Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Methyl(—CH_3)-terminated ZnO Nanowires for Selective Acetone Detection: Novel Approach Toward the Sensing Performance Enhancement Via Self-Assembly Molecules

Mandeep Singh[a], Navpreet Kaur[a], Andrea Casotto[b], Luigi Sangaletti[b], Nicola Poli[a] and Elisabetta Comini[a]*

[a]SENSOR Laboratory, University of Brescia, Via D. Valotti 9, Brescia 25133, Italy.

[b]I-LAMP and Dipartimento di Matematica e Fisica, Università Cattolica del Sacro Cuore, Via della Garzetta 48, 25133, Brescia, Italy

Email: mandeep.singh@unibs.it

1. Pictorial View of Conductometric Sensor Fabrication Using DC Sputtering, TO Packaging and Sensor Embedded in Test Chamber

Figure S1 represents the pictorial view of 3 stages involved in sensing measurements. In the first stage, conductometric sensing devices based on bare and TEOS functionalized ZnO nanowires were prepared as described in the materials and methods section using DC sputtering. Then, the fabricated sensors were mounted on TO package using electro-soldering technique. Finally, the TO package mounted sensors were embedded in a test chamber for sensing measurements.

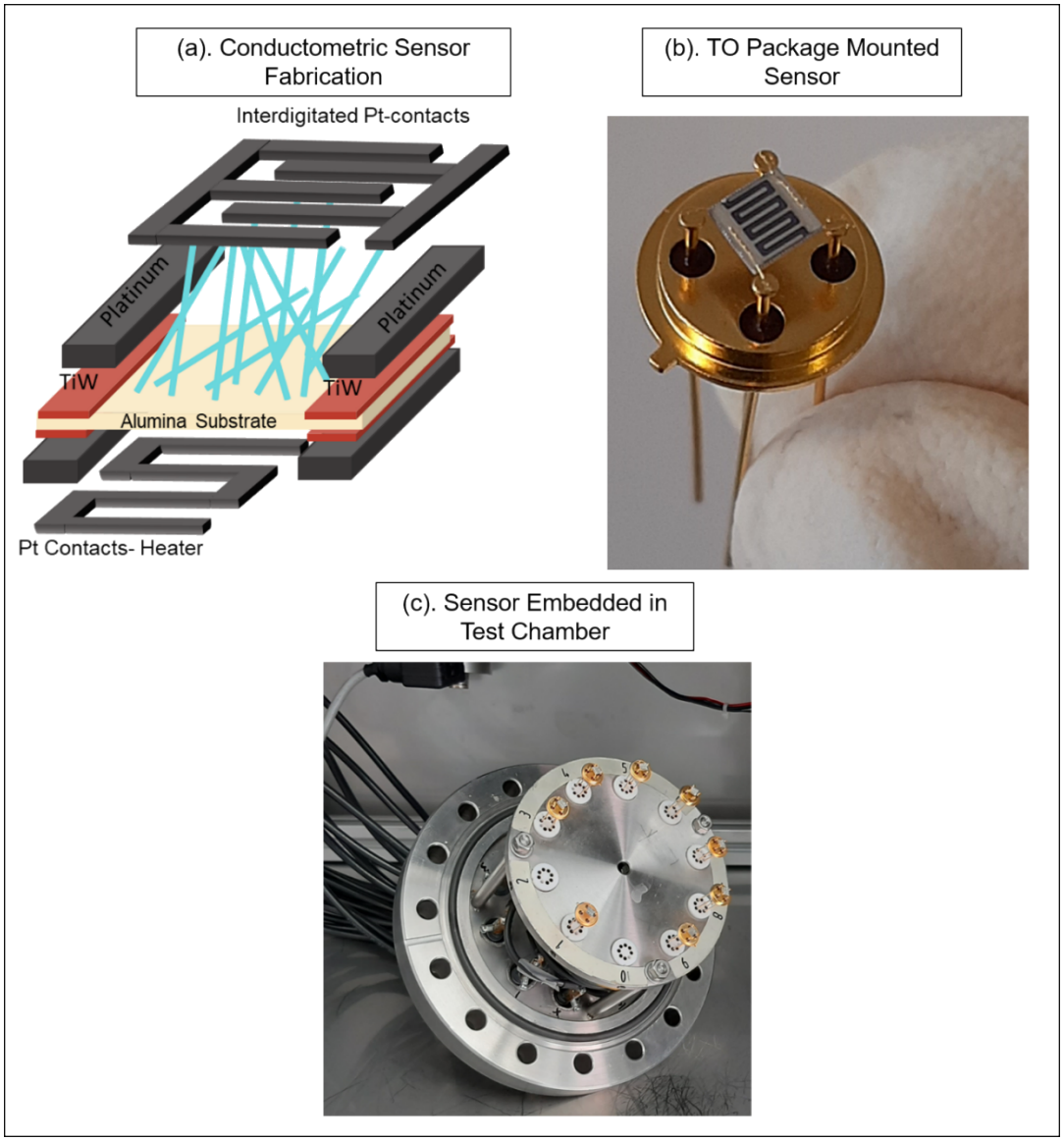

Figure S1. Pictorial view of (a) steps involved in sensor device fabrication using DC-sputtering, (b) TO-packaged sensor and (c) sensors embedded in test chamber.

