Unique detection of organic vapors below their auto-ignition temperature using III-V Nitride based triangular microcantilever heater

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We report on the unique detection of dilute volatile organic compounds below their auto-ignition temperature using a novel AlGaIn/GaN heterostructure based triangular microcantilever heater. With a low input power of 12 mW, the microcantilever heater was found to reach a maximum temperature of 330 °C at the tip, which was verified through infrared microscopy and Raman spectroscopy. Unique threshold voltages were observed for various organic analytes with different functional groups, beyond which the heater current started to increase sharply in presence of analytes, which correlated strongly with their latent heat of evaporation. Dilute vapors with concentrations as low as 50 parts per million (ppm) could be detected selectively with a noise limited resolution down to 5 ppm. On the other hand, the magnitude of change of current for a fixed applied voltage was found to be dependent on the molecular dipole moment of the analytes, which can likely be attributed to the strong surface polarization of AlGaIn. A simple circuit model has been proposed to explain the observations. Heat transfer and Joule heating simulations were performed using

finite element method to model the electro-thermal characteristics of the microcantilever heater, which were in good agreement with the experimental observations.

1. Introduction

Detection of volatile organic compounds (VOCs), which are widely used in industrial processes and household products, is very important due to significant health hazards associated with them.^[1] VOCs are commonly detected using photo-ionization detectors (PIDs),^[2] suspended hot bead pellistors,^[3] or heated metal oxide semiconductor functionalization layers.^{[4]-[7]} The detection methodology using PIDs is based on high-energy photon (typically > 10.5 eV) induced ion generation, while that using hot bead pellistors takes advantage of the exothermic reaction (from auto-ignition of VOCs) to produce a change in resistance. Heated metal oxide (i.e. TiO₂ or SnO₂) based sensing also relies upon a change in resistance, but at a temperature below the auto-ignition temperature of the VOCs. However, all the above techniques suffer from the problem of high power requirement as well as poor selectivity among VOCs, which is often important for proper identification of the source of a problem. Although the last method requires somewhat lower operational power, it involves complicated functionalization process with metal oxides.

Microcantilevers offer excellent avenues for molecular sensing that arises out of their high sensitivity to various physical parameter changes induced by the analyte molecules.^{[8]-[15]} Microcantilever heaters, which are extremely sensitive to changes in thermal parameters,^{[16]-[21]} have been widely utilized for calorimetry,^[16] thermal nanotopography^[17] and thermal conductivity measurements.^[18] Due to the small area of the microcantilever that needs to be heated (i.e. the tip of a triangular microcantilever), they also offer the possibility of reduced power consumption for high temperature operation. However, achieving repeatable and reliable functionalization of a microcantilever, especially over a small area, is a challenge that

1 has thwarted practical applications of microcantilever based sensors. On the other hand,
2 unfunctionalized microcantilevers (typically made of Si) are not particularly sensitive toward
3 a specific analyte, and are generally accepted to be incapable of performing selective
4 detection. Thus, only a handful of studies utilizing uncoated microcantilevers to perform
5 unique molecular detection have been reported so far.^{[13], [22], [23]} In these studies, detection is
6 generally based on changes in physical properties of the media surrounding the cantilever (i.e.
7 viscosity,^[23] thermal conductivity,^[22] or the analyte (i.e. deflagration temperature^[22]).
8 However, these techniques are applicable only to a few specific analytes, and selective
9 detection still remains a major challenge, especially when the analytes are diluted (or present
10 in minute quantities) or have similar physical properties i.e. VOCs.

11
12 III-Nitride heterojunction (especially AlGa_N/Ga_N) based microcantilevers offers a
13 unique opportunity for realizing these microscale heaters, taking advantage of presence of
14 high carrier (electron) density in close proximity to the surface,^[24] which allows for highly
15 efficient surface heating. In addition, strong spontaneous polarization of III-Nitride surfaces
16 allows these heaters to interact better with VOCs, which are typically strongly polar in nature.
17 Finally, AlGa_N/Ga_N heterojunction based heaters are capable of operating at high temperature
18 and harsh environment due to chemical inertness and wide bandgap of III-Nitrides. With
19 commercial availability of high quality III-Nitride heterojunction epilayers on Si, the
20 fabrication of these heaters are also quite straightforward. Although, III-Nitride based
21 microcantilevers have been demonstrated earlier,^{[11], [25], [26]} there is no report so far on
22 triangular microcantilever heaters and their sensing applications.

