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Nanocomposite Films for Gas Sensing

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1. Introduction

Nanocomposite films are thin films formed by mixing two or more dissimilar materials having nano-dimensional phase(s) in order to control and develop new and improved structures and properties. The properties of nanocomposite films depend not only upon the individual components used but also on the morphology and the interfacial characteristics. Nanocomposite films that combine materials with synergetic or complementary behaviours possess unique physical, chemical, optical, mechanical, magnetic and electrical properties unavailable from that of the component materials and have attracted much attention for a wide range of device applications such as gas sensors. Recently, various nanocomposite films consisting of either metal-metal oxides, mixed metal oxides, polymers mixed with metals or metal oxides, or carbon nanotubes mixed with polymers, metals or metal oxides have been synthesized and investigated for their application as active materials for gas sensors. Design of the nanocomposite films for gas sensor applications needs the considerations of many factors, for example, the surface area, interfacial characteristics, electrical conductivity, nanocrystallite size, surface and interfacial energy, stress and strain, etc., all of which depend significantly on the material selection, deposition methods and deposition process parameters. This chapter will summarize recent developments in this new area of research including the fabrication methods currently in use for preparing nanocomposite films, transduction mechanisms for nanocomposite film gas sensors, types of the nanocomposite films suitable for gas sensors application, and the unique gas sensing properties of nanocomposite films.

2. Nanocomposite film fabrication methods

Materials can be deposited in the form of thin film (up to a few micrometer thick) on a substrate by a variety of methods such as physical vapour deposition, chemical vapour deposition, wet-chemical processes such as sol-gel and electrochemical deposition, thermolysis and flame spray pyrolysis etc.. Structural properties and composites of the nanocomposite films are strongly dependent on deposition techniques and deposition parameters. There are many more challenges to deposit composite films consisting of materials of very different nature such as a metal with a polymer or a metal oxide with a metal, than to deposit films of only one type of material. Any deposition process that can be used to prepare nanocomposite films should be able to simultaneously vaporize or coat materials of different nature onto the same substrate to form the composite films. To deposit
composite materials of different natures by precisely controlling their chemical composition, surface morphology, microstructure, and phase remains a challenge. This section will summarize the most common deposition methods used for the fabrication of nanocomposite films for gas sensor applications.

2.1 Physical vapor deposition

Physical vapour deposition (PVD) is referred to a variety of vacuum deposition methods that are used to deposit thin films by the condensation of the vaporized form of materials onto various substrate surfaces. The coating method involves only purely physical processes such as high temperature vacuum evaporation using electron beam or resistance heating, plasma sputter bombardment and pulsed laser deposition. To deposit nanocomposite films by PVD processes, the energy sources, such as electron beam, laser, and plasma, must be able to vaporize component materials under the same processing parameters such as power, energy, temperature and vacuum level, and then condense them at the same time onto a substrate surface to form the composite film.

