Selective room temperature nanostructured thin film alcohol sensor as a virtual sensor array

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Nanostructured SiO\textsubscript{2} thin films fabricated via glancing angle deposition on interdigitated electrodes were used as room temperature alcohol sensors. Both frequency dependent capacitance and impedance were used to analyze sensor response to methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol. Sensor responsivity was examined across the entire percent vapour saturation range for the same set of alcohols and the detection limit for ethanol, as an example, was derived. The response and recovery times for ethanol were determined from a pulse test and the responsivity curves, giving values of 66 s and 76 s, respectively. Sensor lifetime was examined for the same set of alcohols with and without irradiation from a UV-LED. We observed that sensor aging for the detection of ethanol and 1-butanol was greatly reduced under irradiation from the UV-LED whereas the UV-LED had little effect on aging for methanol, 1-propanol and 2-propanol. Using the frequency dependent responsivity curves of our sensors, we developed an algorithm that enables a single sensor to distinguish between methanol, ethanol and 2-propanol in a blind protocol test. In five out of seven trials, the algorithm successfully identified both the alcohol and concentration thereby demonstrating room temperature single sensor selectivity.

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1. Introduction

Gas sensors are used in environmental monitoring, industrial production, personal safety, medical, and military applications [1,2]. Specifically, alcohol sensors have applications such as detecting ethanol for foodstuffs control or detecting methanol in industrial processes [3–5]. Semiconducting metal oxides are frequently used as alcohol sensor materials because they behave as ‘chemiresistors’ where the catalytic oxidation of the alcohol by the semiconducting metal oxide affects the material’s electrical conductivity [6,7]. Several metal oxides, including zinc oxide [2,8–11], tin oxide [5,12–20], titanium dioxide [21], tin doped indium oxide (ITO) [22–24] and silicon dioxide [25] have been previously used as alcohol sensor materials but they often suffer from several limitations including low sensitivity, long response and recovery time and poor selectivity [26]. To improve their sensitivity, the gas sensors are frequently operated at elevated temperatures [1,2,6,8,9–14,16–23,26,27] and there exist few examples of room temperature sensors in the literature. Wang et al. used a single electrospun tin oxide nanofiber for the room temperature detection of moisture and methanol where they demonstrated both high sensitivity and fast response times [15]. Patel et al. used ITO thin films grown by direct evaporation for the detection of methanol at room temperature, and found that the sensitivity of their sensors improved with the addition of a catalytic metal layer on top of their ITO layer or by the addition of a stimulating layer between the ITO and the alumina substrate [24]. Arshak and Gaiden used a screen printing method to prepare thick films based on zinc and zinc ferrite for the detection of methanol, ethanol and propanol at room temperature [28]. They observed that their sensors were most sensitive to propanol at room temperature and that the sensitivity decreased with increasing temperature. Innocenzi et al. used mesoporous silica thin films for the detection of methanol, ethanol, 2-propanol, and 1-butanol at room temperature where they examined the effect of calcination temperature on sensor response [25]. There is currently interest in decreasing the temperature at which thin film alcohol sensors can efficiently operate at, improving their selectivity towards different alcohols and increasing their sensing lifetime towards a given analyte.

By using glancing angle deposition (GLAD), a physical vapor deposition technique that is capable of producing thin films with extremely high surface areas [29], selective thin film alcohol sensors that can function under ambient conditions have been achieved. GLAD is an extension of oblique angle deposition that combines oblique vapour incidence angles, ballistic shadowing and finely controlled substrate motion to give rise to nanostuctured thin films of varying morphologies [30]. In previous work, TiO\textsubscript{2} GLAD thin films have been used as humidity sensors and...
have demonstrated response times below 100 ms [31,32]. We have also previously shown extended sensor lifetime by irradiating our humidity sensors with ultraviolet wavelengths, photocatalytically cleaning the surface [33].

Some sensor development work has used multiple interrogation methods on a single sensor, producing a “virtual” sensor array [34–36]. Such sophisticated readout methods allow identification and quantification of multiple analytes with a single sensor element. Musio and Ferrara probed polymeric sensors from 20 Hz to 10 kHz, successfully distinguishing between methanol, acetone, ethyl acetate and ethanol (all at 200 ppm) [34]. Analogous work using polysulfone films on RFID tags at MHz frequencies [35] and carbon nanotubes on a GHz resonator [36] have shown that virtual arrays can successfully identify and quantify analyte gases. Combining these techniques at a lower frequency range may reduce the cost of readout electronics and enable both identification and quantification of unknown analytes while retaining the subsecond response times characteristic of GLAD gas sensors.

