Humidity sensing is critical in environmental and industrial spaces to monitor air conditions for the wellbeing of the human population and to ensure favorable industrial processes such as storage and performance. In this work, we utilize room temperature ionic liquids (RTILs) as novel sensing elements toward the development of a robust electrochemical humidity sensor for integration in semiconductor technology. For this study, we report and discuss the performances of a non-fluorinated RTIL vis-a-vis a fluorinated RTIL, MMIM[MeSO₄] and EMIM[TF₂N], on exposure to humidity levels 25–65%RH at low (25–45°C) and elevated temperatures (65°C). The electrochemical responses of the RTILs to humidity and temperature are recorded via electrochemical impedance spectroscopy to measure the capacitance changes occurring within the electrochemical double layer. Both RTILs show similar responses to humidity levels and temperatures. This work is the first demonstration of the implementation of RTILs on micro electronic devices toward achieving rapid and sensitive humidity sensing.

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Rising environmental concerns have led to the development of sensors to monitor environmental conditions such as CO₂, VOC’s, particulate matter, temperature, and relative humidity (RH). Humidity sensing finds its usage in a broad range of applications for indoor air quality monitoring in HVAC systems and automobiles, weather monitoring in meteorological stations, greenhouse gas monitoring systems, and textile quality monitoring. Three basic sensor types that have been widely used in commercial and industrial space are capacitive, resistive, and thermal humidity sensors. Over the years, variety of sensing materials such as ceramics, semiconductors, polyelectrolytes, and polymers have been explored and utilized in humidity sensors. Current challenges faced in humidity sensing are sensor drift, accuracy and reproducibility at increased humidity, response time of the sensor, power consumption, and long-term usability. These challenges necessitate the development of a new material system for next generation humidity sensing.

We employ a unique sensing material system- Room temperature ionic liquid (RTIL) to develop a robust humidity sensor toward making it suitable for commercial applications. Room temperature ionic liquids (RTILs) are a class of materials that have been studied for over a century. They have been shown to be useful in several different applications from gas sensing to protein stabilizers in biological experiments. Their highly ionic nature, wide electrochemical window, and ideal thermal and physical properties (See Table I) are ideal for the development of new electrochemical based humidity sensor. This class of materials consists of two major components; an organic cation and inorganic anion. These two components can be tuned depending upon what application the material is being investigated. Bridgeman et al. have previously demonstrated a calorimetric humidity sensor using ionic liquid membranes for food and pharmaceutical quality monitoring. Due to the pure ionic nature of RTILs, when a voltage is applied, this material has shown promise as a potential electrochemical based sensor. The innovation of this study is to interface an RTIL with a sensing platform which results in the formation of multi stack electrochemical double layer (EDL). The charge distribution in the EDL as a result of water adsorption is studied through an AC based technique- Electrochemical impedance spectroscopy (EIS).

Exploring the behavior of this material across different humidity levels and temperature ranges are necessary for the further development of a sensor. The purpose of this paper is to explore the role of the anionic moiety of the RTILs in achieving humidity sensing and then investigate how their sensitivity to humidity is affected at low and elevated temperature and humidity levels.

**Experimental**

**Electrode design and material.**—Commercial humidity sensors utilize interdigitated electrode design (IDEs) for sensing relative humidity. The comb structure of the IDE design allows for higher electric field confinement within a smaller geometry leading to an amplified signal response. Each digit of the IDE is 0.8 mm with digit separation of 0.2 mm and digit widths of 0.2 mm. The IDEs, as shown in Figure 1, were custom designed and ordered through PCB Universe. The interaction of the RTIL with humidity alters the electric field measured by the impedance changes occurring in the system. The electrode material of choice was gold electrodes due to its inert nature and stable electrochemical properties.

**Selection of RTIL candidates.**—RTIL’s consist of cation/anion pairs in various combinations. The cation/anion moieties can be tuned as per application by manipulation of their physical, chemical, and electrical properties. Two candidates, as shown in Figures 2a and 2b, chosen for humidity sensing are 1,3-dimethylimidazolium [MMIM] methyl sulfate [MeSO₄] and 1-ethyl-3-methylimidazolium [EMIM] bis(trifluoromethane)sulfonimide [TF₂N] (Sigma Aldrich, 98% purity) based on their miscibility in water, surface wetting, and viscosity properties.

