Processing and Characterization of Nanostructured Metal Oxides for Gas Sensing Applications

Krithika Kalyanasundaram  Non-member  (Center for Nanomaterials and Sensor Development, State University of New York, Stony Brook, NY, 11794-2275, USA  Email: kkalyana@ic.sunysb.edu )
P. I. Gouma  Non-member  (Center for Nanomaterials and Sensor Development, State University of New York, Stony Brook, NY, 11794-2275, USA  Email: gouma@notes.cc.sunysb.edu )

Keywords : Nanomaterials, metal oxides, gas sensors, nanowires, nanoribbons

1. Introduction

Nanomaterials are defined as those that have at least one of their dimensions \( \leq 100 \)nm. Thus we may visualize them as structures produced by reducing one, two, or three dimensions of a bulk material, thereby resulting in 2D nanolayers, 1D nanowires or 0D nanoclusters (quantum dots). Such length scales are close to atomic sizes and at the nanoscale, the physical, chemical, and biological properties of materials differ in fundamental and valuable ways from the properties of individual atoms and molecules or bulk matter. At such small length scales most of the atoms are surface atoms, thus significantly increasing the effective number of sites available for reactions. Increase in surface area to volume ratio with decrease in grain size also is very important in the field of sensing. Thus reducing the grain size plays a very important role in applications that involve surface reactions like gas sensing. The other factor that becomes predominant at smaller grain sizes is the depletion layer depth or called otherwise the Debye Length (\( L \) or \( \lambda \)). For most nanostructures the value is comparable to their diameter, or their width.

2. Processing of Nanostructured Metal Oxides

The conventional processing techniques for metal oxide nanostructures are illustrated in the schematic below.

A variety of oxides such as ZnO, Ga_2O_3, In_2O_3, CdO, PbO_2 have been fabricated using a solid-vapor process. These involve vaporizing a powder source material at an elevated temperature, and the resultant vapor condenses to form the desired product under specific operating conditions. Novel processing techniques, such as electrosprinning used for producing single crystal nanowires of MoO_3 and WO_3 are also reported in this article.

3. Sensing Behavior of Nanostructured Semiconductor Gas Sensors

3.1 P-n Type Transitions

Semiconductor type transitions can occur during gas sensing involving nanostructured sensing elements. The exact mechanisms of such transitions are not exactly known though there are two possible explanations for it. The first one is a inversion layer formation on the surface that locally causes a transition from an n-p type behavior or p-n type depending on the nature of the adsorbate species. In the other case, the common mechanism that has been suggested is the formation of oxygen vacancies due to a loss of local stoichiometry.

3.2 Nanowires as Sensing Elements

Recently, efforts are focusing in synthesizing one and two dimensional nano-architectures due to their novel electronic transport properties. The figure below shows the morphology of MoO_3 nanowires produced by electrosprinning and their corresponding sensing response towards ammonia. The nanowire sensors show excellent sensitivity (measured as \( R_g/R_{air} \)) and stability (complete removal of baseline drift), compared to the sol-gel-based counterparts. Optimization of selectivity and stability of nanostructured sensors is still underway. The future lies in the successful integration of these nanoassemblies and their arrays with electronics for applications ranging from molecular recognition to bio sensing.

Fig. 1. (Left) HRTEM image of a MoO_3 nanowire; (Right) Sensing response of the nanowire sensor to different concentrations of NH_3
Processing and Characterization of Nanostructured Metal Oxides for Gas Sensing Applications

Krithika Kalyanasundaram*  Non-member
P. I. Gouma*  Non-member

Nanoscience and nanotechnology involve materials and systems with at least one dimension in the range of 1-100 nm that exhibit novel and size-dependent properties. This article reviews the main processing techniques used to fabricate nanomaterials, ranging from sol-gel to vapor deposition to electrospinning. Emphasis is given to metal oxide nanostructures, such as SnO₂ nanoribbons and MoO₃ nanowires. Their electronic properties and their gas detection behavior are presented and discussed. The high surface-to-volume ratio of metal oxide nanostructures has been exploited to develop gas sensors with higher stability, faster response, and higher sensitivity to the analytes of interest than their conventional counterparts. Commonly observed p-n type transition phenomena in nanostructured metal oxides are explained on the basis of the sensing mechanism involved in gas detection by semiconducting oxides and the size-related effects of nanomaterials in the concentration of free charge carriers. Insights are given on the future challenges in resistive gas sensing and how nanotechnology may be helpful in overcoming these burdens.

