

NANOSTRUCTURED POLYMORPHIC OXIDES FOR ADVANCED CHEMOSENSORS

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Abstract. Nanostructured metal oxides have been used as resistive gas sensing elements for the detection of toxic gases, such as ammonia. Two processing techniques for producing nanoparticles and/or nanofibers of semiconducting oxides are described, the sol-gel route and the electrospinning technique. Sensing devices were prepared from these materials. The importance of the oxide polymorphism on the gas sensing behavior is discussed, using MoO_3 as the model system. A generic and simple oxide system-gas detected selection map is proposed based on the findings presented herein as well as on published work in the gas sensor literature.

1. INTRODUCTION

The idea of chemical sensors was introduced by the invention of the pH electrode in 1922, which was used to detect chemical changes [1]. Since then, several sensing technologies based on oxidation-reduction reactions at electrodes were extensively pursued to-date. Gas (such as ammonia) detection often involves the use of glass electrodes which are separated from the sample solution to be analyzed using a plastic membrane [2]. This electrolytic method, however, is expensive and does not provide sufficient gas sensitivity and selectivity. Similarly, other potentiometric and optical chemical sensing technologies lack simplicity and suffer from long detection times [3-4].

Conductimetric sensors based on semiconducting oxides, on the other hand, have been the preferred low-cost detectors for reducing gases. The operating principle of these devices is associated primarily with the adsorption of the gas molecules on the surface of semiconducting oxides inducing electric charge transport between the two materials, that changes the resistance of the oxide [5]. There are a number of ways in which semiconducting oxides in the temperature range of 100 °C – 500 °C can provide *resistance changes* to the introduc-

tion of impurity gases into an air ambient and some generic models for conductimetric or resistive gas sensing have been proposed in the literature [6-7]. As a rule of thumb, the resistance of an n-type semiconducting oxide decreases in the presence of reducing gases while it increases for oxidizing ones.

Among the several parameters controlling the metal oxide gas sensing process, the catalytic and electronic properties and structural configuration of the sensing materials, as well as the nature of gas-oxide interactions, play a key role. There is an increasing trend in chemical sensing to utilize nanostructured materials as gas sensing elements [8-11]. The use of nanoparticles, nanobelts, and nanowires in gas sensing offers high surface areas and unique structural features that are expected to promote the sensitivity of the oxide materials to the gaseous components as well as affecting the temperature dependence on sensing. For resistive type chemical sensors, it was observed that the sensing properties improved with reducing the size of the oxide particles [12]. Nanocrystalline oxide-based chemical sensors were also found to respond extremely fast to gaseous species that may be released from bio-chemical processes, such as CO and amines [13-14].

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Therefore, the work presented involves the use of nanocrystalline films and non-woven nanofiber structures of binary metal oxide systems as gas sensing elements. In particular, his paper focuses on the effect of oxide polymorphism on the sensing behavior of these systems. These materials may exist in several different crystallographic forms (phases) without any change in their composition. Each phase is stable in a given range of temperatures and pressures. Nanoscale processes favor metastable polymorphic configurations for the materials systems studied. A decrease in the average particle/grain size of a polymorphic oxide, such as titania, from a coarse crystal (0.5 μm) to a nanocrystal (e.g. 20 nm size) causes a shift to the onset temperature of the phase transition from anatase to rutile from 1200 $^{\circ}\text{C}$ to 400 $^{\circ}\text{C}$ [15]. The latter temperature is close to the operating temperature of titania-based sensors. The occurrence of a phase reaction during sensing contributes to sensor's degradation [16]. Thus, the issues of polymorphic phase selection for optimized gas sensing are discussed and a correlation is made between the oxide's microstructure and its gas selectivity.

2. EXPERIMENTAL

Two nanofabrication techniques used to produce nanoparticles and nanofibers of metal oxides are described.

Sol-gel processing: A sol is a colloidal suspension of solid particles in a liquid. The sol-gel technique involves the preparation of a sol, the gelation of the sol, and the removal of solvent [17]. A gel is a substance that contains a continuous solid phase enclosing a continuous liquid phase. The continuity of the solid phase gives the elasticity to the gel. The sol may be produced from inorganic or organic precursors. A precursor is a starting compound for the preparation of a colloid. Alkoxides are the most common precursors used. Metal alkoxides have an organic ligand attached to the metal atom or metalloid atom. These alkoxides are used mainly because they react readily with water [18].



where R is the alkyl group, and z is dependant on valency of metal M.