Sputter deposition is one of the PVD processes that uses a sputtering gas such as argon to sputter composite material sources (a target consisting of pre-mixed compounds or a few targets simultaneously sputtering by ions) which then deposits them onto a substrate to form thin films. Nanocomposite films consisting of mixed metal oxides, a metal and a metal oxide, or a metal and a polymer can be deposited by the sputtering method. Pulsed laser deposition (PLD) is another PVD process that can be used to deposit nanocomposite films. The PLD uses a high power focused pulsed laser beam to ablate targets of materials to be deposited to form a deposited thin film on the substrate inside a vacuum chamber. Since laser beams are much easier to transport and manipulate, and does not interact with gas-phase species, the dynamic range of deposition pressures is the largest compared to other vacuum deposition processes. Typical laser wavelengths used in PLD process are less than 250 nm. In such short wavelength, virtually any material can be laser evaporated leading to the possibility for depositing composite films consisting of a variety of materials. Nanocomposite thin film material can be easily deposited by PLD using a target consisting of pre-mixed powder of source materials or ablating multiple targets of different materials simultaneously. The ability of the technique to reproduce the target composition is a unique feature for controlling the composition of nanocomposite films. Fig. 1 shows a typical PLD apparatus used for deposition of Au-WO$_3$ nanocomposite films. The KrF laser beam, operating at 248 nm wavelength, was used to subsequently ablate a rotating WO$_3$/Au composite target, which was formed by mounting a pie-shaped piece of Au target over a circular WO$_3$ target as shown in Fig. 1. The vapours from both Au and WO$_3$ are condensed and mixed on a substrate to form the Au-WO$_3$ nanocomposite film. To improve the film homogeneities, the substrates were rotated along the vertical axis at a speed of 35 rpm (Yang, 2008). High temperature vacuum evaporation is also a PVD process suitable for depositing nanocomposite films. This technique consists of pumping a vacuum chamber to low pressures and heating the material to produce a flux of vapour and condensing it onto a surface. The material to be vaporized is typically heated by using an electrically resistive heater or electron beam until its vapour pressure is high enough to produce a flux. For depositing nanocomposite films, powders of two or more materials were mixed and compressed into pellets for evaporation. It is also possible to vaporize multiple pellets of different materials using multiple heating sources. The flux of each material can be controlled individually by increasing or decreasing the power of
the heating source or exposed area of the materials in the vacuum. Vacuum evaporation is very useful for nanocomposite thin film fabrication due to ease of uniform mixing over a wide range of concentrations.

![Diagram of a PLD apparatus used to deposit nanocomposite films.](image)

Fig. 1. A typical PLD apparatus used to deposit nanocomposite films. The laser beam subsequently ablates rotating WO$_3$/Au composite targets to produce the Au-WO$_3$ nanocomposite films.

2.2 Sol-gel and other wet chemical synthesis

The sol-gel process is a wet-chemical technique that is widely used to deposit nanocomposite films. In this process, sol (or solution) containing sources for component materials, such as metal alkoxydes and metal chlorides precursors for metal oxides, metallic nanoparticles for metals, tetraethoxysilane for silica matrix, catalysers, stabilizers and other additives for porosity generation, was prepared first. The sol then undergoes hydrolysis and polycondensation reactions to evolve gradually towards the formation of a gel-like network containing both a liquid phase and a solid phase. The basic structure or morphology of the solid phase can range anywhere from discrete colloidal particles to continuous chain-like polymer networks. The formation of the nanocomposite film from the sol-gel precursor involves either dip coating or spin coating on a substrate, decomposition and pyrolysis of organic compounds, removal of water and residual organics from the resulting network followed by nucleation and growth of the crystallites. The thermal decomposition behaviour of the gel precursor plays an important role in crystallites size and in film porosity. Sol-gel is an excellent technique for preparing high purity multicomponent films. Various types of nanocomposite films have been prepared by the sol-gel process and used as active materials for gas sensors.

Beside sol-gel process, other wet chemical processes were also used to synthesize nanocomposite films. For example, successive ionic layer deposition (SILD) method was used to prepare SnO$_2$-Au nanocomposites using HAuCl$_4$ and SnCl$_2$ as the precursors (Korotcenkov, 2009). The SILD method consists essentially of repeatedly successive treatments of the substrate surface with solutions of various salts such as acetates, chlorides,
and nitrates of various metals. Electrophoretic deposition process is another wet-chemical process used to incorporate metal nanocrystals into the mesoporous metal oxide films to form metal-oxide nanocomposites films. In the process, the mesoporous metal oxide films are immersed in metallic nanocrystal dispersion. Under applied electrical potential, metallic nanocrystals are infused into the inside of mesoporous oxide film to form the nanocomposite films.