23
24 In this article, we present a novel AlGa_N/Ga_N heterostructure based triangular
25 microcantilever heater (TMH), demonstrated for the first time, which has been utilized to
26 perform selective detection of a number of VOCs belonging to various functional groups,

1 including alcohols, ethers, ketones, alkanes and aromatic compounds. The detection occurs
2 below the auto-ignition temperature of the analytes and the responses have been found to
3 strongly correlate with their latent heat of evaporation and dipole moment. A simple model
4 has been presented to explain the observed responses, which are also correlated with results
5 from numerical simulations.

6 7 **2. Materials and Methods**

8 The triangular cantilevers used in this work were fabricated using AlGa_N/Ga_N
9 heterostructure epitaxial layers grown on a 625 μm thick (111) Si substrate. The
10 microcantilevers were designed to have tapered arms (shown in the inset of **Figure 1a**) to
11 maximize the temperature rise at their tip under an applied bias. We started our process with
12 1.4 cm by 1.4 cm diced pieces of AlGa_N/Ga_N HEMT epi layer grown on Silicon (111) wafer;
13 the details of the wafer can be found in Section I of the supporting information. At first,
14 Cl₂/BCl₃ Plasma was used to isolate the cantilever mesa, followed by another deeper etch to
15 define the Ga_N outline. Then Ti/Al/Ti/Au metal stack was deposited using an electron beam
16 evaporator, followed by rapid thermal annealing to make good ohmic contact. After that the
17 Si at the bottom of the pocket was etched from the backside of the sample using Bosch
18 process, using PECVD SiO₂ as a hard mask. The parameters and details of fabrication can be
19 found in Section I of the supporting information. The total thickness of the cantilever was 2.3
20 μm ; base width of each arm of the cantilever was 25 μm , which reduced to 3 μm at the tip.
21 The arms were 100 μm apart at the base of the cantilever. Details of the wafer structure and
22 the fabrication process are given in Section I of supporting information and also in ^{[25], [26]}.

23
24 The experimental setup used for sensing volatile organic compounds involved a test
25 chamber fitted with an inlet and an outlet. Two mass flow controllers (MFC) were used to
26 control the composition of the VOC vapor (produced by passing ultra-high purity (UHP) N₂

through a bubbler at room temperature), which was diluted with UHP N₂. The outlet of the chamber was connected to a dry pump to quickly remove the analyte from the test chamber. The electrical and sensing characterizations were performed using an Agilent B2902 source measuring unit (SMU).

3. Results and Discussion

The I-V characteristics of the TMH are shown in **Figure 1a** where a linear (low bias) and a saturation region (high bias) can be clearly identified. Because of the significant self-heating of the device, current is generally observed to decrease at higher biases (> 20 V) as tip resistance increases rapidly with rise in temperature. The SEM image of the device is shown in the inset. **Figure 1b** shows >300% change in resistance (from 50 to 200 k Ω) as the bias changes from 0 to 50 V, with a power dissipation of 12 mW at 50 V. For our sensing experiments, dilute analyte vapors were flown into the test chamber for a fixed duration under a constant dc bias applied to the device. The wire-bonded device mounted on a 28-pin dual inline package (DIP) is shown in the inset.

The device response upon exposure to 2000 ppm molar concentration of hexane vapor is shown in **Figure 2a**, where the current changes from 245.8 to 250.2 μ A (1.84% change) in about 30 s, at a device bias of 50 V. The rise time, defined by the time taken by the current to go from 10% to 90% of the steady state value, is found to be ~14 s (**Figure 2a**). The fall time (defined as the time for the maximum signal to decay from 90% to 10% of its value) was found to be ~20 s. Comparable rise and fall times were observed for other analytes as well. For comparison, the response to 2000 ppm molar concentration of water vapor is also shown for a bias of 50 V. Since no response is observed, it confirms the lack of interference from water vapor. In **Figure 2b**, the response of the device to 400 ppm of hexane vapor is shown for two consecutive cycles to demonstrate complete recovery and repeatability of the device.

1 For each phase of exposure, a current change of 1.1% was observed with an increased rise
2 time (25-30 s) and fall time (~ 35 s), which is expected at lower concentration. The same
3 device has been used repeatedly for the same analyte and for different analytes over several
4 months, no hysteresis was observed at any occasion. The variation in sensor response has
5 been observed to be within $\pm 2\%$ of its average value for multiple instances of sensing
6 performed for over a year, showing excellent accuracy and repeatability. Although the I-V
7 characteristics of various devices in the same batch has slight variation ($< 5\%$), the normalized
8 response (e.g. percentage change in current) has been found to be very uniform for all sample
9 devices, with an average deviation of $\pm 3\%$ or less for the response of different devices under
10 various bias/sensing conditions.