Keywords: Nanomaterials, metal oxides, gas sensors, nanowires, nanoribbons

1. Introduction

Metal oxides have been used nearly for four decades in gas sensing applications. The basic principle behind the gas sensing mechanism by metal oxides is the change in their electrical resistance on exposure to a gas, due to electronic exchange. The discoveries by Seiyama et al. in 1962 that ZnO thin films exhibit changes in their electrical conductivity with small amounts of reducing gases, and the same year by Taguchi et al. that SnO₂ partially sintered pellets respond similarly, were the beginning for what has been a rapid gas sensor developmental phase. Since 1968 Taguchi sensors have been mass-produced and with the establishment of Figaro Engineering Inc. in 1969 the SnO₂ based sensors have been commercially available.

1.1 Size Matters: why ‘Nano’ Matters for Gas Sensing

In a talk by Richard Feynman—“There is plenty of room at the bottom”—at the American Physical Society meeting at CalTech, the advantages of having better control over things at smaller dimensions were outlined, which spurred the drive for miniaturization and beating Moore’s law. The book by Eric Drexler titled “Engines of Creation-The Coming of Era of Nanotechnology” came next. With the discovery of a new form of carbon—the nanotube in 1991 by Sumio Iijima and the Nobel Prize winning discovery of C₆₀-fullerene, it seemed that the “nanoage” had really started. This paved the way for an avalanche of research and developmental activities on not only C₆₀ but other nanomaterials as well.

A nano-meter is 10⁻⁹ m. Nanomaterials are defined as those that have at least one of their dimensions ≤ 100 nm. Thus we may visualize them as structures produced by reducing one, two, or three dimensions of a bulk material, thereby resulting in 2D nanolayers, 1D nanowires or 0D nanoclusters (quantum dots). Such length scales are close to atomic sizes and at the nanoscale, the physical, chemical, and biological properties of materials differ in fundamental and valuable ways from the properties of individual atoms and molecules or bulk matter. A wealth of new and interesting phenomena such as size dependent emission or excitation, quantized conduction, single electron tunneling (SET), metal to insulator transition to mention a few, are associated with bulk to nano transition. Quantum confinement of electrons by potential wells of nanometer size may provide one of the most effective methods of modifying the electrical, optical, thermoelectric and magnetic properties of materials.

Table 1. Typical Nanomaterials (adapted from)

<table>
<thead>
<tr>
<th>Size (approx)</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond 1-100 nm</td>
<td>Metals, semiconductors, magnetic materials</td>
</tr>
<tr>
<td>Diamond 1-100 nm</td>
<td>Ceramic Oxides</td>
</tr>
<tr>
<td>Several mm^2-µm^2 in area</td>
<td>Metals, Semiconductors, oxides, sulfides, nitrides, Carbon, layered metal chalcogenides</td>
</tr>
<tr>
<td>Thickness 1-1000 nm</td>
<td>Several materials</td>
</tr>
<tr>
<td>Several nm min all three dimensions</td>
<td>Metals, semiconductors, magnetic materials</td>
</tr>
</tbody>
</table>
that involve surface reactions like catalysis, chemical gas sensing etc. Table 1 (adapted from 14) lists the common dimensionalities found in nanomaterials.

1.2 Nanostructured Metal Oxides  Fig. 1(15) shows the grain size dependence of sensitivity for SnO$_2$ films exposed to CO and H$_2$. Similarly Fig. 2(16) shows the response of an In$_2$O$_3$ film to O$_3$ (ozone) as a function of grain size of the In$_2$O$_3$ film. A two to three order increase in sensitivity$^1$ was observed in the case of the In$_2$O$_3$ films when the grain size was decreased from 60-80 nm to 10-15nm.