2.3 Chemical vapor deposition and flame spray pyrolysis
Chemical vapour deposition (CVD) is a chemical process that can be used to produce thin nanocomposite films. In a typical CVD process, the substrate is exposed to more than one volatile precursor, which reacts and/or decomposes on the substrate surface to produce the desired composite films. However, only few papers reported using the CVD process to produce nanocomposite films for gas sensor applications. Flame spray pyrolysis is a one step combustion process of solution precursors to produce nanocomposite materials of mixed oxides. Particle size can be produced in the range of 10 nm to 100 nm depending on process parameters. A binder and solvent were then used to mix the nanocomposite particles prepared by pyrolysis to form a paste prior to doctor-blade coating on the substrates to form thin films or thick films for gas sensor applications.

3. Transduction mechanisms for nanocomposite film gas sensors
A gas sensor is an electronic device that consists of a transducer and a sensitive element (an active layer such as a nanocomposite film) that relies, for its operating mechanism, on one of its physical and chemical properties. Basically it operates as follows: a charge transfer occurs between gas molecules and the “sensitive” nanocomposite films, resulting in an electrical and/or optical signal that is related to the gas molecules type and number. Due to its nanoscale morphology and aggregation, the surface-to-volume ratio and quantum confinement, nanocomposite “sensitive” films with high sensitivities, improved selectivity and reduced operating temperatures have been demonstrated. The following section summarizes various types of transducers that utilize different operating mechanisms for the nanocomposite film gas sensors.

3.1 Chemoresistive sensors
Chemoresistive response of nanocomposite films is based on the modification of electrical conductivity of the nanocomposite films due to adsorbed gas species. Chemoresistive effects are perhaps the most attractive measurable responses since very precise readings may be achieved with minimal electronics. To fabrication a chemoresistive gas sensor, nanocomposite films are deposited on to a substrate provided with interdigital electrodes made from either Pt or Au. A thin film heater made from Pt or NiCr is always fabricated on the backside of the substrate as a heater to provide high operating temperature requirement. The resistance of the nanocomposite film is monitored when the film is exposed to difference gases. A typical apparatus for testing chemoresistive gas sensor is shown in Fig. 2. The sensor under test was loaded in a glass chamber and the electrical resistance of the sensor was measured by a multi-meter through two conductive needles when a target gas was injected into the chamber. Chemoresistive response is the most common transduction mechanisms for gas sensors based on nanocomposite films.
3.2 Optical sensors

Optical gas sensors are based on the modification of optical responses of a nanocomposite film induced by interaction with gas molecules. This approach presents a number of advantages over the chemoresistive sensor. Electromagnetic waves are described by a certain number of degrees of freedom such as intensity, wavelength, and polarization: optical sensing thus allows multi-parametric detection, which is not possible in electrical sensing where only a single scalar quantity (electrical conductivity) is involved. Optical sensors do not need electrical contacts, do not suffer from electromagnetic noise and may allow optoelectronic integration and have the potential of multi-gas detection. Different optical responses may be involved in optochemical gas sensing, such as reflectance, absorption, surface plasma resonance or photoluminescence. Examples of optical sensors include white light interferometry of polymer nanocomposite films to measure their swelling sensitivity when exposing to gas vapours (Mauro, 2009), optical absorption of Au-TiO$_2$ nanocomposite films for the detection of CO and H$_2$ (Buso, 2008), and surface plasmon resonances of the metal nanoparticles in metal-metal oxide nanocomposites (Yang, 2008 & Fernández, 2005 & Manera, 2008). Recently, nanocomposite films with gas sensing functionality have become a new area of interest for optical gas-sensing applications.