Our thin film sensors are based on the conductance changes of an interdigitated electrode (IDE) substrate coated by a SiO2 GLAD film. The conductance changes due to the catalytic oxidation of the absorbed alcohol by metal oxide surface sites [7]. At room temperature, such sites can irreversibly absorb alcohol molecules, inducing sensor aging. By incorporating an ultraviolet light-emitting diode (UV-LED) of the appropriate wavelength to target the chemical bonds leading to poisoning and subsequent deactivation, we hope to achieve enhanced sensor lifetime thereby enabling room temperature operation. Furthermore, by examining the frequency dependent selectivity of the sensor, there is potential for a single sensor to act as a virtual sensor array, successfully distinguishing between different alcohols and simultaneously determining their percent vapour saturation. In this paper we report the results of our initial experiments for this sensor configuration, including sensor responsivity, detection limits, response and recovery times, lifetime enhancement, and the frequency dependent selectivity towards different alcohols. We develop an algorithm that allows a single sensor to successfully distinguish between three different alcohols in a blind protocol test.

2. Experimental setup

Our sensors were fabricated using countersunk IDE substrates [31] coated with SiO2 (Cerac, 99.99%) GLAD films. The IDEs had 3 μm wide electrodes and 5 μm spacing for a period of 8 μm. The GLAD film consisted of 1500 nm vertical posts deposited with the incident vapor flux at an angle of 81° relative to the substrate normal. Film structure was imaged using a Hitachi S-4800 SEM with ~10 nm of Cr sputtered onto the sample to reduce charging effects while imaging.

Our previously described custom humidity control chamber (volume ~570 cm³) [31] was modified to allow for the testing of methanol (MeOH) (>99.8%, Sigma–Aldrich), anhydrous ethanol (EtOH) (commercial alcohols), 1-propanol (1-PrOH) (ACS reagent, >99.5%, Sigma–Aldrich), 2-propanol (2-PrOH) (ACS certified, Fisher Scientific) and 1-butanol (1-BuOH) (Chromasolv Plus for HPLC, >99.7%, Sigma–Aldrich) by the incorporation of a 500 ml gas washing bottle. Each sensor’s capacitance and complex impedance were measured using a QuadTech 1920 Precision LCR Meter at room temperature (22 °C) over a wide range of frequencies (20, 24, 29, 35, 41, 50, 60, 72, 86, 100, 103, 124, 129, 178, 241, 257, 308, 370, 444, 532, 639, 767, 920, and 1000 Hz).

The frequency dependent responsivity of the SiO2 sensor was tested by cycling between 0% and 100% gas saturation in 5% increments with or without irradiation of a 351 nm UV-LED. The mole fraction is reported as the fraction of the air (in moles) that is alcohol vapour, and was calculated from the ratio of the partial pressure of the alcohol to the total pressure of the alcohol vapour/air mixture. The partial pressure of each alcohol was determined using the Antoine equation:

$$\log(p) = A - \left(\frac{B}{T + C}\right)$$

where $p$ is the partial pressure in mmHg, $A$, $B$, and $C$ are component-specific constants and $T$ is the temperature in °C [37]. The percent vapour pressure was determined based on the ratio (in scm) of alcohol saturated air and clean dry air that were flowed into the sample chamber at any given point. For example, where 100% vapour pressure is indicated, the clean dry air (CDA) was completely saturated by that alcohol at room temperature. The partial pressure and therefore the mole fraction at this temperature could be calculated. The other percent vapour pressure values were determined based on the percentage of alcohol saturated air and CDA that were flowed into the sample chamber.

The detection limits were derived using the following equation where $C_{blank}$ is the average capacitance value measured a probe frequency of 20 Hz under an atmosphere of CDA, and $S_{blank}$ is the standard deviation of those values:

$$C_{lid} = C_{blank} + 3S_{blank}$$

Once $C_{lid}$ was determined, the corresponding mole fraction was read off of the responsivity curves. The detection limit for EtOH was also derived from the responsivity curves as an example.

The sensors response and recovery times for EtOH were determined by exposing a SiO2 sensor to a short rectangular EtOH exposure pulse and measuring the capacitance at a probe frequency of 20 Hz every 3 s for a given period of time. The sensor was exposed to 100% CDA for 1 min, followed by a 5 min exposure to EtOH saturated air, and then a 3 min exposure to 100% CDA.