**Humidity measurement experimental system setup.**—A standard nitrogen chamber was modified to allow for both gas and electrical connections. A small box placed internally within the nitrogen chamber houses the sensor mounted on a ceramic heater placed on top of a digital hotplate [Torrey Pines Scientific, Inc. HS60]. The ceramic heater allows for heating the device under test to 155 °C for 90 minutes to remove any impurities present in the RTIL before being cooled to the test temperature through conduction with N₂ as the carrier gas

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Table I. Selected RTILs for humidity sensing with their physical and electrochemical properties.

| RTIL          | Decomposition Temperature | Electrochemical Window       | Density (g/mL) | Mixing Solvents     | References |
|---------------|---------------------------|------------------------------|----------------|---------------------|------------|
| MMIM[MeSO₄]  | > 300 °C                  | −3.2 V − +1.7 V              | 1.44           | Most Alcohols, DMSO | 17         |
| EMIM [TF₂N]  | 455 °C                    | −2.0 V − +2.9 V              | 1.39           | Acetone, DMSO       | 21         |

Figure 1. Gold interdigitated electrodes used for humidity sensing with RTIL deposited on it.

flowing through the box. A series gas mixing system [Envionics 4000] allowed for mixing the house nitrogen [purity of >95%] with test percentage of humidity being pumped into the chamber through a humidity control unit.

**Signal transduction mechanism for humidity sensing.**—Electrochemical impedance spectroscopy [EIS] was utilized to characterize the impedance changes occurring at the electrode-RTIL interface on exposure to humidity. Low volume of 1 μL of the RTIL of interest is deposited on the sensor through drop cast method. The sensor system is perturbed with AC excitation voltage of 100 mV and a DC offset potential of 1.6 V which is dictated by the electrochemical window of the chosen RTILs. The frequency range of measurement was chosen between 1–10 KHz. EIS measurements for the sensor under test conditions [25–65 °C, 25–65% RH] are done by interfacing a potentiostat [Reference 600 Potentiostat Gamry Instruments] with the sensor system through soldered connections. Baseline measurements were done for the sensor at the test temperature with N₂ in the chamber and 0% RH. The detailed procedure of performing humidity sensing on the RTIL sensor system is shown in Figure 3.

**Results**

**Performance of MMIM[MeSO₄].**—The performance of the non-fluorinated RTIL MMIM[MeSO₄] in sensing humidity levels at elevated, ambient and low temperature and humidity conditions is shown in Figures 4a, 4b, and 4c respectively. The Nyquist plots depict the variations in the real (Zreal) and imaginary components (Zimag) of the impedance as function of the RTIL’s interaction with water molecules over the chosen probing frequency range. At a given temperature, we observe that the diameter of the semicircle decreases with increasing humidity levels which is indicative of decreasing charge transfer resistance (Rct). Interactions of water molecules with the RTIL’s moieties makes the RTIL film conductive. Hence, a smaller Rct is observed with increasing humidity levels makes the RTIL film more conductive as more water molecules come in contact with the RTIL. However, we are interested in exploring the non-faradaic behavior of the RTIL-humidity interaction which is more pronounced than the faradaic charge transfer. The extracted double layer capacitance (Cdl) changes on exposure to humidity at varying temperatures with respect to 0% humidity are tabulated in Tables II, III, and IV. The relative standard deviation (RSD) for n = 3 repeats lies within 10–13% for lower temperature conditions. A higher RSD of ~20% is observed for elevated temperature studies. An increasing change in capacitance is observed with increasing humidity levels as more water molecules interact with the RTIL moieties. This interaction results in an increased charge build up with the EDL thus altering the dielectric permittivity of the EDL and hence the Cdl increases. The capacitance changes

![Figure 2. a) Cation (MMIM) and anion (MeSO₄) of MMIM[MeSO₄]. b) Cation (EMIM) and anion (TF₂N) of EMIM[TF₂N].](image-url)
Figure 4. a) Nyquist plots for MMIM[MeSO4] across humidity levels 0–65%RH at 25°C b) Nyquist plots for MMIM[MeSO4] across humidity levels 0–65%RH at 45°C c) Nyquist plots for MMIM[MeSO4] across humidity levels 0–65%RH at 65°C.

