eng. Jpn. 25: 388 (1992).
- [27]. G. F. Sykes and A. K. St. Clair, J. Appl. Polym. Sci. 32: 3725 (1986).
- [28]. E. Sacher and J. R. Susko, J. Appl. Polym. Sci. 23: 2355 (1979).
- [29]. E. Sacher and H. R. Susko, J. Appl. Polym. Sci. 26: 679 (1981).
- [30]. J. A. Barrie, P. S. Sagoo, and P. Johncock, J. Appl. Polym. Sci. 33: 2253 (1987).
- [31]. D. K. Yang, W. J. Koros, H. B. Hopfenberg, and V. T. Stannett, J. Appl. Polym. Sci. 30: 1035 (1986).
- [32]. D. K. Yang, W. J. Koros, H. B. Hopfenberg, and V. T. Stannett, J. Appl. Polym. Sci. 31: 1619 (1986).
- [33]. C. R. Moylan, M. E. Best, and M. Ree, J. Polym. Sci., polym. Phys. Ed. 29:87(1991).
- [34]. F. Bellucci, L. Nicodemo, and L. Nicolais, Polym. News 17:272 (1992).
- [35]. B. S. Lim, A.S. Nowick, K. W. Lee, and A. Viehbeck, J. Polym. Sci., Polym. Phys. Ed. 31: 545 (1993).
- [36]. K. Okamoto, N. Tanihara, H. Watanabe, K. Tanaka, H. Kita, A. Nakamura, Y. Kusuki, and K. Nakagawa, J. Polym. Sci., Polym. Phys. Ed. 30: 1223 (1992).
- [37]. D. D. Deton, D. R. Day, D. F. Priore, and S. D. Senturia, J. Electron. Mater. 14:119 (1985).
- [38]. T. Tchangai, Y. Segui, and K. Doukkali, J. Appl. Polym. Sci. 38: 305 (1989).

- [39]. D. R. Day, in Polimides: Materials, Chemistry and Characterization (C. Feger, M. M. Khojasteh, and J. E. McGarth, eds.), Elsevier, Amsterdam, 1989, pp. 537-547.
- [40]. T. Yokoyama, N. Kinjyo, and Y. Wakashima, Kobunshi Ronbunshu 43: 597 (1986).
- [41]. J. Crank, The Mathematics of Diffusion, 2nd ed., Clarendon Press, Oxford, 1975, pp. 203- 253.
- [42]. R. Buchhold, A. Nakladal, G. Geralch, K. Sahre, K. J. Eichhorn "Mechanical Stress in micromachined components caused by humidity-induced in- plane expansion of thin polymer films", Thin Solid Films 312 (1998) 232-239.
- [43]. K.Sager, R. Buchhold, A. Nakladal, A. Schroth, G. Gerlach, Molecular-sensitive mechanical properties of thin polyimide-layers and their application in silicon micromechanics, Proc. Micro Mat. '95. Berlin. 255-260.
- [44]. K. Sahre, K.-J. Eichhorn, F. Simon, D. Pleul, A. Janke, G. Gerlach "Characterization of ion-beam modified polyimide layers", Surface and Coatings Technology 139 (2001) 257-264.
- [45]. F. Garbassi and E. Occhiello, Anal. Chim. Acta 197: 1 (1987).
- [46]. Valsaraj *et al.*, "Adsorption of Trace Hydrophobic Compounds from Water on Surfactant-Coated", Separation of Science and Technology SSTEDS, Vol. 27, No. 12, P1633-1642, Oct.1992.

Author: Qamar A. Shams, NASA Langley Research Center, Mail Stop 238 Hampton, VA 23681, USA. Phone: 757-864-8156,Fax:757-864-7607, E-mail: <u>Qamar.A.Shams@nasa.gov</u> Ralph L. Fenner, Fenner Associates, Alpine, CA 91901, USA. Phone: 619 659-0338, Fax: 619 445-7471, E-mail: <u>fenner@fennerassociates.com</u>