In the preparation of transition metal oxides, an alkoxide reaction with an alcohol is often used to adjust the rate of gelation due to alcohol interchange [17]. This method was adopted for processing thin films of MoO_3 . Precursors for molybdenum oxide films are prepared from molybdenum isopropoxide.

These alkoxides were mixed with n-butanol to obtain 0.1M solutions. Since the materials were reactive to atmosphere, the mixing was done inside a glove box under nitrogen atmosphere. After mixing, the sols were mechanically agitated for 5 minutes inside the glove box and then sealed airtight. Ultrasonic agitation was then performed for 2 hours and the sols were allowed to age and settle. In the case of molybdenum oxide sol, a black opaque liquid was obtained after 24 hours of aging.

Electrospinning: This process has been invented by Formhals in 1934 [19]. Fiber formation is driven by the electrical forces on free charges on the surface or inside a polymeric liquid during this process, which involves the polymer solution or melt put in an pipette charged with high electrical potential. Reneker [20] realized first the importance of electrospinning as a nanomaterials synthesis route. This process has recently been used to form nanofibers of polymeric materials with a range in diameter of 40-2000 nm [21-22]. If the polymer is dissolved in non-volatile solvents, water or other appropriate liquids can be used to collect the jet, remove the solvent, and coagulate the polymer fiber. There are several processing parameters that determine whether a bunch of fibers will be form as opposed to a number of discrete droplets. These include the viscosity of the solution, the net charged density carried by the jet, and the surface tension of the solution [23].

A highly exploratory approach to oxide nanowire fabrication was attempted involving the electrospinning of ceramic oxides. In collaboration with Dr. H. Schreuder-Gibson at Natick Soldier Center, non-woven mats of composite polymer-oxide fibers were produced. The starting solutions consisted of 2 ml MoO_3 sol-gel (0.1M) dissolved in 4 ml polyethylene oxide (PEO) in water and ethanol (0.057 g PEO/ml). According to this process, a conducting (Cu) wire was inserted into the composite solution. High voltage (15 kV) was subsequently applied to the copper wire so as to generate an electric field between the solution and a metallic container. As the voltage increased, the electrostatic charge causes a single jet of liquid to form moving towards the metallic substrate. The resulting mats contained 0.88 mmoles of oxide per gram of fiber.

Further processing & characterization: Once the sol-gel solutions or electrospun mats were produced, thin films of the material were deposited on sensor substrates, the former by spin coating and the latter by simple positioning of square pieces of the composite structures that were peeled off the

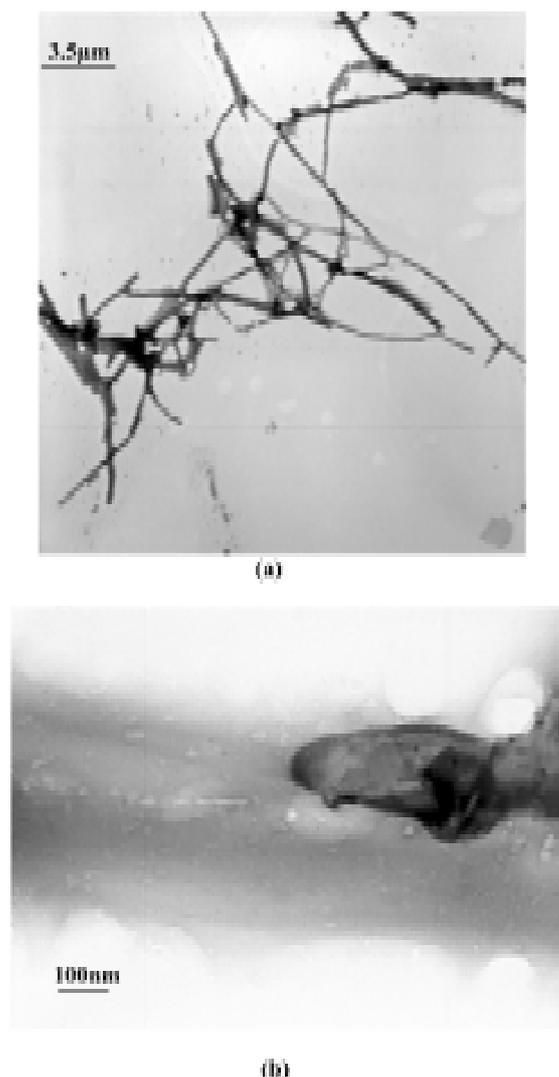


Fig. 1. Transmission Electron micrograph showing the structure of the electrospun mats at high magnification. (a)-(b) The dark contrast features in the images are associated with the location of the amorphous oxide phase; (b) is an enlarged view of a single fiber showing its composite nature.