11
12 In **Figure 3**, temperature profile along the length of the TMH is shown using infrared
13 (IR) thermal microscopy and Raman spectroscopy. The tapered shape of the cantilever gives
14 rise to a sharp temperature variation along the arms, especially near the tip, as observed from
15 the infrared (IR) image of the cantilever (**Figure 3**) recorded using a temperature calibrated
16 Inframetrics PM280 Ultra Cam fitted with IR microscopic lenses (from Sierra Pacific
17 Innovations Corporation). The microcantilever is a two-terminal self-heating device with the
18 conducting channel serving as the heater. The entire V-shaped arm of the cantilever acts as
19 the heater-resistor. Temperature change in the arm, especially near the tip region controls the
20 change in resistance between the two ohmic contacts at the base. To determine the impact of
21 analyte flow on the temperature profile of the cantilever arms, IR images of the cantilever
22 with and without the presence of isopropanol were recorded. In **Figure 3a**, the cantilever
23 (dashed line) is shown at 50 V bias without any analyte flow, the red region at the tip is the
24 hottest spot with a temperature of about 330 °C. **Figure 3b** shows the cantilever image with
25 2000 ppm molar concentration of isopropanol vapor under the same 50 V bias. **Figure 3c**
26 shows a line scan depicting average temperature variation along the arms of the cantilever.

1 Here we see that the peak temperature at the tip is reduced by $\sim 30^\circ\text{C}$ in presence of 2000 ppm
2 of isopropanol vapor, while the temperature profile becomes wider. Interestingly, the side
3 arms adjacent to the tip area exhibit an increase in temperature by $\sim 20^\circ\text{C}$. It is interesting to
4 note that the current in our TMH sensor increased, i.e. the overall resistance decreased, in
5 presence of isopropanol vapor. Thus, any exothermic reaction between the VOC and air can
6 be ruled out in contrast with hot bead pellistors.^[3] In **Figure 3d**, we show the peak
7 temperature at the tip determined by IR microscopy and also from calibrated Raman
8 spectroscopy, details of which can be found in Section II of Supporting Information. The peak
9 temperature was found to vary from 105 to 330 $^\circ\text{C}$ as the applied voltage bias was increased
10 from 20 to 50 V. The temperature was determined by calibrating the IR camera, and the
11 Raman peak shift using an identical cantilever on a temperature controlled hot plate. The
12 voltage bias was swept from 0 to 50 V at 5 V intervals and the steady-state temperature was
13 measured at each bias point, **Figure 3d** shows the 20-50 V bias range where the sensing
14 experiments are done.

15
16 Considering the temperature profiles shown in **Figure 3**, we propose a model explaining
17 the response of the TMH sensor in presence of organic vapors. To facilitate our model
18 description, we assume the overall cantilever resistance to consist of several lumped resistors
19 connected in series, each describing the resistance of a specific zone along the arms of the
20 cantilever. These resistances are shown in **Figure 3a** as R_c (contact resistance), R_1 (side arm
21 resistance), R_2 (resistance near the tip) and R_{tip} (resistance of the tip region). At lower biases
22 ($< 10\text{ V}$), the device exhibits an I-V with almost constant resistance [**Figure 1b**], indicating
23 the absence of any significant self-heating. At higher biases ($> 10\text{ V}$), I^2R loss increases,
24 causing the tip temperature and resistance R_{tip} to go up. However, the temperatures of R_c and
25 R_1 do not increase as much as R_{tip} with an increase in bias voltage, therefore, these resistances
26 do not change significantly. If a volatile vapor is injected into the test chamber, the vapor

1 molecules will initially tend to condense in close proximity of the cantilever, but the heated
2 tip region will cause their immediate evaporation. This results in a net loss of thermal energy
3 from this region (defined by resistance R_{tip}) causing its temperature to become lower. The
4 regions of the side arms away from the tip (defined by resistances R_2 and R_1) do not
5 participate in rapid evaporation of analyte molecules, so the thermal energy loss due to the
6 evaporation of VOCs is not significant there. Since the whole device is under a constant
7 voltage bias, reduction in R_{tip} will cause an increase in voltage drop across R_1 and R_2 (R_c is
8 likely to be much smaller and the voltage drop across it can be neglected). Since R_2 can be
9 expected to be larger than R_1 at high temperature, the voltage drop across it is more
10 significant, resulting in a higher temperature rise in that region and consequently larger
11 increase in resistance. Therefore, the total resistance between the arms of the cantilever is
12 affected by the opposite changes in R_{tip} and R_2 , in agreement with the IR image line scan
13 shown in **Figure 3c** under isopropanol flow. At a moderate bias voltage, i.e. ~ 10 V, even if a
14 VOC vapor actually causes a reduction in R_{tip} (by reducing temperature), the increase in R_2
15 (due to increase in temperature) can compensate for it, since the overall rise in temperature is
16 still low at that bias. Thus, the current can remain unchanged even in presence of a VOC
17 vapor at lower biases. However, as the bias voltage is increased for a given VOC flow,
18 depending on the extent of the temperature drop of R_{tip} region (which correlates with the
19 molar latent heat of evaporation, ΔH_{vap} of the VOC), a threshold voltage bias can be reached
20 where the reduction in R_{tip} would be more than the increase in R_2 , thus an increase in current
21 would be observed. Existence of such a threshold voltage, and its dependence on ΔH_{vap} , has
22 been experimentally observed, and are shown in **Figure 5**.