2. X-Ray Diffraction (XRD) Study of Bare and TEOS Functionalized ZnO Nanowires

In order to investigate the crystalline structure of VLS grown nanowires, XRD spectra of ZnO nanowires were acquired before and after functionalization with TEOS monolayer (see figure S2).

The peaks at 2Θ values 34.30°, 36.20° and 66.41° belong to the (002), (101) and (200) hkl planes of ZnO nanowires.[1–3] Indeed, the occurrence of these peaks confirms the polycrystalline hexagonal wurtzite structure of the nanowires. On the other hand, the peaks indexed (*) belong to the alumina substrate, indicating the immense contribution of the substrate. Furthermore, no changes were observed in the crystalline structure of ZnO nanowires after the functionalization. This indicates that the nanowires' crystalline structure and morphology remain intact after dipping in SAM solution for 18 hours.

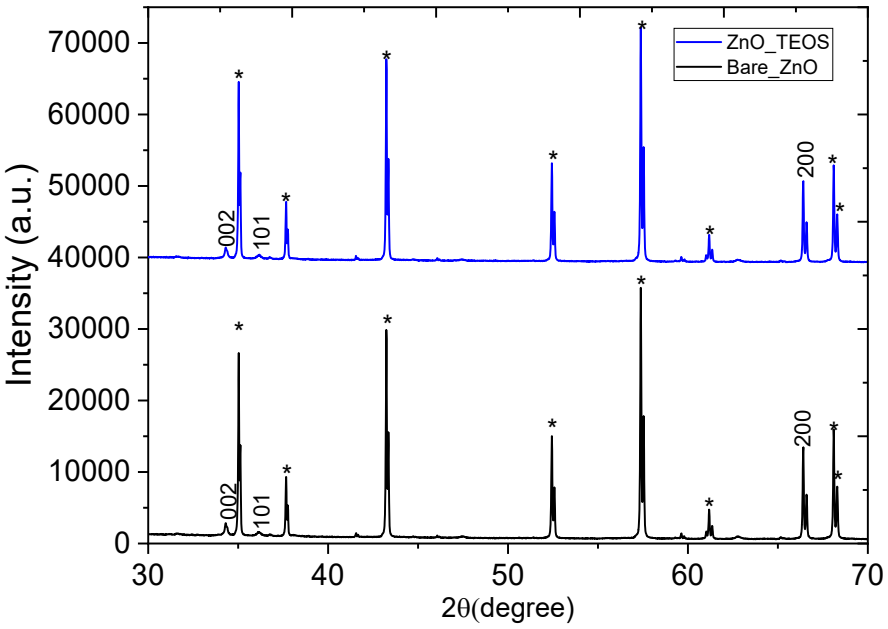

Figure S2. X-ray diffraction pattern of bare and TEOS functionalized ZnO nanowires

3. X-Ray Photoelectron Spectroscopy (XPS) of Bare and TEOS Functionalized ZnO Nanowires

Figure S3 represents the survey scan spectra of bare and TEOS functionalized ZnO nanowires, from which the presence of Zn, O, C, and Si core level peaks is detectable. Indeed, the Si peaks are only observed in TEOS functionalized ZnO nanowires, thus confirming the presence of TEOS monolayer. Furthermore, the absence of any other contaminations also showed the good quality of the samples. In table S1, elemental quantification of C, Zn, O and Si is presented. The elemental quantification has been obtained by evaluating the integrated peak areas of the principal core level peaks, with their respective sensitivity factor, adding the calculated escape depth correction. Please note that the relative error associated with this quantification is about the 10%. For the bare ZnO sample no silicon is detectable.

