Novel Humidity Sensors Based on Nanoscale Hybrid Dielectric Materials

by Zhi David Chen

Humidity sensors are extensively used in industrial processing and environmental control.[1,2] For manufacturing of highly sophisticated integrated circuits in the semiconductor industry, humidity or moisture levels are constantly monitored in wafer processing.[3] There are many household applications for humidity sensors, such as intelligent control of the living environment in buildings and houses, cooking control for microwave ovens, and intelligent control of laundry.[1] In the automobile industry, humidity sensors are used in rear-window defoggers and motor assembly lines. The lithium-ion batteries used in electrical automobiles are manufactured at low humidity levels, which are monitored and controlled by highly-sensitive humidity sensors, called dew point meters. In the medical field, humidity sensors are used in respiratory equipment, sterilizers, incubators, pharmaceutical processing, and biological products. In agriculture, humidity sensors are used for green-house air-conditioning, plantation protection (dew prevention), soil moisture monitoring, and cereal storage. In the general industrial framework, humidity sensors are used for humidity control in chemical gas purification, dryers, ovens, film desiccation, paper and textile production, and food processing.[1]

Humidity/Moisture Measurement Units

Based on measurement techniques, the most commonly used units for humidity measurement are relative humidity (RH), dew point/frost point (DP/FP) and parts per million (PPM).[2] Relative humidity is the ratio of the partial pressure of water vapor present in a gas to its saturation vapor pressure at a given temperature. The RH measurement is expressed as a percentage, which is a relative value because the saturation vapor pressure increases with temperature. Parts per million represents water vapor content by volume fraction (PPMv) or by weight (PPMw) if multiplied by the ratio of the molecular weight of water to that of air. PPMv is an absolute measurement. Dew point is the temperature (above 0 °C) at which the water vapor in a gas condenses to liquid water. Frost point is the temperature (below 0 °C) at which the vapor condenses to ice. DP/FP is a function of the pressure of the gas but is independent of temperature and is therefore defined as an absolute humidity measurement.

Figure 1 shows the correlation among relative humidity, parts per million by volume, and the dew point/frost point. RH measurement covers the higher humidity range, PPMv covers the lower humidity range, and the dew point/frost point covers the entire humidity range. To simplify the terminology, dew point/frost point is usually called simply "dew point." In daily life, relative humidity is typically used for ease of understanding. For trace moisture measurements, it would be better to use dew point or PPMv, because it tells us the absolute amount of water vapor in a gas or air.

The Pros and Cons of Humidity/Dew Point Sensors on the Market

Humidity sensors are divided into two categories: (1) Relative humidity sensors for high humidity measurement; and, (2) Moisture or dew point sensors for low humidity measurement. Most humidity sensors on the market are relative humidity sensors, including ceramic, semiconductor, and polymer humidity sensors.[1,3] It is relatively easier to produce relative humidity sensors because high sensitivity is not required. However, for dew point sensors, extremely high sensitivity is required so that they are able to detect trace moisture levels below 0.5 PPMv or −80 °C DP (see Fig. 1). In addition, dew point sensors can be used for both low humidity and high humidity measurements because of their high sensitivity, but RH sensors cannot be used for low humidity measurement due to their low sensitivity.