23

24 To explain the aforementioned physical phenomena, a theoretical model based on heat
25 transfer and Joule heating has been developed. The model is normalized using a number of
26 experimental observations so that the calculated temperature profiles for known conditions

(i.e. bias and analytes) match well with the measured values. The calibrated model can then be used to predict outputs at conditions for which experimental values are difficult to obtain; it can also lead to valuable information on other quantities such as local variation of resistivity (please refer to Section III in supporting information) and so on. The model is based on the following equations for heat transfer (**Equation 1** and **Equation 3**)^[27] and Joule heating (**Equation 2**) which are solved simultaneously and iteratively using finite element method (using COMSOL Multiphysics and MATLAB).

$$\rho_d C_p \frac{\partial T}{\partial t} + \nabla \cdot (-K_c \nabla T + u \rho_d C_p T) + Q_{\text{vap}} = \frac{1}{\rho} |\nabla V|^2 \quad (1)$$

$$-\nabla \cdot d \left(\frac{1}{\rho(T)} \nabla V - J_e \right) = 0 \quad (2)$$

$$\mathbf{n} \cdot (K_c \nabla T) = q_0 + h(T_{\text{inf}} - T) + \varepsilon \sigma (T_{\text{inf}}^4 - T^4) \quad (3)$$

Equation 1 and **Equation 2** are solved for different domains of the system, whereas **Equation 3** is used as a boundary condition at the interface of the solid and surrounding air domains. Here, ρ_d = material density, C_p = heat capacity, T = absolute temperature, K_c = thermal conductivity, Q_{vap} = heat loss due to evaporation of analyte molecules (when applicable), J_e = electrical current density, V = potential profile, $\rho(T)$ = electrical resistivity as a function of temperature, $\mathbf{n}$ = unit vector normal to the interface, d = thickness of the domain, q_0 = heat source inside the domain, h = temperature dependent coefficient of convection for air,^[26] T_{inf} = temperature far away from the cantilever, ε = emissivity of the solid surface, σ = Stefan-Boltzmann constant. The temperature dependence of the electrical resistivity is modeled using a least square fit of experimental data (Section III in supporting information), which yields the following empirical relation

$$\rho(T) = 0.03 T - 2.04 \quad (4)$$

Since at very low concentration (in parts per million range or below) partial pressure of analyte molecules become very low, they can be considered as ideal gases; and therefore, kinetic theory of gases can be applied to calculate the amount of latent heat taken away from a heated surface by the molecules. For an arbitrary surface area A_h , amount of heat loss Q_{vap} per unit time at a given concentration C and partial pressure P_p is given by (see Section IV in supporting information for derivation)

$$Q_{vap} = \frac{1}{4} A_h P_p C \frac{\Delta H_{vap}}{N_A} \sqrt{\frac{3M}{kT}} \quad (5)$$

Here, ΔH_{vap} = molar latent heat of evaporation, N_A = Avogadro's number (6.023×10^{23} molecules/mol), M = molecular mass, k = Boltzmann's constant (1.38×10^{-23} JK⁻¹).

Using the model described above, calculated temperature profiles are obtained and shown in Section III of the Supporting information where it shows a good match to the experimental results shown in **Figure 3c**. **Figure 4a**, for 50 V dc bias, with and without 2000 ppm of isopropanol vapor flow. For simplicity, we assumed that heat was taken away by the molecules from the tip region (see below for definition). The experimentally determined temperature profiles for the similar conditions were presented in **Figure 3c**, which are reproduced in **Figure 4** for comparison. **Figure 4b** shows an important phenomenon obtained from the theoretical model that explains a number of subsequent observations. Here, the electrical “path length” of the heated tip region (designated by R_{tip} in **Figure 3c**) is shown for different bias voltages with and without 2000 ppm of isopropanol vapor. In this context, electrical path length refers to the length of the hypothetical resistance R_{tip} along the path of the current; which corresponds to the portion of the cantilever that undergoes a negative change in temperature in presence of an analyte vapor. Therefore, in order to calculate the electrical path length of R_{tip} (denoted as L_{tip}), temperature profile at each bias point is obtained for no analyte vapor, and for a given analyte vapor at a certain concentration. That is