3.3 Surface acoustic wave sensors

The operational principle of an acoustic wave gas sensor is a travelling wave combined with a confinement structure to produce a standing wave whose frequency is determined jointly by the velocity of the travelling wave and the dimensions of the confinement structure. Surface acoustic wave gas sensors obtain their gas sensitivity from a chemically active nanocomposite film coated on top of the acoustic device, which interacts with the surrounding gases. The acoustic wave travelling in the coated device particularly penetrates into the adjacent composite film, translates and deforms the film, thereby probing its mechanical properties, its thickness and the acoustic properties at the upper film surface.
The chemical interaction on the surface of a nanocomposite film leads to a change in acoustic wave propagation, which in turn yields a change of the electrical response of the sensor. The quartz crystal resonator is the most common device used as an acoustic-wave-based sensor. The simple geometry of the device and the predominant thickness-shear mode of the propagating wave are propitious conditions for a comprehensive derivation of the acoustic-electrical behaviour of quartz crystal devices. Examples of surface acoustic wave gas sensors using nanocomposite films include TiO$_2$-porphyrin nanocomposite thin film coated on a quartz crystal was used to detect volatile organic compounds such as ethanol, acetone, 2-propanol, cyclohexane, toluene and o-xylene (Arshad, 2008) and a polyaniline-indium oxide nanocomposite thin films gas sensor was fabricated on AT-Cut quartz crystal microbalance (QCM) of Ag electrodes for analyze CH$_4$ and CO$_2$ gases (Yan, 2009).

4. Types of nanocomposite films

Nanocomposite films consists of nanocrystalline or amorphous phase of a least two different materials. Depending on the nature of the component materials, micro/nanostructure and surface/interfacial characteristics, various unique gas sensing properties can be realized by using nanocomposite films as the active layer. Improvement in gas sensitivity, selectivity, stability, as well as reduction in the response time and operating temperature has been demonstrated by various types of nanocomposite films. In the following section, the fabrication and unique gas sensing properties of various types of nanocomposite films such as metal-metal oxide, mixed metal oxides, polymers mixed with metals or metal oxides, or carbon nanotubes mixed with polymers, metals or metal oxides will be described.

4.1 Metal-metal oxide nanocomposite films

Nanocomposite films that consist of metal nanoparticles dispersed in a matrix of metal oxides have recently attracted much interest as materials for gas sensors. Metal-metal oxide nanocomposites have physical properties that differ from those of the nanostructured single phase metal oxides. The metal nanoparticles play both passive and active roles in the sensing process. The presence of metal nanoparticles increases the active surface area and improves gas diffusion inside the film. Metal nanoparticle also reduces the electrical resistance and increases the optical absorption of metal oxide. Metal nanoparticles such as platinum (Pt), palladium (Pd), gold (Au), palladium (Pd) and silver (Ag) also show catalytic properties that can modify the analyte-metal oxide chemical interactions and enhance the sensing process. The interfacial region between metal nanoparticle and metal oxide also has very different electron band structure than inside the bulk semiconducting metal oxide, which also contribute to the unique gas sensing properties of this type of nanocomposite.

Fabrication

The amount and distribution of the metallic nanoparticles in a metal oxide matrix is an important parameter to be controlled in order to obtain highest gas sensing sensitivity. Diverse methodologies including PVD, impregnation, sol-gel, and electroless plating have been used to introduce metal nanoparticles into the metal oxide matrix. For example, reactive magnetron sputtering was used to deposit Pd-doped SnO$_2$ nanocomposite films with tetragonal SnO$_2$ structure and columnar nanograins at the substrate temperature of 300 °C and discharge gas pressure of 1.5, 12, and 24 Pa. The discharge current was fixed at 80...
mA, and the discharge voltage showed a value between 280 and 260 V, depending on the discharge gas pressure. It was found that a porous film could be formed at a high discharge gas pressure and a low substrate temperature (Shen, 2009). Metal–metal oxide nanocomposite films can also be deposited by the PLD. For example, gold-zinc oxide nanocomposite films have been synthesized by subsequent laser ablation of zinc and gold targets using either an UV KrF excimer or a frequency tripled Nd:YAG laser. The optical properties of the gold-zinc oxide nanocomposite films can be tailored by proper choice of the relative number of laser pulses used for the ablation of the gold or zinc targets (Gyorgy, 2008). Surface plasma resonance (SPR) gas sensors using very thin Au-WO$_3$ nanocomposite thin films were also fabricated by PLD and the content of Au in the composite films was also varied by altering the relative laser ablation time on Au and WO$_3$ targets, respectively (Yang, 2008).