Table II. Capacitance change of MMIM[MeSO4] & EMIM[TF2N] with respect to 0% RH at different humidity levels at 25°C.

| RTIL        | 25%RH    | 45%RH    | 65%RH    |
|-------------|----------|----------|----------|
| MMIM[MeSO4]| 1.8 μF ±12% | 7.1 μF ±13% | 23.8 μF ±13% |
| EMIM[TF2N] | 21.56 nF ±8%  | 51.4 nF ±16% | 530 nF ±8% |

Table III. Capacitance change of MMIM[MeSO4] & EMIM[TF2N] with respect to 0% RH at different humidity levels at 45°C.

| RTIL        | 25%RH    | 45%RH    | 65%RH    |
|-------------|----------|----------|----------|
| MMIM[MeSO4]| 1.2 μF ±10% | 3.2 μF ±10% | 9 μF ±9% |
| EMIM[TF2N] | 2.2 nF ±13%  | 30.4 nF ±6%  | 83 nF ±16% |

Table IV. Capacitance change of MMIM[MeSO4] & EMIM[TF2N] with respect to 0% RH at different humidity levels at 65°C.

| RTIL        | 25%RH    | 45%RH    | 65%RH    |
|-------------|----------|----------|----------|
| MMIM[MeSO4]| 152 nF ±17% | 343 nF ±18% | 617 nF ±18% |
| EMIM[TF2N] | 1.2 nF ±14%  | 9.3 nF ±6%  | 15.5 nF ±14% |

for MMIM[MeSO4] are greater since there is a strong hydrogen interaction between MeSO4⁻ and water molecules. The symmetry of the anionic moiety could be another factor that positively impacts the interaction of the RTIL with the water molecules. MMIM[MeSO4] shows greater sensitivity to humidity at lower temperature conditions and their sensitivities are tabulated in Table V. The loading of water molecules within the RTIL moieties is affected at elevated temperatures. We hypothesize this to be the consequence of decreased interstices formation between the cationic and anionic moieties of the RTIL leading to lesser loading on water molecules and hence the lower capacitance changes.

Performance of EMIM[TF2N].—The behavior of the fluorinated RTIL EMIM[TF2N] toward increasing humidity levels at varying temperature conditions was investigated. The Nyquist plots for the response of the RTIL at 25, 45, and 65°C for increasing humidity levels (25–65%RH) are shown in Figures 5a, 5b, and 5c respectively. The decreasing diameter of the semicircle with increasing humidity at any given test temperature suggests decreasing Rct.

The change in capacitance as tabulated in Tables II, III, and IV shows an increasing capacitive (Cdl) behavior with increasing humidity levels across all temperatures being studied. The RSD for n = 3 repeats lies between 8–16% across the temperature conditions studied. EMIM[TF2N] shows similar trend in capacitance behavior toward humidity as MMIM[MeSO4] across temperature and humidity conditions under investigation. The capacitance changes for MMIM[MeSO4] are greater in magnitude than EMIM[TF2N] indicating that MMIM[MeSO4] is more sensitive to humidity levels than EMIM[TF2N]. The sensitivity of EMIM[TF2N] across varying temperatures is tabulated in Table V. This can be attributed to the fact that TF2N contains electron withdrawing fluorinated groups which cause weaker RTIL and water interactions. The structural composition of the fluorinated anionic moiety may also hinder the interaction between the RTIL and the water molecules thus contributing to the overall decreased sensitivity of EMIM[TF2N].

Table V. Sensitivities of MMIM[MeSO4] & EMIM[TF2N] to humidity levels across varying temperatures.

| RTIL        | 25°C    | 45°C    | 65°C    |
|-------------|---------|---------|---------|
| MMIM[MeSO4]| 386 nF/%RH | 42.7 nF/%RH | 13.5 nF/%RH |
| EMIM[TF2N] | 8.6 nF/%RH  | 1.5 nF/%RH  | 0.2 nF/%RH  |
Figure 5. a) Nyquist plots for EMIM[TF$_2$N] across humidity levels 0–65%RH at 25°C b) Nyquist plots for EMIM[TF$_2$N] across humidity levels 0–65%RH at 45°C c) Nyquist plots for EMIM[TF$_2$N] across humidity levels 0–65%RH at 65°C.

**Discussion**

**Electrical double layer formation in RTILs.**—The moieties of RTILs form an ordered structure of alternating cation and anion stacks when it comes in contact on a charged electrode surface as shown in Figure 6a. An electrical double layer (EDL) is formed at this contact interface upon application of voltage bias. Typically, a thin layer formed closer to the charged surface consists of Stern layer wherein the charges of the RTIL moieties strongly adhere to the charged electrode surface through electrostatic forces. Beyond the Stern layer is the diffuse layer which compensates for the net unbalanced charges on the charged electrode surface. The Stern layer in conjunction with the diffuse layer forms an electrical double layer (EDL), until which the influence of electrostatic forces is observed. This EDL interface is often compared to mimicking a capacitor which accounts for the large capacitances observed during RTIL-humidity interactions. The double layer capacitance is primarily driven by two factors: 1. Dielectric constant, 2. Debye length. The RTIL-water interactions result in modulation of these factors thereby, changing the double layer capacitance with varying humidity levels. RTILs are unique in a way that they allow for the formation of multiple double layers through the cation/anion stacking feature. The multi EDL capacitor can be thought of as individual capacitors connected in parallel formed by the stacking of the moieties as shown in Figure 6b. The average absolute capacitance ranges ($C_{Total}$) of the multi EDLs formed by the selected RTILs on exposure to humidity levels across the test temperatures are tabulated in Table VI. The chosen RTILs show differentiability in their response to humidity across the wide range of humidity percentages (25–65%RH) and temperatures (25–65°C) being investigated.