1 why, it is important to note that L_{tip} strongly depends on the concentration and nature of the
2 analyte. Here in **Figure 4b**, we see that before 14 V bias, L_{tip} is not significant (uniform
3 temperature distribution over most of the cantilever length), indicating negligible effects of
4 analyte vapor on temperature distribution. However, after 14 V the value of L_{tip} starts
5 becoming significant in presence of isopropanol. Although, L_{tip} starts to increase after 14 V,
6 the threshold voltage for isopropanol has been experimentally observed to be ~ 18 V (please
7 refer to discussions on **Figure 5** below), which can be explained based on our earlier
8 discussions, which postulated an increase in R_2 offsetting any change in R_{tip} (denoted by R_2 in
9 **Figure 3c**) below 18 V. Consequently, the total resistance ($R_{\text{tip}} + R_2$) remains unchanged
10 below 18 V, keeping the tip current unchanged. After 20 V, L_{tip} increases almost linearly with
11 bias voltage, which indicates the extension of the R_{tip} region along the side arms toward the
12 base of the cantilever. Due to the tapered nature of the cantilever, this extension of the R_{tip}
13 region is expected to saturate as the wider edges of the region would not heat up at the same
14 rate (with change in voltage) as the cantilever tip. This saturation effect of L_{tip} can be clearly
15 seen in **Figure 4b** above 40 V. This behavior has important consequences on device sensing
16 performance at higher bias voltages which will be discussed below in relation to **Figure 5** and
17 **Figure 6**.

18
19 **Figure 5a** shows the percentage change in current caused by dilute vapor (2000 ppm
20 molar concentration) of four different VOCs: isopropanol, methanol, hexane and acetone, as
21 the applied voltage bias was varied from 15 to 50 V. Seven readings were averaged at each
22 bias point and a 5-points moving average filtering was performed to ensure better consistency
23 and noise reduction. From the measured data points, the approximate uncertainty in the
24 threshold voltage was estimated to be ± 0.1 V. As can be seen from **Figure 5a**, each analyte
25 corresponds to a distinct threshold voltage (V_{th}) below which it does not cause any noticeable
26 change in current. Although the current nearly saturates after ~ 20 V, tip temperature still

1 keeps on increasing with an increased bias due to the higher power dissipation (i.e self-
2 heating), which is why we still need to increase the voltage bias to observe the sensor
3 response despite having a fairly constant current through the device. In the present work, V_{th}
4 is arbitrarily defined using a current magnitude change of 0.1% or higher (considering our
5 noise level of 0.04% and a signal to noise ratio of >2.5) in presence of an analyte; however,
6 for a low noise environment, it can be defined at a lower value as well. To determine the V_{th}
7 from our measurements we use the following methodology; if within a voltage range of 0.2 V
8 the change in current is at least 0.1% (in presence of an analyte vapor), then the mid-value of
9 that voltage range is defined as V_{th} . The threshold voltage for each analyte was observed to be
10 very consistent over multiple sets of experiments performed in a period of more than six
11 month utilizing several identical devices. To verify if a generic correlation indeed exists
12 between ΔH_{vap} and V_{th} , as predicted by our model, threshold voltages of seven different
13 analytes with latent heat varying over a wide range were determined. The plot of V_{th} versus
14 ΔH_{vap} is shown in **Figure 5b**, where an excellent linear correlation is observed. This is in
15 agreement with our proposed model (please refer to the explanation of **Figure 3**, where a
16 correlation between V_{th} and ΔH_{vap} was predicted), and clearly indicates that such a well-
17 defined correlation can be utilized to perform selective detection of VOC vapors from their
18 unique threshold voltages. It should be noted here that the temperature of the tip (measured
19 using the IR camera) at the threshold voltage was always lower than the auto-ignition
20 temperature for all the seven VOCs studied, ruling out any combustion related effects. Also,
21 as mentioned above, no effect of water vapor of similar molar concentration (2000 ppm) was
22 observed (see **Figure 2**) even up to a bias of 50 V, which is much higher than the expected V_{th}
23 of 23 V based on its ΔH_{vap} of 40 kJ/mol. This, therefore, rules out any interference from water
24 vapor in realistic sensing environments. To investigate any dependence of the V_{th} on analyte
25 concentration, detection was performed with much diluted (down to ~50 ppm concentration)
26 vapor of isopropanol, ethanol and toluene. The V_{th} values were found to increase only by