Sensor lifetime was tested by cycling between 0% and 100% gas saturation in 100% steps using CDA as the carrier gas and a dwell time of 2 min in the absence and presence of a 351 nm UV-LED, chosen to attack the 3.5–3.6 eV C–O bond that is responsible for irreversible absorption of alcohols on the SiO2 surface [38].

To demonstrate the virtual array concept, a series of blind tests were performed by having one researcher (NAB) select an alcohol and percent vapour saturation for that alcohol to be tested at. The sensor was then tested by measuring the impedance, phase, and capacitance over the range of previously listed frequencies using a dwell time of 10 min for a total of 8 cycles under irradiation from the UV-LED. The same sensor was tested at two different percent vapour saturation values for each alcohol, yielding 10 unique sets of data. The data was then given to another researcher (MTT), who was unaware of the alcohol’s identity and concentration. The data was analyzed using an algorithm (discussed below) to determine the identity of the alcohol and the vapour concentration based on the previously established frequency dependent responsivity curves.

3. Results and discussion

For a wide variety of practical applications, the lifetime of a sensor towards a given analyte is of great importance. Sensor aging can be minimized by operating the sensor at elevated temperatures thereby minimizing irreversible absorption of an alcohol, but this requires incorporation of a microheater into the sensor, increasing sensor cost. Photoinduced desorption of the alcohol by incorporating a LED of the appropriate wavelength into the sensor setup can provide an alternate method to improve the lifetime of a sensor and allow the sensor to be operated under ambient temperatures. However, to successfully measure the changes in conductivity due to the absorption of the alcohol and not the generation of charge...
carriers created in the semiconducting metal oxide due to irradiation by the UV-LED, an appropriate sensor material had to be selected. SiO$_2$ was chosen, as there are few examples of this material being used an alcohol sensor in the literature [25], and it would allow for us to study the effect of UV-LED-induced lifetime enhancement for alcohol sensing without introducing photoinduced charge carriers into our measurements.

Shown in Fig. 1 is an SEM image depicting the structure of our SiO$_2$ sensor deposited on an IDE. The metallic IDE can be identified, as can the defects the IDE induces into the SiO$_2$ structure. These defects have been previously shown to increase response times when compared to homogeneous defect-free thin films, and it was proposed that these defects act as high diffusivity channels to the bottom of the sensor, mimicking the effect of etching the thin film [39].

Our sensor configuration and proposed mechanism for sensor lifetime enhancement using the UV-LED is shown in Fig. 2a. There are two types of irreversibly absorbed alcohol species that can be formed on the surface of a metal oxide that may lead to sensor aging: an alkoxo species resulting from the dissociative chemisorption of the alcohol on a weak Lewis acid site adjacent to a strong basic Lewis site and an undissociated species absorbed on a strong Lewis site [38]. Because the theoretical C–O bond energy in alcohols is very difficult to accurately calculate, and given the large uncertainties in calculated values (reported methanol C–O bond dissociation energies vary from 63.13 to 92.1 kcal/mol), we used the thermodynamic values to select the appropriate UV-LED [40,41].

Based on the thermodynamic C–O bond energies in the alcohols examined (3.47–3.59 eV), we choose a UV-LED of an appropriate wavelength to span that energy range [42]. Shown in Fig. 2b is the measured power profile of the 351 nm UV-LED that we selected: the C–O bond energies of MeOH, EtOH, n-PrOH and n-BuOH are indicated. Given the LED's power profile and the fraction of photons above the bond energy, we anticipated that the UV-LED would successfully enhance the sensor lifetime for all of the alcohols examined. However, the efficiency was expected to correlate with the fraction of total photons available (e.g. the fraction above alcohol C–O bond energies) to desorb the C–O bond responsible for the irreversible absorption of the alcohols to the surface, e.g., MeOH should be most affected by the LED, while EtOH should be the least affected.

To examine the potential of our room temperature SiO$_2$ GLAD sensors, we challenged their responsivity against the same five alcohols methanol, ethanol, 1-propanol, 2-propanol and 1-butanol across a broad concentration range. Shown in Fig. 3 is an example of the raw sensor data collected for a typical measurement cycle of our sensor's response to EtOH with and without UV-LED irradiation. From this figure, the high degree of reproducibility of our sensor across a broad range of EtOH concentrations can be seen. Sensor responsivity with and without a UV-LED to a broad range of alcohol mole fractions is shown in Fig. 4. The UV-induced change in response curves does not follow a trend for the different alcohols; EtOH and 1-BuOH show higher capacitance values under UV irradiation, while MeOH, 1-PrOH and 2-PrOH show lower capacitance...
values. Given this variation, UV-induced electron transfer processes to the SiO$_2$ are probably not significant for our devices.