mats. Stabilization heat-treatment of these structures followed at 500 °C for two different times of 1 hr and 8 hrs. TEM imaging and electron diffraction studies were performed using a Philips CM12 transmission electron microscope with LaB₆ cathode and an incident energy of electrons of 120 keV. SEM studies were also carried out on a LEO-1550 Field Emission Gun Scanning Electron Microscope in order to compare the morphology of the films obtained by the two techniques. Secondary electron imaging was used. All the films were observed directly (without any special specimen preparation techniques).

Sensing tests were carried out in the gas flow bench setup at SUNY-Stony Brook. The primary sensing gases were ammonia and nitrogen dioxide. The gases were controlled through 1479 MKS Mass flow controllers. The combined flow rate of the gases in the presence of either NH₃ or NO₂ was maintained at 1000 sccm. The gas mixture is passed through a tube furnace (Lindberg/Blue), which can be heated at a programmed rate. The sensor is placed inside the tube furnace with quartz tube (1" diameter and 24" length) and is electrically connected to outside leads using gold wires. Sensing experiments were carried out at 450 °C. Electrical resistance measurements of the sensing films as a function of the gas concentration were carried out using an Agilent 34401 digital multimeter.

3. RESULTS AND DISCUSSION

3.1. Morphology of the nanostructured sensing elements

The as-spun composite fibers varied in diameter between 50-500 nm. The electron diffraction patterns obtained from the material reveal typically amorphous structures in the as-received state. The features of darker contrast on the fibers shown in Fig. 1 are the oxide components. These are found to have three distinct morphologies, including: a) long chunks attached to a single polymer fiber; b) aggregates linked to intertwined fiber structures; and c) continuous segments interrupting the PEO structure, with slightly larger diameter than the rest of the fiber. Following the stabilization heat-treatment, the PEO fiber "support" burnt off and the fiber mat shrank. The oxide structures consisted of nanowires of 100 nm length and 5-20 nm width, as well as a wide size distribution of nanoparticle aggregates of MoO₃ as shown in Fig. 2.

The as-received and heat-treated microstructures of the sol-gel processed films were found to be amorphous and equiaxed grain nanocrystalline (20-60 nm) respectively, and have been discussed elsewhere [24].

3.2. Polymorphic phase stability and gas sensing behavior

The MoO₃ system has been extensively used for detecting a variety of gases [25-30]. Recent work performed by the author and co-workers [31-32] has demonstrated that the α -phase of MoO₃ is used as a selective ammonia-sensing probe. In order to demonstrate the dependence of gas sensitivity on the type of polymorph used for sensing the observed p