Currently dew point (moisture) sensors on the market include ceramic sensors, polymer sensors, aluminum oxide film sensors, and chilled-mirror hygrometers.[1,2] All sensors on the market have some advantages and drawbacks. The chilled-mirror dew point hygrometers have very high precision, and thus are used as the standard for calibration of other sensors. But they have very high cost.[1,3] Ceramic sensors show very good stability (no drift), but respond very slowly with a response time of 5 minutes for a 63% step change from low humidity to high humidity. Polymer sensors with the sensor-heating technology respond very fast either from dry to wet or from wet to dry. But they do not have a wide measurement range. The mainstream polymer sensors have low sensitivity with the measurement range down to only −60 °C DP. Because of polymer's elastic property, polymer sensors cannot withstand high pressure. In addition, polymer sensors have some drift and hence need calibration every two years. Aluminum oxide film sensors are based on amorphous or γ-Al_2O_3 obtained by anodization. For simplicity, the amorphous/γ-Al_2O_3 based sensors are called γ-Al_2O_3 sensors. Aluminum oxide (γ-Al_2O_3) sensors have extremely high humidity sensitivity with the measurement range down to -110 °C DP or 1.3 parts per billion by volume fraction. Their temperature coefficient is also very small. However, γ-Al_2O_3 sensors exhibit long-term drift when exposed to higher moisture levels because the γ-Al_2O_3 phase is unstable and reacts with moisture to form boehmite (γ-$Al_2O_3.H_2O$), leading to long-term drift.[3-10] Our group has also fabricated γ-Al_2O_3 dew point sensors, which exhibited very large drift (see Fig. 2). Between tests, the sensor was placed on the desk in the laboratory, which exposed it to a humidity level of ~20 – 30%. It is clear that the γ-Al_2O_3 sensor had large drift when exposed to moisture. The drift was much faster initially and the drift rate was lowered after a few days. Commercial γ-Al_2O_3 dew point sensors are usually aged for three months before release to the market, but still require frequent calibration (6 months) and storage in dry environment.[11] They cannot be exposed to air, which is inconvenient to users.

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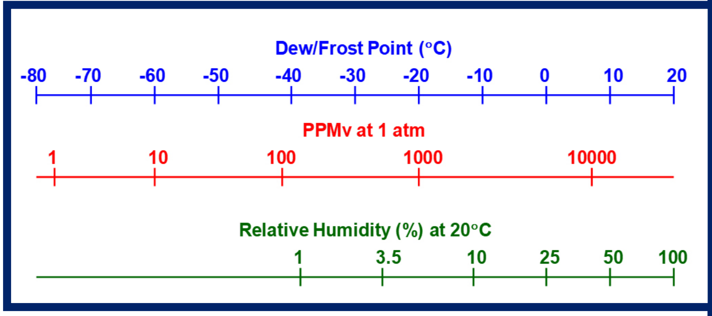

Fig. 1. *Correlation among humidity units: dew/frost point, parts per million by volume fraction (PPMv), and relative humidity.*

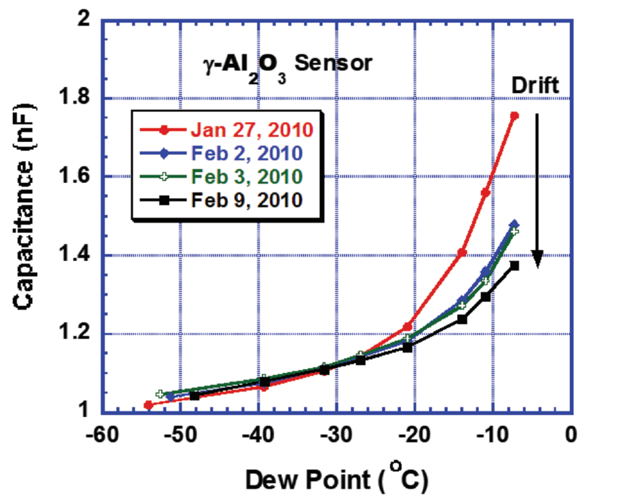

Fig. 2. *Capacitance vs.dew point of an γ-Al_2O_3 moisture sensor. Large drift after exposure to air (20 – 30% RH) for two weeks.*

Novel Hybrid Dielectric Sensing Materials

Most humidity sensors are capacitive structures where porous humidity-sensing materials are used as dielectric materials. When the humidity level in the environment changes, the amount of water molecules adsorbed in the inner surfaces of pores changes, resulting in change of the dielectric constant of the porous dielectric material. This leads to change of the capacitance and hence the impedance of the sensors.

A material considered as a humidity-sensing material for capacitive sensors must have the following properties: (1) dielectric, (2) porous, and (3) humidity-sensing. However, there are many humidity-sensing materials that are not porous. Using the following hybrid dielectric material scheme, non-porous humidity-sensing materials, if deposited by atomic layer deposition, can be converted into porous humidity-sensing dielectric materials. In this article, I present novel humidity sensors based on hybrid dielectric materials as shown in Fig. 3.[12,13] A porous dielectric material, which may not be humidity sensing, is formed on a conductive substrate. A nanoscale humidity-sensing film (<10 nm) is deposited conformally on the inner surfaces of the pores using atomic layer deposition. A thin metal film (<50 nm) is deposited as the top electrode. The conductive substrate is used as the bottom electrode.