1 ~0.75 V as the vapor concentrations were reduced 40 fold from 2000 to 50 ppm (discussed in
2 detail in **Figure 6**). This indicates that V_{th} remains effectively constant, and thus can be used
3 to reliably identify VOCs over their significant detection range, especially for indoor
4 environments.^[28]

5
6 Since III-Nitrides have strong polarization properties, it is interesting to explore possible
7 correlations between the magnitude of the molecular dipole moment of the analyte VOC and
8 the magnitude of current change caused at a fixed applied bias. **Figure 5c** shows the
9 percentage change in current for seven VOCs (measured at a constant bias of 50 V) plotted
10 against their dipole moment. We find that as the dipole moment of the analyte VOC increases,
11 the response magnitude also increases, which is expected since the molecules with higher
12 dipole moment are expected to have stronger interaction with the highly polar AlGaN
13 surface.^[29] This would cause a larger change in tip temperature and hence in the overall
14 magnitude of the current change. Although the physical mechanism of molecular interaction
15 is unclear to us at present, it is possible that the polar AlGaN surface is responsible for
16 attracting the polar VOC molecules toward it, (which is dependent on the dipole moment) and
17 allowing them to condense to a certain extent. When the condensed molecules evaporate, the
18 latent heat taken away (and hence the response magnitude) is therefore also proportional to
19 the molecular dipole moment. For example, acetone, in spite of having a rather low ΔH_{vap} ,
20 still caused the largest change in current at 50 V, since its dipole moment is the highest among
21 all the analytes studied. If multiple analytes have very similar dipole moments, the change in
22 current depends on their latent heat of evaporation, which is clearly evident from **Figure 5b**
23 with respect to isopropanol, ethanol and methanol. Here all three have similar dipole moments
24 (in the range 1.6 – 1.7 D), so the one with highest latent heat of evaporation (isopropanol)
25 caused the largest change in current. We would like to point out here that the effect of
26 polarization is clearly observed only at high bias voltages. At low bias voltages, closer to the

1 V_{th} for a particular analyte, the response is primarily controlled by the temperature
2 distribution of the tip (please refer to earlier discussions). Although polarization effect is also
3 present for this bias range, it is insignificant compared to the other effects. However, at high
4 bias voltages (i.e. over 45 V, which is much higher than the V_{th} of analytes considered here),
5 effective surface area of the hot zone near the tip tends to saturate (temperature still keeps
6 increasing though), allowing the surface polarization to play a dominant role in controlling the
7 heat transfer to the analyte molecules, and consequently the device response. The power
8 dissipation and the tip temperature keep on increasing as the bias voltage goes up; however
9 the device response has been found to be stable at 50 V bias in spite of significant self-heating.
10 In regular ambient environment, the devices have been tested for up to 90 V bias repeatedly
11 for several days and it has been concluded that a 50 V bias could certainly be used for reliable
12 and repeatable results. While a smaller bias (18-32 V) is sufficient for detecting V_{th} , a larger
13 voltage bias of 50 V is required to observe the other modality of the sensor that is related to
14 the dipole moment of the analytes.

15
16 In order to establish the utility of V_{th} for uniquely identifying an analyte, we performed
17 systematic measurements of device characteristics as a function of analyte concentration. The
18 results are shown in **Figure 6** for three different analytes, isopropanol, ethanol and toluene,
19 which were chosen to cover a wide range of ΔH_{vap} . As observed from **Figure 6a**, the V_{th}
20 values corresponding to different analytes changed only slightly (0.6 – 0.75 V) when their
21 concentration was reduced from 2000 ppm to 50 ppm. As the analyte concentration is
22 increased, more molecules are able to interact with the cantilever, thus causing the V_{th} to
23 reduce. Although, the relatively small magnitude of change in V_{th} is unclear to us at this point,
24 nonetheless, V_{th} is obviously an important parameter that can be utilized in a practical sensor
25 to uniquely identify different VOCs over a specified range of concentration.