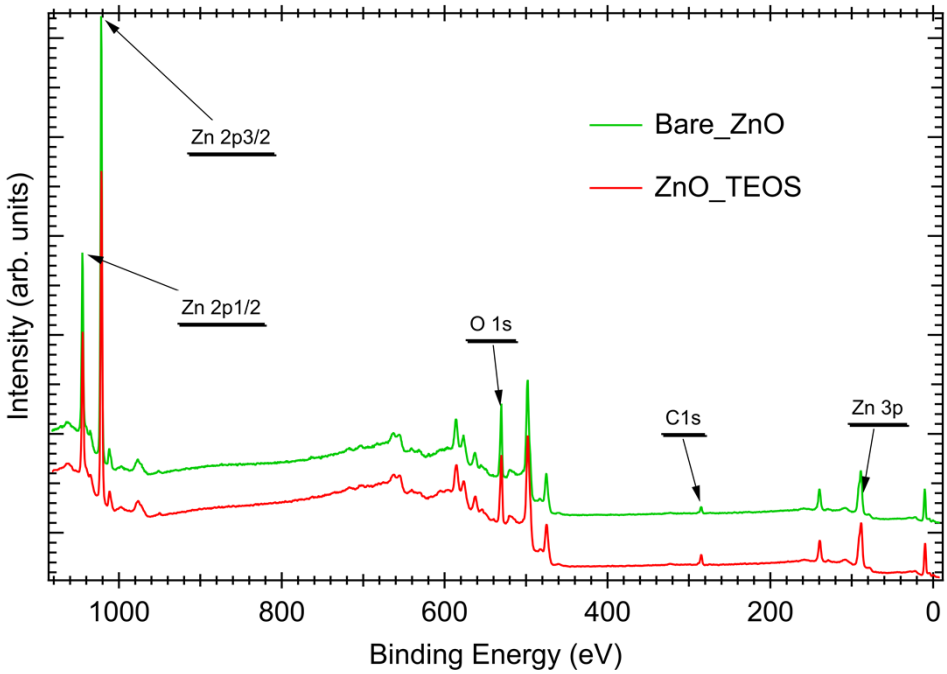

Figure. S3. XPS Survey spectra of bare and TEOS-functionalized ZnO nanowires. The core levels of the elements present in the samples are indicated by arrows, while the other peaks are related to Auger signals. The intensity is normalized on the Zn 3p signal.

Quantification	C	O	Zn	Si
ZnO_TEOS	16.6 %	46.7 %	36.0 %	0.7 %
Bare_ZnO	12.6 %	48.6 %	38.8 %	/

Table S1. Elemental quantification obtained from the integrated area of selected XPS peaks.

4. Dynamic Response Curves of TEOS Functionalized ZnO Nanowires, Detection Limits and Sensor Response/Recovery times

Figure S4 showed the comparison of dynamic responses along with response values of TEOS functionalized ZnO NW's for different gas analytes at 250 ^{o}C in air. Clearly, the sensor exhibits the highest dynamic response for 50ppm of acetone, as compared to other gas analytes. Instead, among all the gases, the response for CO is the lowest. These results confirm the excellent selectivity of TEOS functionalized sensor for acetone detection.

On the other hand, table S2 showed the values of detection limits along with parameters A and B for bare and TEOS functionalized ZnO NW's sensors. At optimal working temperature, the lowest detection limit for acetone i.e. 1 ppm was observed for TEOS functionalized sensors. Hence, not only the response but also the ability to discriminate acetone molecules was improved after

functionalization. This is mainly due to the molecular interactions that occur between TEOS methyl groups and acetone.

