

## New Generation Devices for Gas (Liquid) Sensing

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### Abstract

We present a short review and novel approach for the construction of conductometric sensors demonstrating considerably higher sensitivities than traditional metal oxide sensors. Sensor platforms do not require film-based technology, operate at room temperature, and can be obtained without the use of time consuming self-assembly processes. A combined nanopore coated micro-porous array, is deposited with nanostructure directing acidic metal oxide island sites which vary in their Lewis acidity, decorate the micropores, and control an electron transduction process. The interaction of analytes with these island sites varies in a predictable manner and can be modified through *in-situ* functionalization of their Lewis acidity through formation of the oxynitrides or oxysulfides. Micropores allow rapid Fickian diffusion of the analytes to the active nanostructured island sites whose reversible interaction with the analyte dominates the sensor response. We require only that the island sites be deposited at sufficiently low concentration so as not to interact electronically with each other. Highly accurate repeat placement of the nanostructured island depositions is not required. The nanoporous walls of the microarray act as a phase match for the deposition of a diversity of nanostructures that are selected for deposition from a variety of solution-based sources and the forgiving deposition process requires a minimum of energy consumption and time. Comparisons to a variety of metal oxide systems are considered. Observed sensitivities and the sensor system reversibility can be predicted from the recently developing IHSAB model.

**Keywords:** Sensors; Directing nanostructure; Metal-oxide; Island sites; Acid/base theory; IHSAB principle; Extrinsic semiconductors

### Introduction

Because the requirements for the detection, monitoring, and transformation of environmental constituents are increasing at a significant rate developing sensor interfaces must be sensitive to low level exposures and have fast response times [1]. As concerns about the impact of gases on health and environmental concerns increase, the reliable detection of several gases over a range of temperatures has become a priority. Included in this group, NO<sub>x</sub> associated with air pollution, combustion, and respiratory disease [2,3] is critical. NO is the primary monitor of an asthmatic attack and can also provide rapidly accessed noninvasive disease [4] detection. NH<sub>3</sub>, which plays an especially important role in urban environments [5,6], also is produced albeit at much lower levels, during an asthma attack. SO<sub>x</sub> and H<sub>2</sub>S [7-9] as well as NO<sub>x</sub> play an important role in automotive and industrial exhaust, acid rain, photochemical smog, and corrosion [3] and natural gas venting. PH<sub>3</sub> is an extremely toxic gas used for fumigation in agriculture and is a byproduct in the production of methamphetamines [10,11]. Advances in gas sensor technology used to monitor these exemplary gases have been driven by sensitivity, selectivity, stability, response time, and durability. Here, we review a new solid-state device technology which detects analytes by measuring an electrical property of a detection interface and from this measurement we can evaluate an interacting gas. Conductometric gas sensors can be made to consist of a sensitive interface layer decorated by nanostructure island sites. The nanostructure decorated interfaces that can be easily constructed, do not demand complex self-assembly, are much easier to implement and reproduce than film depositions, and require far fewer starting materials. These attributes suggest enhanced energy efficiency both in the transduction mechanism and in the simplicity of a design involving minimal manufacturing time. Metal oxide sensors have been the most commonly used solid-state sensor. These sensors [12,13] use the metal oxides of tungsten (WO<sub>3</sub>), nickel (NiO), copper (Cu<sub>x</sub>O), aluminum (Al<sub>2</sub>O<sub>3</sub>), titanium (TiO<sub>2</sub>), tin (SnO<sub>x</sub>), or zirconium (ZrO<sub>2</sub>). The most

commonly cited types of oxide sensors in the literature are based off thin films (<1 micrometer). However, in some cases thick films are used, doped with noble metals or various nanoshapes designed to effect grain boundaries [13-20]. These metal oxide sensors must be heated to elevated temperatures that range from 100 to 600°C depending on the analyte [13,21-23]. For effective monitoring of a given analyte, the temperature must be precisely controlled. The necessary heating results in a significant power drain on the system. The required temperature ranges means that these configurations can be greatly affected by an impinging combustion or flue gas, severely impeding the correct identification of the gaseous species in the flow. The figure compares the typical metal oxide configuration to the potential configuration for PSi sensors, which maybe heat sunk (Figure 1). The required temperature control of typical metal oxide sensors and the necessity to generate the sensing interface from film technology are two key problems that can be overcome with the technology that we summarize below. We describe a conductometric gas sensor that can be made to consist of an easily designed sensitive hybrid nano/microporous interface transformed through the introduction of select nanostructures. This hybrid structure facilitates rapid Fickian [24,25] diffusion into a microporous framework whose nanoporous wall covering serves to provide a phase match for the selectively deposited nanostructures. In contrast to both thin and thick films, which may respond in minutes [26] due to slow diffusion, the current structure, with which analyte interaction is diffusion dominated, allows a response in less than two seconds [27].