The other factor that becomes predominant at smaller grain sizes is the depletion layer depth or called otherwise the Debye Length (L or \(\lambda\))$^2$. For most nanostructures the value is comparable to their diameter (in the case of spherical particles/nanotubes/nanowires), or their width (in the case of nanobelts and other flat nanostructures). Under such conditions the surface chemical processes strongly influence the electronic properties. A nanowire can go from a completely insulating state to a completely conducting state$^3$.

Quantum confinement effects become pronounced when dimensional anisotropy sets in.

2. Basic Mechanisms of Gas Sensing in Semiconductor

The most quoted model to explain the resistance change in a metal oxide semiconductor sensor suggests that, in air, oxygen adsorbs on the surface, dissociates to form O*, where the electron on the oxygen, is extracted from the semiconductor$^3$. This electron extraction tends to increase the resistance (assuming an n-type semiconductor, whose majority charge carriers are electrons). In the presence of a combustible gas, like say H$_2$, the hydrogen reacts with the adsorbed O*, to form water and the electron is re-injected in to the semiconductor, tending to decrease the resistance. A competition results between the oxygen removing the electrons and the combustible gas restoring these electrons. So, the steady state value of resistance of the metal oxide depends on the concentration of the combustible gas. This could be illustrated in the following way, by considering the competing reactions:

\[
\text{O}_2 + 2e^- \rightarrow 2O^- \quad \text{(1)}
\]

\[
\text{H}_2 + \text{O} \rightarrow \text{H}_2\text{O} + e^- \quad \text{(2)}
\]

The higher the concentration of H$_2$, the lower will be the density of O* and hence the higher will be the electron density in the semiconductor, and this lowers the resistance.

Another model that may exist or co-exist is that the combustible gas, if chemically active, extracts a lattice-oxygen from the metal oxide, leaving vacancies that act as donors. The oxygen from the air tends to re-oxidize the metal oxide, removing the donor vacancies. Thus, there is a competition between the oxygen removing the vacancies and the combustible gas producing donor vacancies. The density of donor vacancies (and therefore the resistance) depends only on the concentration of combustible gas because the oxygen partial pressure is constant (as when operating in air)$^3$.

2.1 Surface States in Ionic Crystals Like SnO$_2$

In an ionic crystal like SnO$_2$, both anions and cations have poor coordination at the surface. The positively charged Sn ions at the surface have an incomplete shell of negative oxide ions around them. With too few negative ion neighbors, the positively charged ions are more attractive to electrons. So their conduction-band-like orbitals can be at a lower energy than the conduction band edge and can ‘capture’ electrons from the bulk. They also can bond well with a ‘basic’ molecule such as OH$^-$, which has an electron pair to give to the bond$^{14}$.

The surface anions on the other hand do not have their quota of positive ions around them so their anionic-like orbitals can be at an energy level higher than the valence band edge. They can capture holes or give up electrons to the bulk. They can also bond well with an acid molecule like H$^+$ which has a pair of unoccupied orbitals. Actually at low temperatures it is expected that the ionic solids will normally be covered by chemisorbed water, the OH$^-$ bonded to the surface at cationic and the H$^+$ at anionic sites. At higher temperatures these water molecules can be driven off leaving the active sites open for interaction with bases or acid gaseous species or with electron-donor or electron-acceptor gaseous molecules.

---

$^1$ Sensitivity is calculated as the ratio of resistance in gas to the resistance in air in the case of oxidizing gases and in the case of reducing gases it is calculated as the ratio of resistance in air to resistance in gas.

$^2$ It is a measure of field penetration in to the bulk (the mechanism of formation of this layer will be provided in the next section).


The electronic energy levels in the bandgap are termed “surface states” and for semiconductors there are both donor and acceptor levels present on the surface. If there is no carrier exchange between the surface states and the bulk of the semiconductor the bands remain flat and the energy band model is as shown in Fig. 3 (18). In Fig. 4 we see what happens if the electrons move from the region of high EF, the near surface region of the semiconductor, to a region of lower EF, the surface states (18). This separation leads to a double layer voltage that either raises or lowers the energy of the surface states. This movement of bands near the surface is called “band bending”.

The electrical double layer formed may be of three types depending on the movement of electrons in to and out of the double layer. They are:

1) Accumulation layer- This type of layer forms when electrons are injected in to an “n-type” semiconductor (Fig. 5)
2) Depletion or Exhaustion or space charge layer- This forms when electrons are extracted from the conduction band of the n-type semiconductor (Fig. 6)
3) Inversion layer- This type of layer forms in FET devices when a very strong oxidizing agent such as fluorine is present.