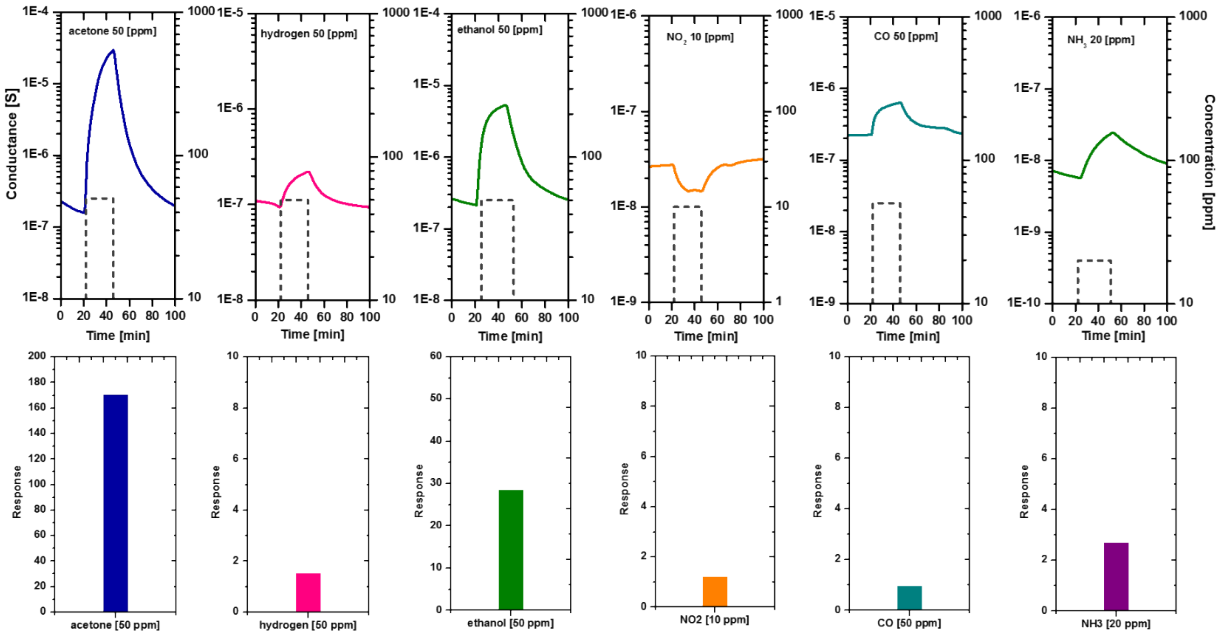

Figure. S4. Dynamic Response curves of TEOS functionalized ZnO nanowires along with corresponding response bar graphs for acetone and other interfering gases at 250 ^{o}C in air.

Samples	A	B	Detection limits
ZTEOS (250 ^{o}C)	0.9	1.3	1 ppm
Bare ZnO (250 ^{o}C)	0.4	1.3	2 ppm
ZTEOS (200 ^{o}C)	0.3	1.2	2.5 ppm

Table S2. Sensing parameters of bare and TEOS functionalized ZnO nanowires obtained by fitting the calibration curves with power law.

Furthmore, figure S5 represents the response and recovery times of ZTEOS sensor towards 50ppm acetone at two different measurents conditions. Specifically, figure S5a showed the response and recovery time of sensing data represents in figure 4 i.e. gas-in time= 30 min. and recovery-time= 60 min. was maintained during the measurements. While, in figure S5b response and recovery times was calculated from the dynamic response represented in figure 6a (gas-in time = 10 min. and recovery-time = 30 min.). Indeed, in both cases response and recovery times are calculated as the time required by each sensor to reach 80 % of the response and 90 % of the baseline, respectively.

The response and recovery times of ZTEOS sensor as shown in figure S5a was found to be 13min. and 29 minutes respectively. While, response and recovery times determined from figure S5b were found to be much lower i.e. 5min. and 18 min. respectively. This indicates that these times value highly dependent on the chosen measurement conditions. Moreover, our measurement chamber used in experimental setup has a volume of 1L to host multiple sensing devices simultaneously. However, using a 200 sccm flow it takes 5-10 minutes to completely fill or empty the chamber. This means that if this time is also considered, much lower values of response and recovery times can be expected.

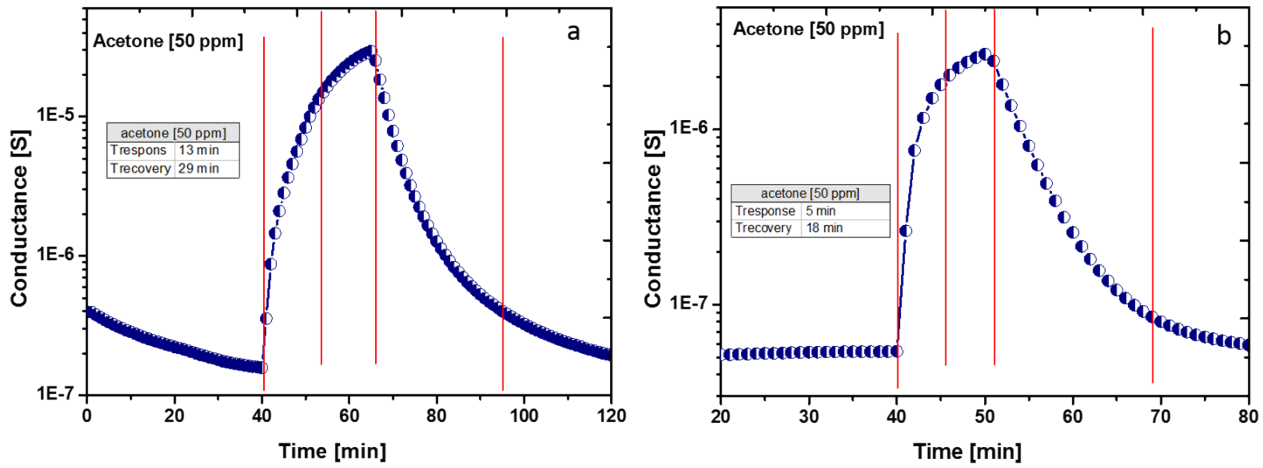

Figure S5. Response and recovery times of ZTEOS toward 50ppm acetone at different gas-in and recovery times (a) gas-in time= 30 min. and recovery-time= 60 min. and (b) gas-in time = 10 min. and recovery-time = 30 min. Gas-in time means that the analyte was maintained for given minutes inside the test chamber, while recovery-time signifies the time given for sensors to recover the baseline as the air flow was restored.

References

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