1 In order to identify the threshold voltage, it is also important to observe the dependence
 2 of current magnitude change at the threshold voltage. In the post-threshold biasing region,
 3 more and more analyte molecules can interact with the heated cantilever tip as the effective
 4 area of the hot zone (corresponding to R_{tip}) increases with bias voltage. Increased temperature
 5 also increases the convection flow, creating a low pressure region in the vicinity of the heated
 6 tip of the cantilever. This causes faster circulation of analyte vapor around the cantilever tip
 7 resulting in more molecules to interact with the tip per unit time. Therefore, just above the
 8 threshold voltage, for the same analyte concentration, current is mostly governed by the
 9 effective area of the heated tip region as shown in **Figure 6b**, where the analyte with the
 10 lowest threshold voltage has the lowest threshold current (see definition below) because of the
 11 smaller effective area of hot zone at that voltage. Extrapolating all the curves towards low
 12 concentration gives a noise limited resolution of ~ 5 ppm. The threshold current is calculated
 13 by first taking a voltage bias which is 0.1 V above the threshold voltage. Then the change in
 14 current is measured in presence of an analyte vapor of a certain concentration. The threshold
 15 current response (i.e. normalized change in current) is then defined by the following relation

$$16 \quad \frac{\Delta I}{I_0} = \frac{(I_{vap} - I_0)|_{V_{th}+0.1} - (I_{vap} - I_0)|_{V_{th}}}{I_0|_{V_{th}+0.1} - I_0|_{V_{th}}} \quad (6)$$

17 Here, I_{vap} and I_0 are the currents measured with and without analyte vapor, respectively. The
 18 same is also done for dry UHP N_2 instead of analyte to obtain the background response for the
 19 carrier gas (dry UHP N_2) and the noise signal, which was found to be within 0.04% over the
 20 entire bias range (15 to 35 V). **Figure 6b** also shows a linear relation between threshold
 21 current response with logarithm of concentration, which is common for many sensors.

22 Above the threshold voltage, percentage change of current in presence of a particular
 23 VOC depends on the concentration of analyte vapor. We define sensitivity of the sensor as the
 24 percent change in current for one decade change in analyte concentration; change in current is

calculated at threshold voltage using **Equation 6**. We denote this sensitivity by S , which is calculated using the following expression,

$$S = \frac{\frac{\Delta I}{I_0}|_{C_2} - \frac{\Delta I}{I_0}|_{C_1}}{\log\left(\frac{C_2}{C_1}\right)} \quad (7)$$

where C_2 and C_1 are the vapor concentrations ($C_2 > C_1$). **Table 1** shows the sensitivity of the TMH sensor for 50 and 2000 ppm concentration of isopropanol, ethanol, toluene and acetone vapors. We find that an analyte with a higher threshold voltage leads to higher detection sensitivity, which is also evident in **Figure 6b**, where the slope of the fitted line is higher for such an analyte. **Table 1** also lists the rise and fall times of the sensor for different analytes. It is observed that the rise/fall times are similar for all four analytes at high concentration (2000 ppm), however at low concentration (50 ppm) they start to deviate quite significantly (by up to 10 s). The rise/fall time decreases by several seconds as the voltage bias (i.e. cantilever temperature) goes up.

We also estimated the limit of detection (LOD, in terms of vapor concentration), from our simulation results, corresponding to the threshold current response assuming it to vary over the range of 0.001% and 0.1%. The results are presented in **Figure 7a** for 3 different analytes. Interestingly, all the responses can be seen to merge asymptotically at low concentration, which is supported by our experimental results, as shown in **Figure 6b**, where the extrapolated curves also intersect at low concentration. Such an intersection of extrapolated responses for various analytes is however expected, since at very low concentration (i.e. below detection level), the various analyte vapors would produce very similar response to the carrier gas alone (i.e. N_2), which is basically defined by the system noise. The LOD for different analytes at 0.001% threshold current response are tabulated in **Figure 7b**.

1 The TMH sensors used in this work were studied over a period of at least a year, both in
2 open air and in a closed chamber; and were subjected to much higher applied biases (up to
3 ~90 V) than those reported here. However, no noticeable change in device characteristics was
4 observed in this time frame, which underscores high measurement reliability as well as
5 thermal and chemical stability of these sensors.

6 7 **4. Conclusions**

8 In conclusion, we have demonstrated novel AlGaIn/GaN heterostructure based triangular
9 microcantilever heaters, and utilized them to perform unique detection of VOCs down to the
10 low ppm (down to 5 ppm limited by noise) range with high specificity, while operating below
11 their auto-ignition temperatures. It has been observed that for a particular VOC, over a certain
12 concentration range, a well-defined threshold voltage exists, which varies linearly with the
13 molar latent heat of evaporation. The response magnitude for a VOC at a fixed voltage bias
14 was found to be related to the molecular dipole moment. A simple model has been proposed
15 to explain the response of the sensor to different VOCs.

16 17 18 19 20 **Acknowledgements**

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Table Caption

Table 1. Sensitivity, rise time and fall time for different analytes at threshold voltage.

Figure Caption

Figure 1. (a) I-V characteristics of V-shaped micro cantilever heater sensor. Inset shows the SEM image of the device. (b) Change of power and resistance with bias voltage. Photograph of a wire-bonded device mounted on a dual inline package (DIP) is shown in the inset.