Dot- and rod-shaped Au-TiO$_2$ nanocomposite films were prepared by a sol-gel method for SPR sensing of alcohol vapours. For the synthesis of Au-TiO$_2$ nanocomposite films, firstly, a sol using titanium isopropoxide, isopropanol and acetic acid with a molar ratio of 1:6:1.3 was prepared. Then, a colloidal solution containing Au spherical nanoparticles was prepared and mixed with the sol. Colloidal gold was synthesized by reducing HAuCl$_4$ with tris-sodium citrate in water and then dispersed in ethanol by using poly(n-vinylpyrrolidone) as a stabilizer. The mixed sol was spin coated onto fused silica slides following by drying and heat treatment to form the thin films (Manera, 2008). Other metal-metal oxide nanocomposite films prepared by sol-gel processes include the SnO$_2$-Ag nanocomposite (Gong, 2006); Au-TiO$_2$-NiO nanocomposites (Gaspera, 2010) and Au-TiO$_2$ nanocomposite films for sensing vapour organic compounds by Surface Plasmon Resonance and optical absorption (Fernandez, 2005). Beside sol-gel process, other wet chemical processes were also used to synthesize metal-metal oxide nanocomposite films. SnO$_2$-Au nanocomposites were deposited by the SILD method on a substrate coated with un-doped SnO$_2$ films of thickness ~50–55 nm using HAuCl$_4$ and SnCl$_2$ as the precursors. The thickness of the SnO$_2$–Au nanolayer on the surface of the SnO$_2$ films was controlled through the number of deposition cycles (Korotcenkov, 2009). A significant limitation in SILD deposition relates to the repeated treatment of the growing film, which is necessary for the synthesis of the multilayer, but it can cause re-dissolution of the film in the solution during repeated treatment. Electrophoretic deposition process can also be used to deposit metal-metal oxide nanocomposite films. For example, the mesoporous TiO$_2$ on ITO/glass was immersed in Au nanocrystal dispersion in chloroform. A potential of 25 or 50 V was applied to infuse the Au nanocrystals inside the mesoporous TiO$_2$ film to form the Au-TiO$_2$ nanocomposite films. The ligands such as dodecanethiol on the Au nanocrystals prevented aggregation. The films were highly conductive, and are suitable for sensor applications (Patel, 2007 & Mehul, 2008).

**Unique properties**

Metal-metal oxide nanocomposite films combine the catalytic property of metal and gas reactivity of semiconducting metal oxide, thereby possess unique gas sensing properties unavailable from either the metal or metal oxide alone. Metallic nanoparticles activate or dissociate the detected gas on their surface. These activated products are easier to react with the adsorbed oxygen species on the metal oxide surface, resulting in a change of resistance. In addition, direct exchange of electrons between the semiconductor metal oxide and metallic nanoparticles causes a change in the width of the depletion layer of the semiconductor oxide, leading to a change in sensing properties. The embedded metal
nanoparticles can reduce the sensing temperatures, improve the selectivity, and increase the surface area of the metal oxide.

Sun et al. (Sun, 2009) investigated the Pd-doped SnO$_2$ nanocomposite films for H$_2$ gas sensing. They found that the composite films show reversible response to H$_2$ gas and their sensitivity is better than undoped SnO$_2$ films. Fig. 3a shows the sensitivity of undoped and Pd-doped SnO$_2$ thin films measured at 100, 125 and 150 °C when exposed to 250 ppm H$_2$. The Pd-doped SnO$_2$ has a sensitivity about one or two orders of magnitude higher than the undoped SnO$_2$ at each temperature investigated. Fig. 3b shows the response transients of two films at 150 °C. For undoped and Pd-doped SnO$_2$, the response time was 14 and 10 min, respectively. Clearly Pd-doped SnO$_2$ reduces the response time.