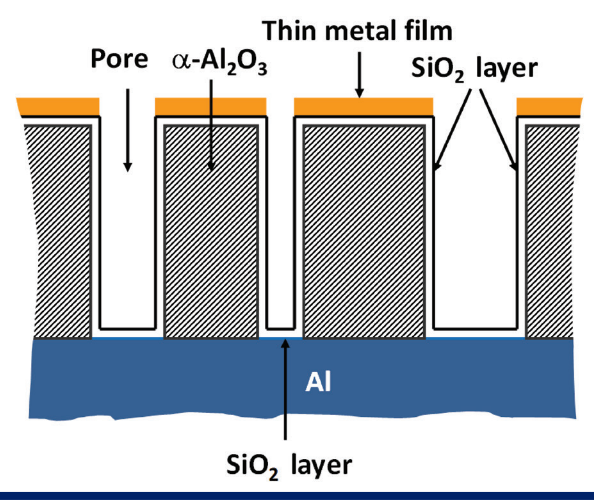

Fig. 3. *Novel schematic α-Al_2O_3/SiO_2 hybrid dielectric sensor structure: Conformal SiO_2 film deposited on the inner surface of pores of α-Al_2O_3 structures by atomic layer deposition. (US Patent 9,285,334 and Chinese Patent 201410246545.)*

α-Alumina(Sapphire)/Silicon Dioxide Hybrid Dielectric Sensors

It is well known that α-Al_2O_3 is synthetic sapphire, which is extremely stable. A porous α-Al_2O_3 film serves as the porous dielectric material. Among various other dielectric materials, SiO_2 is the most stable and has been used in silicon-based integrated circuits for several decades. In addition, SiO_2 is also highly humidity-sensitive because it is hydrophilic. SiO_2 is used as the nanoscale humidity-sensing film here. The schematic hybrid dielectric sensor structure is shown in Fig. 3.[12,13] To form wire bonding for the sensor electrodes on conductive substrates, the sensor electrode structure is described in detail in a US patent.[14]

Porous α-Al_2O_3 (sapphire) films were formed on aluminum substrates by anodic spark deposition.[15-19] Then, conformal SiO_2 thin films of ~3 – 10 nm were deposited on the surface, pore walls, and pore bases of the porous α-Al_2O_3 films by atomic layer deposition (ALD). Because SiO_2 growth is controlled at the atomic scale, very uniform and conform SiO_2 thin films can be obtained. SiO_2 thin films deposited at the pore bases also serve as insulators. Without them, the α-Al_2O_3 sensors would fail due to short-circuiting. The entire sensor structure consists of α-Al_2O_3 and SiO_2, where SiO_2 serves as the humidity-sensing material. Without amorphous/γ-Al_2O_3, the α-Al_2O_3(sapphire)/SiO_2 hybrid dielectric sensors are highly stable when interacting with water molecules. A conducting film, e.g., platinum, gold, Ti, TiN, TiO_2, and their combinations, is deposited on the top of the porous structure, to serve as the top electrode. The aluminum substrate serves as the bottom electrode.

Atomic layer deposition was used to obtain atomic layer control of the thin film growth as this technique is based on sequential self-limiting surface reactions. Because of the self-limiting effect and monolayer-by-monolayer deposition, the molecules cannot accumulate at the pore entrance and uniform films can be deposited on the entire inner walls of the high-aspect-ratio pores.[20-24] Because water molecules can diffuse through SiO_2, the presence of a stable porous dielectric material that is not reactive with water molecules, such as α-Al_2O_3, is of critical importance. The α-Al_2O_3(sapphire)/SiO_2 hybrid dielectric sensor showed very stable performance as shown in Fig. 4. The sensor was tested at varying dew points, generated by a humidity generator through mixture of dry N_2 and water vapor. Between tests, the sensor was left exposed to a humidity level of ~40 – 50% RH, with no special care taken to control the exposure. From Fig. 4, it is seen clearly that no drift occurred for the sensor exposed to air (40 – 50% RH) for 40 days except for small random variations. For comparison, a γ-Al_2O_3-based moisture sensor exhibited large drift after exposure to air for only 13 days (see Fig. 2). The sensitivity of the α-Al_2O_3/SiO_2 moisture sensor in the range from −70 °C DP to −80 °C DP is ~1.8 pf/°C DP, which is sufficient for dew point measurements.