Of these the most important type of layer for gas sensing is the depletion layer. It was mentioned earlier that the depletion layer forms in an ‘n-type’ semiconductor when electrons are extracted from it. Similarly in a p-type semiconductor this type of layer will form when holes are extracted from it. In an n-type semiconductor the double layer forms between the negatively charged surface states and the positively charged donor (immobile) ions in the bulk of the semiconductor. In a p-type semiconductor the double layer forms between the positively charged surface states and the negatively charged acceptor ions in the bulk.

2.1.1 N-p Type and P-n Type Transitions in Semiconductor Gas Sensors

Semiconductor type transitions can occur during sensing. The exact mechanisms of transition are not exactly known though there are two possible explanations for it. The first one is an inversion layer formation on the surface that locally causes a transition from an n-p type or p-n type transition depending on the adsorbate. An inversion layer forms on the surface of an n-type semiconductor in the presence of a strong oxidizing agent which results in the formation of an acceptor surface state. If the surface state energy level is close to the valence band edge then to bring the Fermi level close to the surface state, the surface Fermi energy must be close to the valence band. In such a situation the acceptor surface state is so low in the band diagram that it extracts electrons from the valence band leaving a substantial hole concentration. This results in a local n-p type transition.

In the other case, the common mechanism that has been suggested is the formation of oxygen vacancies due to a loss of...
local stoichiometry \(^{(19)}\). In general, the conductivity of a semiconductor is given as,
\[
\sigma = -q\mu n + q\mu p \quad \text{........................................... (3)}
\]
where \(n\) and \(p\) are the electron and hole concentrations respectively, \(q\) is the associated charge and \(\mu\) is the associated charge mobility. When the concentration of either of the charge carriers becomes larger than the other, there is a shift in the type from \(p\) to \(n\) or \(n\)-to \(p\). It has been found that the values of \(n\) and \(p\) depend on the generation of inter-band traps due to the formation of vacancies or impurity substitution. It has been found in \(\text{MoO}_3\) that there is a \(p\)-\(n\) type transition \(^{(20)}\). This might be due to the formation of oxygen vacancies that leads to excess electrons or incorporation of oxygen atoms in to these vacancies that leads to excess holes. When either of these values exceeds a threshold level there is a transition from one type of conduction to other.

2.1.2 Importance of ‘nano’ Barsan’s analysis originally carried out in \((21)\) and \((22)\) showed that, for grains/ crystallites large enough to have a bulk region unaffected by the surface phenomena i.e. when the grain diameter \(d \gg \text{Debye length } \lambda_D\) the surface charge carrier density \(n_s\), is given by
\[
n_s = n_b \cdot \exp\left(-\frac{qV_s}{k_BT}\right) \quad \text{........................................... (4)}
\]
For the limiting case when the crystallite size \(d \leq \lambda_D\), the activation energy related to the Debye length as
\[
\Delta E \sim k_BT \cdot \left(\frac{R}{2\lambda_D}\right) \quad \text{........................................... (5)}
\]
where, \(R\) is the radius of the cylindrical filament produced by sintering small grains. If the value of \(\Delta E\) is comparable to thermal activation, then we have a homogeneous electron distribution in the filament and flat band conditions.

Some of these parameters like the concentration of free charge carriers (electrons), the Hall mobility \(\mu\), the Debye length \(\lambda_D\) and the mean free path of the free charge carriers \(\lambda\) have been calculated for single crystal \(\text{SnO}_2\) surfaces for various temperatures \((21)\) and are listed in Table 2.

If \(\Delta E\) is comparable to the thermal energy then a homogeneous electron concentration is attained in the grain and leads to the flat band case. For grain sizes lower than 50 nm, it has been shown that complete depletion of charge carriers occurs inside the grain and a flat band condition results for almost all temperatures except a few.