The influence of Pd doping on the microstructure of SnO$_2$ thin films was investigated by SEM and TEM. Fig. 4a and b shows the SEM secondary electron images of undoped and Pd-doped films, respectively, while the corresponding TEM images are shown in Fig. 4c and d. It is clear that the undoped film has larger pores and grain size than the Pd-doped film. The histograms of the grain size distributions measured by TEM are plotted in the insets of Fig. 4c and d. The grain size distributions of both films are fitted with a log-normal distribution. The average grain size of the undoped and Pd-doped SnO$_2$ films is 15 and 9 nm, respectively. Knudsen gas diffusion and depletion layer models were employed by Sun et al. to evaluate the microstructure influence on the gas sensitivity. Their results suggest that the microstructure of the Pd-doped film is critical for improving the gas sensitivity, but cannot account for the total sensitivity enhancement. They believed that other mechanisms could also play important role and the electronic and chemical activities of Pd could be the primary factors for the sensing enhancement (Sun, 2009).

Au-TiO$_2$ nanocomposite films were used by Buso et al. (Buso, 2008) as both optical and chemoresistive sensors for the detection of CO and H$_2$. Tests performed at 360 °C show CO- and H$_2$-induced reversible variations in the optical absorption of thin Au-TiO$_2$ nanocomposite films. The absorbance changes are strongly dependent on both the testing wavelength and the film microstructure. The reactant gases CO and H$_2$ were suggested to initially adsorb into the titania matrix. Once oxidized the liberated electrons then flow to
and are trapped on the gold nanocrystals. Gas adsorption in the matrix sites near the Au nanoparticles could lead to local changes in refractive index of TiO$_2$, which, in principle, are capable of affecting the absorption spectral changes. Mehta et al. (Mehta, 2005) investigated In$_2$O$_3$-Ag nanocomposite films having well-defined individual nanoparticle size and composition for ethanol gas sensing application. For a pure In$_2$O$_3$ nanoparticle film with particle size of 11 nm, they observed the sensitivity of 325 and the response time of 8 s at 400°C for 1000 ppm ethanol, while for In$_2$O$_3$-Ag nanocomposite film, the sensitivity increases to 436 and the response time is reduced to 6 s. They believed that Ag additives form a p-type Ag$_2$O, which interact with n-type In$_2$O$_3$ to produce an electron-deficient spacecharge layer. In the presence of ethanol, interfacial Ag$_2$O was reduced to Ag, creating an accumulation layer in In$_2$O$_3$ resulting in increased sensitivity (Mehta, 2005). Gong et al. (Gong, 2005) discovered that SnO$_2$-Ag nanocomposite films have very high sensitivity to hydrogen sulfide: as low as 1 ppm concentrations of H$_2$S at low working temperature of 70°C can be detected by the composite films. The SnO$_2$-Ag films are also less sensitive to common interference gases such as Cl$_2$, HCl, SO$_2$, C$_6$H$_{14}$, CO, C$_3$H$_8$. Korotcenkov et al. deposited a SnO$_2$-Au nanocomposites film over a pure SnO$_2$ surface and studied its response to reducing gases such as CO and H$_2$ (Korotcenkov, 2009). They found that by increasing the thickness of the SnO$_2$-Au nanocomposite layer, the sensor response and the recovery times were decreased. The ZnO films with embedded noble-metal nanoparticles (Pt, Au and Ag nanoparticles) also exhibit enhanced sensitivity and fast initial recovery behavior compared to those without metal nanoparticles (Mishra, 2005).
Due to the localized surface plasmon resonance (SPR) of the metal nanoparticles, metal-metal oxide nanocomposite films can also be explored as plasmonic-based optical gas sensor using their unique optical properties. SPR responses of Au-WO$_{3-x}$ and Ag-WO$_{3-x}$ nanocomposite films with either stoichiometric ($x = 0$) and non-stoichiometric ($x > 0$) structures were simulated using effective medium theory and Macleod’s general characteristic matrices method for various metal percentages and film thicknesses in the Kretschmann configuration at the wavelength of 632.8 nm. The simulation results predicted that the Au-WO$_{3}$ and Ag-WO$_{3}$ nanocomposite thin films with 40-80% metal fractions and film thickness of 30-50 nm are applicable for optical gas sensing (Deng, 2008). We also observed that SPR response of Au-WO$_{3}$ nanocomposite films changed when exposed to low ppm of NO gas which indicated that gas sensing using the SPR responses of metal-metal oxide nanocomposite films is feasible (Yang, 2008). Thin films composed of Au nanoparticles dispersed inside a TiO$_2$-NiO mixed oxide matrix were also investigated by Gaspera et al. (Gaspera, 2010) as hydrogen sulfide optical sensors using the Au-localized SPR. The detection sensitivity is found to be down to a few ppm of H$_2$S and almost no interference in response is observed during simultaneous exposure to CO or H$_2$. The high sensitivity and selectivity of the Au-TiO$_2$-NiO nanocomposite film for H$_2$S detection is believed to be due to direct catalytic oxidation of H$_2$S over the Au-TiO$_2$-NiO nanocomposite film (Gaspera, 2010). Manera et al. (Manera, 2008) discovered that dot- and rod-shaped gold nanoparticles embedded TiO$_2$ thin films possess optical absorption sensing responses towards different kinds of alcohol vapours in the spectral range corresponding to the SPR peak of the gold nanoparticles. Total attenuation SPR measurements in controlled atmosphere by them revealed that the sensing property is due to variation of the thickness and the real part of the active sensing layer refractive index. Au-TiO$_2$ film is another metal-metal oxide nanocomposite film that was investigated for optical gas sensing of different vapour organic compounds (Fernández, 2005). All the above results clearly indicate that metal-metal oxide nanocomposite films offer a real opportunity for optical gas sensing with rapid and sensitive response to many common gases.