It can be seen that the sensor has a logarithmic response to the both the MeOH (Fig. 4a) and EtOH (Fig. 4b) concentrations over the entire concentration range examined when irradiated with the UV-LED. Furthermore, there is very little hysteresis shown during the testing cycle for these two alcohols with or without irradiation from the UV-LED. However, there was not a logarithmic response of the sensor to 1-PrOH, 2-PrOH and 1-BuOH over the concentration range examined. The sensor was somewhat insensitive to the concentration of 1-PrOH and 1-BuOH below 30% vapour saturation and below 60% for 2-PrOH. Slight hysteresis was observed during the testing of 2-PrOH and a large degree of hysteresis was observed during the testing cycle for both 1-PrOH and 1-BuOH. Irradiation with the UV-LED also demonstrated opposite effects on the hysteresis for 2-PrOH when compared to 1-PrOH and 1-BuOH. When the responsivity of the SiO$_2$ sensor towards 2-PrOH was tested without irradiation from the UV-LED, a larger degree of hysteresis was observed. However, when the sensor was tested for its responsivity towards 1-PrOH and 1-BuOH, the hysteresis was increased by UV-LED irradiation. These hysteresis loops arise from differing chemical potentials in the adsorption and desorption reactions, and depend strongly on the surface pore structure. In the case of the 1-BuOH, the LED irradiation may be suppressing adsorption due to the increased fraction of available power as compared to 1-PrOH and 2-PrOH. However, this remains speculative, and detailed experiments would be required to address these effects.

From the responsivity curves, the detection limits (as mole fractions) for EtOH with and without LED irradiation were determined to be $1.9 \times 10^{-4}$ and $3.4 \times 10^{-4}$, respectively. The lower derived detection limit under UV-LED irradiation is likely due to the interference of the UV-LED with the alcohol adsorption. For the same partial pressure in the ambient atmosphere, there is less alcohol absorbed on the sensor surface with UV-LED irradiation than without. While these detection limits are not very low, they were determined for an unoptimized system and could be improved by optimizing the sensor structure. For example, Steele et al. demonstrated that for humidity sensing, using a thicker film or decreasing the deposition angle relative to the substrate normal improved the sensitivity at the lower percent humidity range [32].
To verify that our sensor exhibits short response and recovery times, the sensor was exposed to a short rectangular EtOH pulse under UV-LED irradiation. (Fig. 5). The change in capacitance as a function of time was measured, and using the responsivity curves established in Fig. 4, the mole fraction could be determined from the capacitance. It can be seen that there is a sharp increase in the sensor response upon initial exposure of the sensor to EtOH vapour followed by a characteristic absorption isotherm. After ∼5 min exposure, the sensor was then exposed to CDA and the sensor recovered very quickly. From these results, a 10–90% response time of 66 s and a 90–10% recovery time of 76 s were determined.

The normalized capacitance results with and without UV-LED irradiation are given for MeOH in Fig. 6a, EtOH in Fig. 6b, 1-PrOH in Fig. 6c, 2-PrOH in Fig. 6d and 1-BuOH in Fig. 6e to determine if UV-LED irradiation influences sensor lifetime. The data shown in Fig. 6 has been normalized to the sensor’s response at t = 100 min to the 100% step change in alcohol concentration. When the SiO2 sensor was irradiated by the UV-LED, the sensor aging was inhibited for the detection of certain analytes, indicating that the lifetime of the sensor can be enhanced by the incorporating of a UV-LED. The UV-LED was particularly effective in reducing aging for ETOH sensing (Fig. 6b) and 1-BuOH sensing (Fig. 6e). For ETOH sensing, over the course of 3.5 days, the UV-LED-irradiated sensor’s response is reduced to about 75% of its initial response; the unirradiated sensor is reduced to about 20%.