3. Fabrication of Nanostructured Metal Oxides

This section attempts to provide a brief outline of the methods commonly used for the fabrication of nanostructured metal oxides. For the sake of simplicity this section will be divided into two portions. The first portion will deal with the conventional methods for fabrication of semiconductor sensors- thick and thin film production methods. The latter half of the section will focus on some unconventional metal oxide nanostructures like nanobelts, nanowires, nanodiskettes and the general approaches for their synthesis. The conventional methods are outlined in the schematic below. A brief overview of each of these techniques is also provided.

3.1 Thin Film Technologies

3.1.1 Sol-gel Method Sol-gel method has been used for a long time for the production of nanomaterials. This is a room or slightly elevated temperature process. The process involves the hydrolysis of a metal organic compound such as a metal alkoxide \((23x24)\) (usually, or can be hexachlorides as well), or inorganic salts such as chlorides \((25x26)\) to produce a colloidal sol. The hydrolysis can take place with the help of alcohol, acid or base. The sol is then allowed to age and settle. This is referred to as the gelation step.

The versatility of the process lies in the flexibility available for the form of the end product such as
- The sol can be coated on the substrate by either spin/dip coating to form a ‘xerogel’ film
- The solvent from the sol can be evaporated to precipitate particles of uniform size and then these can be screen printed
- The sol can be allowed to gel completely to obtain either a xerogel or an aerogel.
- The sol can be spun cast to form ceramic fibers
Sol-gel processing also allows one to introduce second phase particles producing doped metal oxides or mixed metal oxides\(^{(27)}\) hence helping to improve the gas sensitivity and selectivity of the gas sensing matrix.

3.1.2 Spray Pyrolysis It involves the atomization of a liquid precursor through a series of reactors, where the aerosol droplets undergo evaporation, solute condensation within the droplet, drying, and thermolysis of the precipitate particle at higher temperature to form a microporous particle which then gets sintered to give a dense particle \((28)\).

The advantages of using a spray pyrolysis are as follows:
- The process makes use of the wide variety of available
solution chemistries compartmentalizing the solution in to unique droplets, thereby retaining very good stoichiometry on the particle surface. This is particularly useful for the synthesis of single and mixed metal oxides

- A variety of particle morphologies can be obtained such as core-shell morphologies, porous particles for catalyst support, fibers, nanocomposites, quantum dots and hollow nanoparticles, to mention a few.

There are a variety of spray pyrolysis processes, and a few of them are aerosol thermolysis, flame spray pyrolysis, aerosol decomposition, spray roasting, and aerosol decomposition.

### 3.1.3 PVD and CVD

Chemical Vapor Deposition (CVD) involves exposing a substrate of choice to a mixture of volatile precursors that react and/or decompose on the substrate to give the desired product. A wide variety of CVD techniques that are in use are as follows:

1. Atmospheric pressure CVD (APCVD)
2. Atomic layer CVD (ALCVD)
3. Low pressure CVD (LPCVD)
4. Metal organic CVD (MOCVD)
5. Microwave plasma assisted CVD (MPCVD)
6. Plasma enhanced CVD (PECVD) \(^{(29)}\)
7. Metal organic MBE (ultra high vacuum MOCVD) \(^{(30)}\)

Physical vapor deposition (PVD) uses physical means rather as opposed to chemical vapor deposition techniques. The various techniques are

1. Sputtering
2. Evaporation
3. Pulsed LASER deposition

Both PVD and CVD offer enormous amount of control over the film thickness, stoichiometry and microstructure. Hence these films usually have highly controlled properties. But the only disadvantage is that these film deposition techniques are slightly expensive.

A variety of oxides such as ZnO, Ga₂O₃, In₂O₃, CdO, PbO₂ have been fabricated \(^{(31)}\) using a solid-vapor process (see Fig. 7 from reference \(^{(31)}\)). It involves vaporizing a powder source material at an elevated temperature, and the resultant vapor condenses to form the desired product under specific operating conditions (temperature, pressure, atmosphere, substrate etc.).

### 3.2 Thick Film Technologies

**Screen Printing**

Screen printing involves mixing of the high purity oxide powder with organic deflocculant additives like terpineol or propadyol along with inorganic binders like ethyl silicate/ ethyl cellulose \(^{(32)(33)}\). The paste should have the correct rheological properties. In addition, adherence to the substrate and correct thermal shrinkage properties are necessary to obtain a good film.