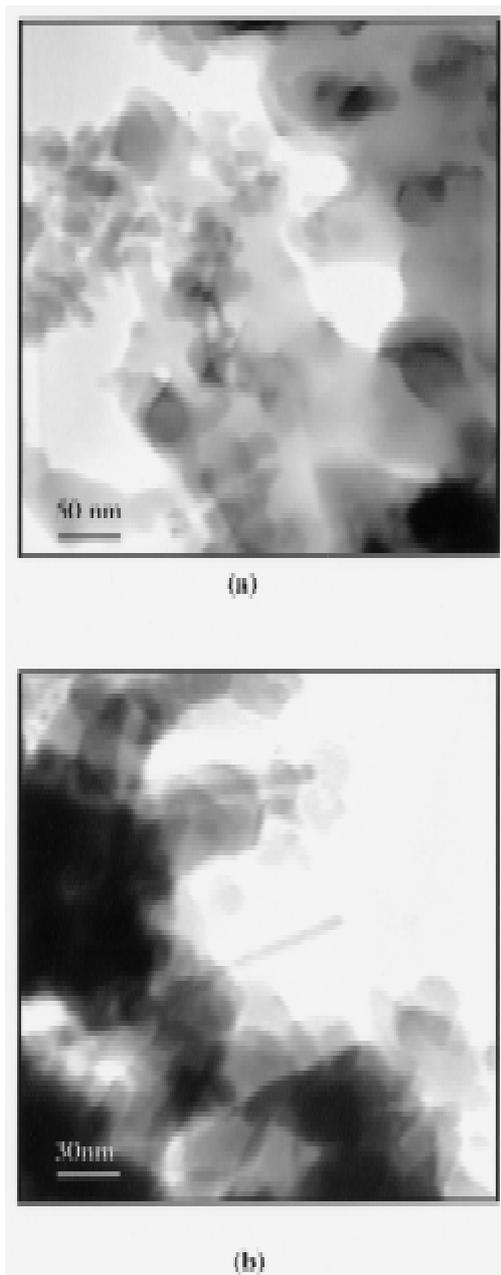


Fig. 2. Transmission Electron micrographs showing the structure of the heat-treated electrospun mats in which the PEO component is burnt off and the resulting material consists of nanosize particulate aggregates in (a) and also some fine nanowires (in (b)).

to n type transitions in oxides are presented and discussed, using MoO_3 as the model system.

The response of sol-gel processed MoO_3 films to NH_3 was obtained under two different processing conditions- after heat treatment at 500°C for a) 1 hour and b) 8 hours. Figs. 3a and 3b show the response of the sensor to ammonia after 1 hour and 8

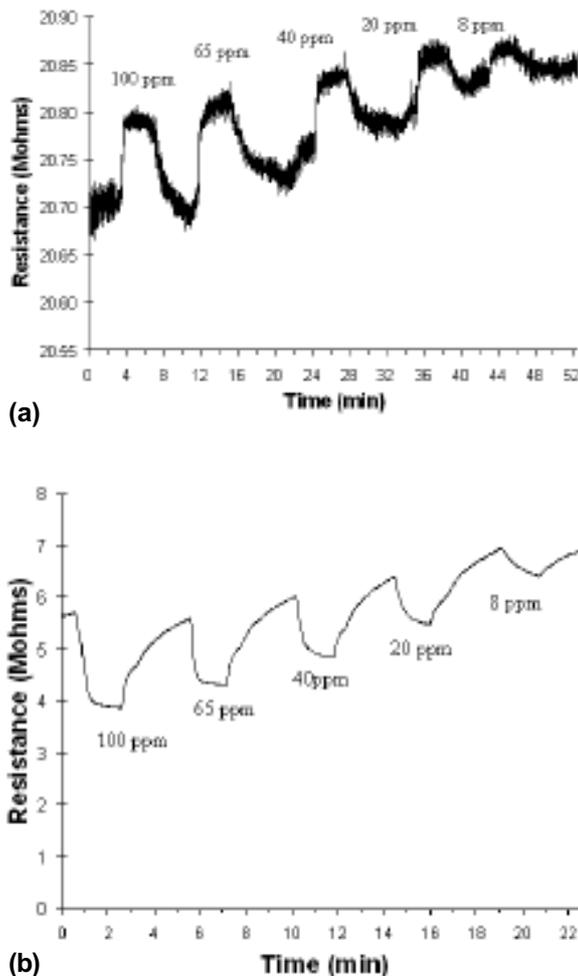


Fig. 3. Sensing responses to 100ppm of ammonia for (a) the specimen heat-treated at 500°C for 1 hr; and (b) for 8hrs.

hours respectively. From Fig. 3a, the response time is in the order of 20-30 seconds and the recovery time is 5-7 minutes. The signal contained a lot of fluctuations and the sensitivity was not as high as that obtained using sputtered sensing films [13]. The resistance increased on exposure to ammonia, (which is counterintuitive finding considering MoO_3 as n-type semiconductor based on previous work) might be due to phase variation, defects (both electronic and atomic) or formation of non-stoichiometric oxides. However, after heat treatment for 8 hours, the expected response was obtained as shown in figure 1b (the resistance dropped in the presence of the reducing gas).

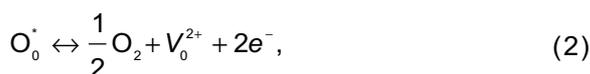
The apparent p to n transition in the semiconductor type of the oxide is possibly due to the stabilization heat treatment. This kind of effect has been

recently reported elsewhere [33]. The conductivity of a semiconductor can be represented in terms of the carrier density and mobility of the individual charge carriers by the Eq. (1)

$$\sigma = -qn\mu_n + qp\mu_p, \quad (1)$$

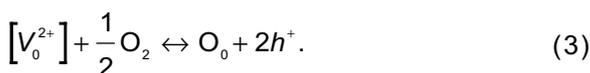
where n and p are the number of electron and hole carriers respectively, q is the charge associated with the charge carrier and the μ values represent the corresponding mobilities. All these four parameters are dependent on temperature and the values of n and p which determine whether it is an n-type or p-type semiconductor vary with the generation of inter-band traps due to the formation of vacancies or impurity substitution.