| RTIL     | $C_{Total}$ (25°C, 25–65%RH) | $C_{Total}$ (45°C, 25–65%RH) | $C_{Total}$ (65°C, 25–65%RH) |
|----------|-----------------------------|-----------------------------|-----------------------------|
| MMIM[MeSO$_4$] | 1–17 μF                    | 35–500 nF                   | 50–100 nF                   |
| EMIM[TF$_2$N]  | 0.02–0.5 μF                | 0.1–165 nF                  | 20–200 nF                   |

AC perturbation of the system through EIS captures only the impedance changes occurring within the EDL as result of RTIL-
RTIL- Humidity interaction.—Application of an external stimuli such as potential and temperature modifies the interaction forces between the cationic and anionic moieties of the RTILs. We present a hypothesis that the interaction between cationic and anionic moieties begin to weaken and stretch out the bonds between the moieties to form interstitial spaces under the influence of the applied DC offset potential. Water molecules dock into these interstices on exposure to varying humidity levels through van der Waals interaction and hydrogen bonds\textsuperscript{19} as shown in Figures 7a and 7b. The anionic moieties and the structures of the RTILs play a significant role in the RTIL-humidity interaction. The anionic symmetry and structure impacts the capacitance response depending on how the structure permits for the RTIL-humidity interaction. The chosen RTIL candidates under investigation- MMIM[MeSO\textsubscript{4}] and EMIM[TF\textsubscript{2}N] show similar trends across temperatures and humidity levels. Our study reveals that MMIM[MeSO\textsubscript{4}] is almost 30–70 times more sensitive to EMIM[TF\textsubscript{2}N] to humidity across temperatures. However, both RTIL candidates show a greater capacitance change across the humidity levels at lower temperatures than at elevated temperature which could be due to the alteration in interstices formation at these conditions thus affecting the RTIL-humidity interaction mechanism. An increasing capacitance response with increasing exposure to humidity levels across all temperatures for the two chosen RTILs is observed. We attribute this behavior to the fact that exposure of the RTIL to humidity causes the electrochemical window of the RTIL to shrink leading to higher capacitance response at higher humidity levels\textsuperscript{20}.

Conclusions

In this paper, we have explored the behavior of a non-fluorinated RTIL and a fluorinated RTIL toward humidity at lower and elevated temperatures toward the development of humidity sensor for integration into semiconductor IC’s. The perturbations in the electrical double layer formed by both the RTILs in response to the humidity levels and temperature conditions is captured by the capacitance responses of the system through EIS. Overall, both the RTILs showed similar behavioral trends across low and elevated humidity and temperature conditions. However, the non-fluorinated RTIL MMIM[MeSO\textsubscript{4}] showed greater sensitivity to humidity than the fluorinated RTIL EMIM[TF\textsubscript{2}N] due to stronger hydrogen interactions. The measurement time to capture the RTIL-humidity interaction dynamics was $\sim$1 minute. However, operating the RTILs at a DC offset potential within its electrochemical window (ECW) is of utmost importance for RTIL based sensing. ECW defines the range of DC potentials within which the RTIL remains stable and its properties are retained.\textsuperscript{17} An appropriately chosen DC offset potential affects the charge density at the electrode surface in turn affecting the impedance changes. Higher operating DC offset potentials generate higher charge densities at the surface which are counterbalanced by the higher concentrations of ions. A single monolayer of ions is formed creating an overcrowded state of ions in the EDL which can be leveraged to generate an increased capacitance response when exposed to different humidity levels.\textsuperscript{18}
interactions between the non-fluorinated anionic moiety with humidity. MMIM[MeSO₄] shows promise as a unique humidity sensing material for further development as humidity sensor. Further research will be performed to understand the behavior of the RTIL anionic moieties for temperatures ≥100°C and to study the effects of scaling electrode geometries, and RTIL sensing volumes.

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