The advantages of using screen printing are that it is a very efficient way to produce cheap and robust chemical sensors. Also it offers excellent control over the obtainable thicknesses.

### 4. One dimensional Nanostructures used in Sensing

Recently there have been a lot of reports of synthesis of 2D and 1D nanostructures such as nanowires, nanobelts, nanorods, nanodiskettes of metal oxides, with a large surface area to volume ratio. A few of these nanostructures are depicted in Fig. 8. These novel nanoassemblies are expected to possess unique properties such as very high sensitivities to single molecules or few ppb of gases, quantum confinement to mention a few.

---

\(^{(29)}\) Reprinted, with permission, from the Annual Review of Physical Chemistry, Volume 55, ©2004 by Annual Reviews

www.annualreviews.org
4.1 Nanobelts as Sensing Elements  
Nanobelts of SnO$_2$ have been synthesized using thermal evaporation of commercially available SnO$_2$ nanopowders. Single crystalline nanobelts that are dislocation free and ultralong (200 nm wide, length that is 5-10 times of the width) have been produced [35]. Figure 8 gives the TEM image of the SnO$_2$ nanobelts and the sensing response to 250 ppm ethanol. The sensor response as defined by its sensitivity ($\Delta G/G$ where G is the conductivity) is 41.6. It is believed that in the case of single crystalline SnO$_2$ nanobelts, almost all of the adsorbed species are active in producing a depletion layer, thus making the nanobelts to act as a pinched off FET whereas in a polycrystalline or a thick film sensor only a small fraction of the adsorbed species, near the grain boundaries is active in modifying the electrical transport properties.

In another work [36] V$_2$O$_5$ nanobelts have been synthesized using a mild hydrothermal treatment with high yield. These nanobelts were found to be highly selective towards ethanol up to concentrations of about 10ppm. V$_2$O$_5$ with its layered structure can accommodate foreign species between its layers, and in the case of nanobelts (with the water or other molecules intercalated), the large layer spacing permits the gas molecules to reach the active sites easily.

4.2 Nanowires as Sensing Elements  
There has been a lot of research on SnO$_2$ since the first Taguchi sensor was discovered and in order to realize the sensing potential for various gases it is necessary to use other semiconductor oxides. Molybdenum trioxide is a wide band gap semiconductor that has been widely used in catalysis of hydrocarbons [37], the selective catalytic reduction of NOx by NH$_3$ [38], etc. Table 3 lists data from

![Fig. 8. (Top) TEM image of SnO$_2$ nanobelts; (Bottom) Response of the SnO$_2$ nanobelts to 250ppm ethanol at a working temperature of 400°C and 30%RH][35]†7

![Fig. 9. (Top) HRTEM image of a MoO$_3$ nanowire; (Bottom) Sensing response of the nanowire sensor to different concentrations of NH$_3$]

Table 3. Literature survey of the common synthesis routes and gas sensing properties of MoO$_3$

<table>
<thead>
<tr>
<th>Material</th>
<th>Dopants</th>
<th>Synthesis route</th>
<th>Gases tested for</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO$_3$</td>
<td>-</td>
<td>Sol-gel</td>
<td>CO</td>
<td>(39)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Sol-gel</td>
<td>$O_3$</td>
<td>(40)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Sol-gel</td>
<td>$NH_3$, NO$_2$</td>
<td>(20)</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>-</td>
<td>IBD</td>
<td>$NH_3$, NO$_2$</td>
<td>(20)</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>-</td>
<td>R.F. Sputtering</td>
<td>CO</td>
<td>(39)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>R.F. Sputtering</td>
<td>$NO_2$</td>
<td>(41)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>R.F. Magnetron</td>
<td>$NH_3$</td>
<td>(42)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>R.F. Magnetron</td>
<td>$H_2$</td>
<td>(43)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>R.F. Magnetron</td>
<td>CO</td>
<td>(44)</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>-</td>
<td>IR irradiation of a Mo foil</td>
<td>CO, CH$_3$OH</td>
<td>(45)</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>-</td>
<td>PLD</td>
<td>$NH_3$</td>
<td>(46)</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>-</td>
<td>Reactive Sputtering</td>
<td>$NH_3$</td>
<td>(47)</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>TiO$_2$</td>
<td>Sol-gel</td>
<td>CO</td>
<td>(40)</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Sol-gel</td>
<td>$O_3$, CO, NO$_2$</td>
<td>(48)</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>WO$_3$</td>
<td>Sol-gel</td>
<td>C$_2$H$_5$OH, NO$_2$</td>
<td>(40)</td>
</tr>
<tr>
<td></td>
<td>WO$_3$</td>
<td>Sol-gel</td>
<td>$O_2$</td>
<td>(49)</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>Cr$_2$O$_3$</td>
<td>Oxide Milling and Pelletization</td>
<td>Humidity</td>
<td>(50)</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>V$_2$O$_5$</td>
<td>Oxide Milling and Pelletization</td>
<td>Humidity</td>
<td>(51)</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>V$_2$O$_5$</td>
<td>RF magnetron</td>
<td>$H_2$</td>
<td>(52)</td>
</tr>
</tbody>
</table>