Performance of α-Alumina(Sapphire)/ Silicon Dioxide Dew Point Meters

α-Al_2O_3(sapphire) is a thermodynamically stable phase. In combination with SiO_2, hybrid dielectric sensors do not exhibit any long-term drift, do not require recalibration, and can be stored anywhere, as shown earlier. The unique pore structure of the α-Al_2O_3 sensors allows them to respond very quickly to changes in humidity levels. The respond speed of α-Al_2O_3(sapphire)/SiO_2 sensors is the fastest among dew point sensors that do not use sensor-heating technology.

As an example of α-Al_2O_3(sapphire)/SiO_2 hybrid dielectric sensors, ASPT SRP-100 portable dew point meters and ASPT T80/T100 dew point transmitters are being manufactured and marketed by Advanced Semiconductor Processing Technology (ASPT). Table I shows, as an

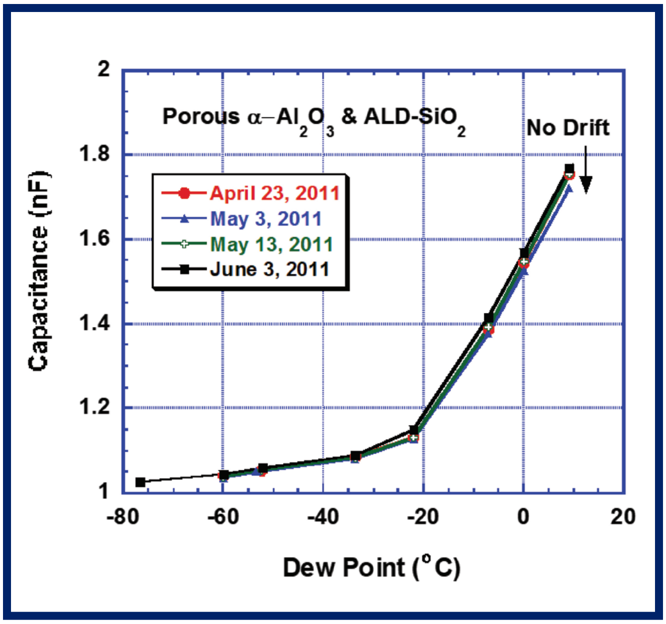

Fig. 4. *Capacitance versus dew point of an α-Al_2O_3/SiO_2 hybrid dielectric moisture sensor. No drift after exposure to air (40 – 50%RH) for 40 days.*

example, the technical data of ASPT T80 and T100 transmitters and SRP-100 portable meters. Performance of various dew point sensors available on the market are compared with ASPT sensors as shown in Table II. The Vaisala polymer sensor using sensor-heating technology has the fastest response. The response speed of the ASPT sensor without sensor-heating ranks the second after the Vaisala polymer sensor. The Michell ceramic sensor has the slowest response (5 min for 63% step change from dry to wet). The measurement of response times for both ASPT sensors and Vaisala DMT 152 was carried out in our company lab by a 63% dew point step from −60 °C to −20 °C (dry to wet) and from −20 °C to −60 °C (wet to dry). The response times of Michell Easidew, GE Panametrics, and Xentaur Cosa LPDT were measured by Xentaur company.[25] The accuracy of all sensors are close to each other. Regarding the measurement range, the GE γ-Al_2O_3 dew point sensor has the widest range and Vaisala polymer sensor has the narrowest measurement range. For long-term stability, only the ASPT sensor and the Michell sensor remain stable without recalibration.

Table I. Technical data of ASPT T80, T100, and SRP-100.