Figure 2. (a) Response of the device to 2000 ppm of hexane and water vapor at 50 V dc bias. In presence of hexane vapor flow, the current increased by about 1.84%; whereas water vapor did not cause any change in current. (b) Response of the device to 400 ppm of hexane in two consecutive cycles to demonstrate the repeatability of the sensor behavior. Each time, there was a change of about 1.1% in current; rise time and fall time are, however, longer than that in (a) as concentration is five times lower.

Figure 3. (a) False color infrared image of the cantilever shown in **Figure 1a** under 50 V bias. The outline of the cantilever is super-imposed on the thermal image. Lumped resistors R_c , R_1 , R_2 and R_{tip} represent different regions of the device and are used to model it. (b) The cantilever under same bias, but in presence of isopropanol vapor with a molar concentration of 2000 ppm. (c) Line scan of temperature along the cantilever as shown in (a) and (b). Inset shows the equivalent circuit based on the model resistors shown in (a). (d) Temperature calibration of the heated cantilever with different bias using calibrated IR microscopy and Raman spectroscopy with identical linear trend.

Figure 4. (a) Simulated temperature profiles for the heated cantilever in intrinsic condition and in presence of 2000 ppm of isopropanol vapor at 50 V bias. (b) Electrical path length of the heated tip resistance (denoted by R_{tip}), L_{tip} as a function of bias voltage for 2000 ppm of isopropanol vapor.

Figure 5. (a) Composite plots of normalized change in current (%) with change in voltage for isopropanol, methanol, acetone and hexane at 2000 ppm molar concentration; showing a distinct voltage for each analyte below which there is no change in current. (b) Dipole Moment (μ) and latent heat of evaporation (ΔH_{vap}) for different volatile organic compounds (VOCs). (c) Linear relation between threshold voltage of sensing (V_{th}) and latent heat of evaporation (ΔH_{vap}) for different VOCs at molar concentrations of 100, 400 and 2000 ppm. V_{th} is observed to vary slightly with the change of concentration. (d) Correlation between normalized change in current (%) at 50 V and dipole moment (μ) for VOCs at 100, 400 and 2000 ppm molar concentration. Linear relation for each analyte concentration has been observed; least square fit parameters for the fitted straight lines are given in the table in the inset.

Figure 6. (a) Dependence of V_{th} on molar concentration of isopropanol, ethanol and toluene. As it is found out, change in threshold voltage is no more than 0.75 V for all three of these analytes. (b) Change in current at threshold voltage for the same analytes. This limits the detectability of the threshold voltage as concentration goes down. Extrapolated curves indicate a noise limited resolution of 5 ppm with a sensor noise level of 0.04% change in output current.

1 **Figure 7.** (a) Theoretical lowest concentration of isopropanol, ethanol and acetone that can be
2 detected for a given change in current at threshold voltage. System noise level of 0.04% has
3 been shown here, indicating a theoretical noise limited resolution below 2 ppm. (b) A
4 compilation of theoretical lower limits for various analytes at 0.001% change in current at
5 threshold voltage.

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Table 1. Sensitivity, rise time and fall time for different analytes at threshold voltage.

Analyte	V _{th} (V)			Sensitivity (%)	Rise Time (s)			Fall Time (s)		
	2000 ppm	1000 ppm	50 ppm		2000 ppm	1000 ppm	50 ppm	2000 ppm	1000 ppm	50 ppm
Isopropanol	18.0	18.2	18.7	0.172	15	21	54	22	30	78
Ethanol	23.0	23.2	23.75	0.224	14	21	51	19	27	72
Toluene	27.0	27.1	27.5	0.251	17	24	58	23	32	83
Acetone	29.0	29.1	29.6	0.256	14	22	53	20	27	75

Figure 1

Figure 2

Figure 3

Figure 4

(b) Dipole Moment (μ) and Latent Heat of Evaporation (ΔH_{vap}) of VOCs

Analyte	μ (D)	ΔH_{vap} (kJ/mol)
Hexane	0.08	31.5
Toluene	0.36	32.3
Isopropanol	1.66	45.4
Ethanol	1.69	38.6
Methanol	1.7	35.3
Acetone	2.69	30.5
Diethyl Ether	1.15	27.3

Figure 5

Figure 6

(b) Theoretical Detection Limit of Analytes for 0.001% Change in Current at Threshold Voltage

Analyte	Detection Limit (ppb)
Isopropanol	502.42
Ethanol	465.31
Methanol	455.93
Toluene	448.51
Hexane	441.65
Acetone	432.72
Diethyl Ether	408.33

Figure 7