The most common synthesis routes for nanostructured MoO₃ thin film sensors are sputtering and sol-gel as can be seen from table 3. But in order to produce novel 2D nanoassemblies our group has used a novel approach (53)(54) to produce single crystalline, one dimensional nanowires. It is a single step process that makes use of electrosprinning to produce a polymer/metal oxide nanocomposite fibrous mat (55). The nanocomposite is then heat treated at an elevated temperature to attain crystallinity and also to burn off the polymer.

The metal oxide nanowires obtained are single crystalline and have a uniform oxide polymorph distribution. The exact mechanism of formation of these nanowires is not fully elucidated yet, but the polymer nanofibers encapsulate the amorphous metal oxide sol-gels and facilitate the formation of single crystal nanowires. We have produced WO₃ and MoO₃ nanowires and used them for sensing NO₂ and NH₃ gases.

Fig. 9 shows the morphology of MoO₃ nanowires produced by electrosprinning and their corresponding sensing response towards ammonia. The unit cell parameters for the MoO₃ single crystal nanowires are: a=3.9630, b=13.856, c=3.6966, A=0.2860, C=0.2688, Z=4 and it belongs to the space-group Pbmm(62). The nanowire sensors show excellent sensitivity (measured as Rg/Rair) and stability (complete removal of baseline drift), compared to the sol-gel nanostructured thin films (53)(54).

5. Summary

This review explores the significance of nanostructured metal oxides in the field of gas sensing. Apart from the thin film sensors, recently there have been a lot of efforts in synthesizing one and two dimensional nanarchitectures due to their novel electronic transport properties. Excellent sensitivities and ease of production have been achieved with these nanomaterials. Optimization of selectivity and stability of these sensors is still underway. The future lies in the successful integration of these nanoassemblies and their arrays with electronics for applications ranging from molecular recognition to bio sensing.

References

Nanostructured Metal Oxides for Gas Sensing Applications

Kirthika Kalyanasundaram (Non-member) received her Bachelors in Engineering in Metallurgy from the National Institute of Technology, Tiruchirappalli, India. Currently she is a Doctoral student at the Center for Nanomaterials and Sensor development at the State University of New York at Stony Brook working with Prof. P. I. Gouma. Her research interests are in the area of development of novel nano metal oxides for selective gas sensing, to be used in electronic nose applications.

P. I. Gouma (Non-member) is an Associate Professor at the Department of Materials Science and Engineering and the Director of the Center for Nanomaterials and Sensor Development at the State University of New York (SUNY) in Stony Brook. Her research focus is on the processing and characterization of advanced materials, such as nanostructured metal oxides and bio-composites for selective chemosensors and electronic noses. Dr. Gouma was invited by the National Academies to participate at the GDEST Workshop on the Future of Sensors and Sensor Systems. She also serves as an Associate Editor of the Journal of the American Ceramic Society and in the Editorial Board of Sensor Letters and The American Journal of Nanomedicine. She has published over 70 peer-reviewed articles on advanced materials, and she can be reached at SUNY Stony Brook, 314 Old Eng. Bldg, Stony Brook, NY, 11794-2275; Ph: +1 (631) 632 4537; Fax: +1 (631) 632 8052; Email: pgouma@notes.cc.sunysb.edu.