MoO_3 is an n-type semiconductor in the stable state. In a metastable state, however, oxygen vacancies might exist in different proportions leading to either excess electrons near conduction band or holes near the valence band. A typical oxygen vacancy creation might be represented by the following quasi-chemical reaction (2) as reported in literature [52].



where O_0^{\cdot} represents an unstable oxygen atom in an oxygen site and V_0^{2+} represents an oxygen vacancy with double positive charge.

When oxygen is incorporated into these vacancies, a reversible reaction (3) occurs as shown below.



When the hole concentration drops below a threshold value or when Eq. (2) is favored to Eq. (3), p to n shift occurs due to formation of donors near the conduction band.

Thermoelectric tests performed on the samples, for MoO_3 films prepared by sol-gel technique and heat treated for 1 hour showed a mixed p and n type behavior when sampled at different areas. The tests performed on the sensor heat treated for 8 hours showed only n-type response. Electron microscopy studies revealed a two-phase structure consisting of a mixture of α - and β - MoO_3 for the specimens heat-treated for 1hr and only α - MoO_3 for the specimen that underwent the 8 hr heat treatment.

3.3. Oxide-Gas Sensor System Selection Process

The detection process of oxidizing/reducing gases by semiconducting metal oxides involves the change in the conductivity of the oxide in the presence of the gas due to catalytic red-ox reactions occurring at the oxides' surfaces [5]. These catalytic reactions are controlled by the electronic structure of the oxide system used as well as by the chemical composition, crystal structure, and relative orientation of the surfaces of the oxide phase(s) exposed to the gas [34]. Metal oxides are polymorphic compounds and nanocrystalline processing may be used to stabilize oxide polymorphs that would otherwise be energetically unstable under normal testing conditions [34-35]. The reported variations in the gas sensing response of the model oxide system described above were found to correlate with the crystallographic modifications of the oxide during processing/testing. It is therefore claimed herein that the ability for selective detection of a particular gaseous analyte in the presence of interfering gas mixtures (i.e. sensor selectivity) is largely determined by the chosen crystalline polymorph (specific crystallographic phase) of a stoichiometric and pure metal oxide used for sensing. A simplified model of the polymorphic phase selection process for the sensing of a particular class of gases is discussed below and specific examples are given from the catalysis and gas sensing literature.

Semiconducting metal oxides show *surface sensitivity* to redox reactions involving gases. For example, during hydrocarbon oxidation reactions, hydrogen abstraction occurs at (001) and (100) crystal phases of MoO_3 while oxygen addition occurs at the (010) basal plane [36]. The local environment of active sites (available for gas adsorption, hydrogen extraction, or oxygen addition) and the orientation of the surface containing these active sites, vary for different phases of a given system, and thus the catalytic behavior of these phases is variable. Oxygen basicity is found to increase with decreasing Mo-O bond strength occurring at different surfaces [37]. Surface oxygen vacancies formed under reduction conditions may influence gas adsorption processes. They may result in slightly reduced metal oxide surfaces which undergo re-oxidation by gaseous oxygen (adsorption-based sensing) or they may order and give rise to crystallographic shear structures that accommodate non-stoichiometric metal oxide compositions known as Magneli phases (reaction-based sensing). The presence of ordered

vacancies and crystallographic shear structures provides a mechanism for selective oxidation.

Considering the two main polymorphs of MoO_3 , the α -phase (orthorhombic) has a layered structure with (010) basal plane which is built up of double chains of edge-sharing $[\text{MoO}_6]$ octahedral connected through vertices while the β -phase (monoclinic) has a ReO_3 -type structure. The ReO_3 type structure does not contain the Wan der Waals gap of the α - MoO_3 . Therefore, α - MoO_3 upon reduction in catalysis forms the $\text{Mo}_{18}\text{O}_{52}$ structure instead of the ReO_3 type Mo_8O_{23} shear structure [36]. It was shown in gas sensing tests performed by the author [31-32, 37] which are not reported here, that the α -phase is selective to ammonia and highly sensitive to amines (which are moderate bases) and the sensing mechanism is consistent with the reduction of MoO_3 and the formation of ordered phases, which suggests reaction-based sensing process. On the other hand, the ReO_3 -type structure of MoO_3 is structurally very similar to that of WO_3 [38] that was found to be selective to NO_2 . An adsorption (chemisorption) based sensing mechanism is most likely active in this case that doesn't affect the bonds in the metal oxide surface.