Technical Specifications	
Dew Point Range	–80 to +20 °C dew point (T80, SRP100) –100 to +20 °C dew point (T100)
Output Signal	4 to 20 mA
Accuracy	±2 °C dew point
Response Time—63% [90%] step change @ 3000 sccm	15 s [45 s] (Step: –60 °C to –20 °C) 1 min [3 min] (Step: –20 °C to –60 °C)
Operating Temperature	0 to +50 °C –30 to +50 °C (extended version)
Repeatability	0.5 °C dew point
Supply Voltage	8 V to 28 V DC
Operating Pressure	5 MPa 15 MPa (extended version)

Summary

A novel α-alumina(sapphire)/silicon dioxide humidity sensor using the hybrid dielectric material technique has been described. The hybrid dielectric material consists of an insulating porous dielectric material and a nanoscale humidity-sensing film deposited conformally on the inner surfaces of the pores using atomic layer deposition. These sensors exhibit long-term stability, fast response, and durability at extremely high/low humidity levels.

Acknowledgments

The author is grateful to his graduate and postdoctoral students in assistance in experiments, including Ibrahim Yucedag, Mengmei Liu, Riasad Badhan, and Bojie Chen. He is thankful to engineers of Advanced Semiconductor Processing Technology (ASPT) in both USA and China in assistance in research and development of the dew point sensor product, including Lei Han, Neha Nehru, Jingbo Tong, Fangdong Huang, Yunju Huo, and Tian Huang. He is also thankful to financial support from Kentucky Science and Engineering Foundation, USA, Chengdu High-Tech Zone Entrepreneur Award, and Chengdu City Talent Program, Chengdu, Sichuan, China.

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Table II Performance comparison of various dew point sensors

Dew Point Sensors	Measurement Range (dew point)	Accuracy (dew point)	Response Time (63% dew point step change @ 3000 sccm)	Recalibration
Vaisala DMT 152 (Polymer)	–80 °C – –20 °C	±2 °C (<–40 °C) ±3 °C (>–40 °C)	–60 °C to –20 °C: 9 s* –20 °C to –60 °C: 42 s*	Every 2 years
Michell Easidew (Ceramic)	–100 °C – +20 °C	±2 °C	–60 °C to –40 °C: 5 min –40 °C to –60 °C: 15 min	No
GE Panametrics (γ-Al_2O_3)	–110 °C – +20 °C	±2 °C (>–65 °C) ±3 °C (<–65 °C)	–60 °C to –40 °C: 1 min 17 s –40 °C to –60 °C: 8 min 20 s	Every 0.5 year
Xentaur Cosa LPDT (γ-Al_2O_3)	–100 °C – +20 °C	±3 °C	–60 °C to –40 °C: 1 min 17 s –40 °C to –60 °C: 2 min 30 s	Every 0.5 year
Retronic LDP-1 (N/A)	–70 °C – +85 °C	±2 °C (>–50 °C) ±3 °C (<–50 °C)	Dry to wet: 13 s Wet to dry: 10 min	Every 2 years
ASPT T100 (α–Al_2O_3/SiO_2)	–100 °C – +20 °C	±2 °C	–60 °C to –20 °C: 15 s –20 °C to –60 °C: 60 s	No

**The sensor-heating technology is used. The response time data for Vaisala and ASPT sensors are from our tests, and those for GE, Michell, and Xentaur sensors are from Xentaur tests[25] except for Retronic LDP-1, which are from its data sheet.*

About the Author

Zhi David Chen is a professor of electrical and computer engineering at the University of Kentucky, visiting professor at the University of Electronic Science and Technology of China, and co-founder and chief scientist of Advanced Semiconductor Processing Technology (ASPT) in the U.S. and China. He received his BS degree in 1984 and MS degree in 1987 in optoelectronic engineering from the University of Electronic Science and Technology of China, Chengdu, Sichuan, China. He obtained his PhD degree in electrical engineering from the University of Illinois at Urbana-Champaign in 1999. He has published about 100 papers in refereed journals and over 60 conference presentations with many high-impact papers. He pioneered the synthesis of titanium oxide nanotubes using anodic oxidation. He received numerous awards including National Expert of China Thousand Talent Program (2012), U.S. National Science Foundation CAREER Award (2001), the Second Prize Paper Award of Industrial Automation and Control Committee at the 27th Annual Conference of IEEE Industry Application Society (1992), and Chinese National Invention Award (the 3rd Prize, 1995). He currently serves as a member-at-large of the ECS Dielectric Science and Technology Division, and is a member of the *ECS Transactions* Editorial Advisory Board. He may be reached at zhi.chen@uky.edu.

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