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functionalized (nitridation, sulfidation) allowing the tuning of response across a broad range of acidity and basicity and analyte interactions [25]. In addition, the sensor platforms are capable of operation under extremely small magnetic field control [27]. The devices have the potential for adaptation to solar pumped sensing, micro-reactor, and solar assisted micro-reactors to achieve difficult but important chemical transformations, extending the development of basic heterogeneous catalyst sites and potential acid/base pairing combinations [28]. The technology has now been applied to the characterization of volatile liquids including the alcohols, acetone, chloroform, additional polar and nonpolar solvents, and more complex liquids including isoprene.

The nature of liquid sensing has been completely reevaluated [29]. The responsiveness of PS sensor systems is superior to other metal oxide systems. The PS sensors operate at room temperature, are easily constructed with simple deposition techniques (vs. spray pyrolysis, magnetron sputtering, and other film coating techniques) and are much easier to fabricate and use than nanorod or nanowire configured systems [25]. A short comparative table is given (Table 1).

### Comparisons to currently utilized sensors

Test devices have been built and characterized providing not only complementarity with, but also a significant superiority to

| Gas               | Gas Concentration Lower Exposure Limit (LEL) | Response sensitivity          | Operating Temperature | Material   | Method  | Authors  |
|-------------------|--|-------------------------------|-----------------------|--|---|--|
| H <sub>2</sub> S  | 1 ppm  | 5900 <sup>a</sup>             | 200°C                 | Ag (8 nm)-doped SnO <sub>2</sub>                         | DC magnetron sputtering (SnO <sub>2</sub> ); Ag film coating          | Jin et al. [30]                                |
| H <sub>2</sub> S  | 3 ppm; 1 ppm LEL                             | 40% <sup>b</sup> ; unreported | 74°C                  | Ag-doped SnO <sub>2</sub>                                | Polymeric sol-gel   | Gong et al. [31]                               |
| H <sub>2</sub> S  | 2.5 ppm                                      | ~85% <sup>b</sup>             | 400°C                 | SnO <sub>2</sub>   | Spray pyrolysis   | Griessler et al. [32]                          |
| H <sub>2</sub> S  | 0.5 ppm                                      | ~1.4 <sup>a</sup>             | 300°C                 | SnO <sub>2</sub>   | Flame spray pyrolysis (FSP) (nanopowders); Spin coating (sensor)      | Liewhiran et al. [33]                          |
| H <sub>2</sub> S  | 10 ppm                                       | ~1.45 <sup>a</sup>            | 300°C                 | CuO  | Heating in open-air high purity copper foils (nanowires)              | Shao et al. [34]                               |
| H <sub>2</sub> S* | 1 ppm<br>0.5 ppm                             | ~ 5 <sup>a</sup><br>~ 4       | 25°C<br>25-100°C      | PS untreated<br>Nanostructure decorated PS               | Nanopore covered μ-pores  | Lewis et al. [35]<br>Baker et. al              |
| SO <sub>2</sub>   | 50 ppm                                       | ~40% <sup>b</sup>             | 300°C                 | SnO <sub>2</sub>   | Spray pyrolysis   | Griessler et al. [32]                          |
| SO <sub>2</sub>   | 20 ppm                                       | ~3.8 <sup>a</sup>             | 300°C                 | SnO <sub>2</sub>   | FSP (nanopowders)<br>Spin coating (sensor)                            | Liewhiran et al [33]                           |
| SO <sub>2</sub>   | 5 ppm  | ~45% <sup>b</sup>             | 350°C                 | 0.15 wt% V <sub>2</sub> O <sub>5</sub> /SnO <sub>2</sub> | Simultaneous precipitation technique (nanopowder); painting (sensor)  | Das et al. [36]                                |
| SO <sub>2</sub> * | 1 ppm  | ~ 5 <sup>a</sup>              | 25°C                  | PS untreated   | Nanopore covered μ- pores   | Lewis et al. [35]                              |
| CO                | 50 ppm                                       | 8 <sup>a</sup>                | 350°C                 | 0.2 wt% Pt/SnO <sub>2</sub>                              | FSP (nanopowders); Thermophoresis (sensor)                            | Mädler et al. [37]                             |
| CO                | 500 ppm                                      | N/A <sup>c</sup>              | 200 - 400°C           | SnO <sub>2</sub>   | FSP (nanopowders); Drop coating (sensor)                              | Sahm et al. [38]                               |
| CO                | 10 ppm                                       | N/A                           | 150°C                 | CuO  | Soft chemistry (nanospheres); Thick film screen printing (sensor)     | Hübner et al. [39]                             |
| CO*               | 1 ppm  | ~ 3 <sup>a</sup>              | 25°C                  | PS, SnO <sub>2</sub> treated                             | Sn electroless solution   | DeBoer et al. [40]                             |
| NO <sub>2</sub>   | 5000 ppb                                     | 20 <sup>a</sup>               | 220°C                 | SnO <sub>2</sub>   | FSP (nanopowders); Drop coating                                       | Sahm et al. [38]                               |
| NO <sub>2</sub> * | <500 ppb                                     | ~ 10 <sup>e</sup>             | 25°C                  | PS, TiO <sub>2</sub> treated                             | TiO <sub>2</sub> nanoparticle solution doped nanopore covered μ-pores | Laminack et al. [39]                           |
| NH <sub>3</sub>   | 100 ppm                                      | 3.1 <sup>a</sup>              | 200°C                 | CuO  | Heating in open-air high purity copper foils (nanowires)              | Shao et al. [34]                               |
| NH <sub>3</sub> * | <500 ppb                                     | ~ 50 <sup>e</sup>             | 25°C                  | PS, Au <sub>x</sub> O treated                            | Au electroless solution   | Ozdemir et al. [41]                            |
| PH <sub>3</sub> * | <500 ppb                                     | ~ 10 <sup>e</sup>             | 25°C                  | PS, Au <sub>x</sub> O treated                            | Au electroless solution   | Ozdemir et al. [38,42]<br>Laminack et al. [43] |
| H <sub>2</sub> S  | 50 ppb                                       | N/A                           | 25-200°C              | ZnO  | Nanorods  | Wang et al. [44]                               |
| H <sub>2</sub> S  | 1 ppm  | N/A                           | RT <sup>d</sup>       | In <sub>2</sub> O <sub>3</sub>                           | Nanowires<br>2-3 min response   | Zeng et al. [45]                               |
| NH <sub>3</sub>   | 10 ppb                                       | N/A                           | RT                    | W <sub>18</sub> O <sub>49</sub>                          | Ultrathin (5 nm)<br>Nanowire bundles                                  | Zhao et al. [46]                               |
| NH <sub>3</sub>   | 100 ppb                                      | N/A                           | 300°C                 | SnO <sub>2</sub>   | Coupling SnO <sub>2</sub> nanowire to MEMS microhotplate              | Meier et al. [47]                              |
| CO                | 100 ppb<br>(Quote <5 ppm)                    | N/A                           | 300°C                 | SnO <sub>2</sub>   | Single nanowire   | Hernández-Ramírez et al. [48]                  |