From the above, it is suggested that ammonia and amines can be best sensed by "loosely bound" layered oxide structures, such as the orthorhombic MoO_3 phase that enable the reaction of lattice oxygen with the gas and provide easy mechanisms for accommodating the off-stoichiometric M:O ratio. On the other hand, oxidizing gases, such as NO_2 , may be easily adsorbed on ReO_3 -type crystals. Oxidizing gases destroy oxygen defects.

CO and hydrocarbons typically react with adsorbed oxygen from the environment and may be sensed by rutile-type structures [14], such as the polymorphs of SnO_2 and TiO_2 . Since a given crystal structure may be sensitive to more than one gases, sensing tests at different temperatures need to be carried out so as to identify the optimum operating temperature for the specific sensor. It is important to remain within the phase stability field of the particular polymorph of the oxide. As discussed above, phase stability depends on the grain/particle size of the sensing element (oxide crystal), the operating temperature and pressure conditions, and the presence of impurities and these are some critical factors to consider when selecting a sensor material.

Summarizing, the sensing systems of interest are binary metal oxides that are classified into three groups according to their crystallographic characteristics. These include:

Group A of oxides having the rutile structure: The following oxides have stable polymorphs that belong to this group (TiO_2 , SnO_2 , CrO_2 , IrO_2 , β - MnO_2 , etc.). The rutile structure is tetragonal, however it is often described as a distorted hexagonal close packed oxide array with half the octahedral sites occupied by the metal [38]. Alternate rows of octahedral sites are full and empty. The rutile structure is regarded as an ionic structure.

Group B of oxides having the ReO_3 structure: The cubic ReO_3 structure is closely related to the perovskite structure [38]. The unit cell contains metal at corners with oxygen at edge centers. A few oxides form this structure, including WO_3 , β - MoO_3 , UO_2 .

Group C of oxides having a weakly bonded layered structure: The α - MoO_3 unique 2D layered structure is a typical representative of this group.

On the other hand, the gases to be sensed may be categorized into the following types: Reducing Gases (**Type I** and **Type II**), and Oxidizing gases (**Type III**). Type I gases include CO and volatile organic compounds, such as methane, propylene, etc. Type II gases include NH_3 and amines, while Type III refers to O_2 , NO, NO_2 .

It is claimed that Type I gases may be sensed selectively by a metal oxide having the crystal structure of the Group A, Type II gases by those of Group C and Type III by group B. A simplified matching of oxides to gases as the one described above is the first step in the selection process of the sensing element and it is based on the primary nature of gas-oxide interactions (i.e. chemisorption vs reaction-based sensing). The next step is to match a specific oxide within a designated group to a single gas of a certain type.

For Group A-Type I and Group B-Type III interactions the adsorption/desorption characteristics of the gas to the surface of the metal oxide are the key factors determining sensitivity, selectivity, response and recovery times. Therefore, preliminary BET measurements (gas adsorption tests) or other chemical analysis techniques that provide chemisorption related information (e.g. Raman spectroscopy) may be carried out for several oxides of this group with the specific gas of interest to determine which oxide behaves optimally.

For Group C-Type II interactions, it is the strength of the M-O bond on the exposed surface that determines which gas will be sensed with high sensitivity. At the same time, the electronic structure of the gas to be detected needs to be considered, espe-

cially with respect to the ease of exchanging electrons with the metal oxide surface. Crystal growth and patterning techniques allow for growing metal oxide along a preferred crystallographic orientation.

There are several other factors that may influence the selection of a given metal oxide for selective gas sensing, and these include the stability of the sensor at the operating temperature, the structural stability of the chosen metal oxide, the temperature dependence of the sensing process. However, these may be accounted for easily once the proper choice of metal oxide phase has been made. The correlations made may serve as a guide for building multisensor arrays of inherent specificity.

4. CONCLUSIONS

Nanostructured metal oxides offer high sensitivity and fast response to gas sensing of harmful chemical species. Electrospinning has been explored as a novel synthesis technique for oxide nanofibers. These early attempts have produced 100 nm long nanowires and fine nanoparticles of transition metal oxides. Polymorphic stability was found to affect the sensing response of nanostructured materials used in gas detection. A simple correlation of certain crystal structures of binary metal oxides with their sensitivity to different classes of gases is proposed.

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