The results of the testing shown in Fig. 6a and c indicate that illumination with 351 nm photons did slow down the sensor aging. Decay time to 80% of the initial response for ETOH was extended by a factor of 8 from ∼8.3 h to ∼66.7 h. However, the 351 nm photons did not slow down the sensor aging when either MeOH, 1-PrOH or 2-PrOH was tested. It is unclear why the UV-LED did not have the anticipated effect on MeOH sensing, as the photon energy and wavelength of light should be sufficient to prevent poisoning and deactivation of the sensor’s surface and we selected a UV-LED with a nominal wavelength such that desorption of the alcohol is only favourable reaction given the photon energy. Because the UV-LED was ineffective for enhancing the MeOH sensor’s lifetime, we propose that another chemical species may be responsible for the deactivation of the MeOH sensor, possibly formaldehyde or formic acid, the products of the MeOH oxidation reaction [24] or the decomposition products resulting from irradiation of MeOH with the UV-LED. The C–O bond energies of formaldehyde (6.94 eV) and formic acid (6.94 eV for C=O and 4.60 eV for C–O) are much higher than those for MeOH, suggesting that these products could not be removed by irradiation with the 351 nm UV-LED. We attempted to characterize our films after alcohol desorption by FTIR, but were unable to detect any chemical species absorbed on the surface of our films that may be responsible for the aging of our sensors.

We used the responsivity test results described in Fig. 4 to characterize the response of our sensors to the different analyte gases. Sensor response may be written as

\[ Z = f(G, C, \omega) \]
matches, and the concentration and uncertainty was calculated using a Gaussian fit to the histogram of the concentrations reported by each match.

Initial attempts to distinguish between all five gases studied here failed, due to significant overlap between the impedance curves of 1-BuOH and 1-PrOH. When these two gases were removed from the blind test, the ability of a single SiO₂ sensor to distinguish between MeOH, EtOH, and 2-PrOH over different concentrations vastly improved. In five of the seven blind trials, the algorithm correctly identified the gas and approximate concentration. The failure of two of the seven blind trials may be due to the similarity in $M_{\text{standard}}$ values when comparing the $Z_{\text{standard}}$ values for EtOH at 100% vapour saturation and MeOH at 60% vapour saturation. Furthermore, even though the sensors that were used to measure the responsivity curves were fabricated in an identical manner as those that were used for the blind tests, the blind tests were performed on a fresh, previously unused sensor so the calibration curves may not necessarily reflect the expected performance of the sensor.

As an additional test of the technology’s potential, we compared the sensor response from the both the visible and blind tests with additional standard curves for H₂O. In this case, Sample I was identified as H₂O at 80% RH; all other identifications remained the same. The sensing approach presented here relies on detecting differences in the dielectric constant for different analyte-SiO₂ systems. Presently, we are limited to a frequency range of 20 Hz to 1 kHz; extending this range should improve the discriminatory power of this approach.

### 4. Conclusions

We have demonstrated room temperature identification and quantification of unknown alcohols in a blind trial utilizing a GLAD nanostructured SiO₂ thin film sensor and UV-LED irradiation. The lifetime of the alcohol sensor was greatly enhanced for both EtOH and 1-BuOH detection whereas the UV-LED had little effect on the aging for MeOH, 1-PrOH and 2-PrOH. Using the frequency dependent responsivity of a LED-illuminated single sensor towards MeOH, EtOH and 2-PrOH at varying concentrations, single sensor selectivity was achieved. These proof of concept results provide motivation for future work.

Several routes to improving the sensors’ performance exist. The frequency range used here was from 20 Hz to 1 kHz; extending this frequency range to lower frequencies may provide additional discriminating power for this algorithm, improving the specificity of the virtual sensor array. As seen above in Fig. 4 (sensor responsivity with LED on and off curves), turning the LED off for the same measurements would double the virtual array, probably further improving specificity. Operation of the sensor under mild heating conditions (i.e. 50°C) may further improve upon the lifetime and sensitivity of the sensor, but incurring an additional fabrication cost.

This technique may also be applied to the conventional approach of sensor arrays composed of different materials. An array of GLAD gas sensors could be fabricated with different deposition angles and materials, both of which have been shown to modify individual sensor responsivity [32]. We expect that the combination of LED irradiation and frequency selective probing would greatly increase the effective selectivity or range of analytes for such arrays.

Lastly, sensor performance in humid air or in the presence of other contaminants requires investigation. Humidity may drastically alter sensor performance and to date, few studies have investigated sensor performance for the detection of alcohols under humid conditions [2,26]. The initial experiments performed here indicate that the single virtual sensor array concept is worth
References


Biographies

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