Sensitivity=(R<sub>air</sub>-R<sub>gas</sub>)/R<sub>air</sub> × 100%  
 Sensitivity=R<sub>air</sub>/R<sub>gas</sub>  
 N/A=Not Available  
 RT=Room temperature  
 From  $\Delta = \frac{\Delta R(\text{deposited}) / R_0(\text{deposited})}{\Delta R(\text{untreated}) / R_0(\text{deposited})}$

Table 1: Lower exposure limit of various gas sensor materials and methods.

alternate technologies. They operate in an unsaturated mode over wide temperature and pressure ranges. Pulsed mode operation ensures low energy consumption and high analyte selectivity. Extensive Diffusion/Absorption/Desorption Modeling based on a non-empirical approach that permits predictive analytical modeling of Mixed Gas interactions and Interface modifications has been developed [30]. In contrast to optical systems, the sensors have minimal alignment requirements. There is no need for high Q cavities such as those used for Fabry-Perot devices.

## Summary

The simple design allows the sensors to operate in saturated or unsaturated mode over wide temperature ranges with insensitivity to temperature drift. When the sensors are heat-sunk, the configuration allows reliable performance at a surface temperature  $\approx 100^\circ\text{C}$ , even in elevated temperature environments (e.g., combustion or flue gas) in sharp contrast to typical metal oxide sensors. The PSi sensor design allows for rapid response ( $\approx 2$  s), high sensitivity (near-ppb), and reversibility to the gas response. Ease of modification with a diversity of clearly mapped and readily generated gas-selective nanostructured materials, provides a range of sensitivities for a broad range of gases as well as being formatable for sensor arrays (response matrix). Energy-efficient-low power requirements (microwatts- less than watch battery), and sensitivity-weak physisorptive processes produce a conductometric response with  $\Delta G \leq 2$  Kcal/mole. Low energy magnetic field, signal enhancement can be achieved with transition metal nanostructures deposited to a semiconductor surface. Contaminated sensors are readily rejuvenated using an HF technique. Does not require film-based technology or lengthy self-assembly. Nanostructure island sites provide faster response, greater sensitivity. Pulsed mode operation ensures low analyte consumption and high analyte selectivity, as well as the ability to rapidly assess false positive signals using FFT techniques. Ready use for the development of solar pumped sensors Liquid phase organic solvent detection as a function of moderate temperatures has also been demonstrated.

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