4.2 Mixed metal oxides

Transition metal oxides have promising gas sensing performance due to their catalytic properties. Some transition metal oxides are stable, have low electric resistance and good gas sensing properties at low operating temperature, while others have high electric resistivity and require high operating temperatures. Some of the oxides are more sensitive to oxidizing gases while others are more to reducing gases. It is therefore a natural approach to combine metal oxides of different properties with an appropriate proportion so that gas sensor performance can be modified as desired.

Fabrication

Although PVD, sol-gel and pyrolysis can be used to deposit mixed metal oxide nanocomposite films, sol–gel method is the most cost-efficient method as it represents a simple processing alternative to the vacuum deposition techniques. Various mixed metal oxide nanocomposite films have been prepared by the sol-gel process. For example, cobalt oxide-SiO$_2$ nanocomposite films were deposited on glass substrate by Musat et al. (Musat, 2008) using [Co(CH$_3$COO)$_2$].4H$_2$O, tetraethoxysilane and CH$_3$(CH$_2$)$_2$N(CH$_3$)$_3$Br surfactant as starting materials. After each layer was deposited on a substrate by dipping, the gel film was dried at 70 °C and then pre-heated in air at 400 °C. The procedure was repeated 2 or 3
times. The stabilized films were then post-heated treated in air at 500 °C for cobalt oxide crystallization. The effect of withdrawal speed, number of layers and thermal treatment on the crystalline structure, morphology, Co-doping states, optical, electrical and gas sensing properties of the thin films were investigated. When using sol-gel process for the deposition of ZnO-SiO$_2$ nanocomposite films, zinc acetate (Zn(CH$_3$COO)$_2$·2H$_2$O) was used as the ZnO nanoparticles source, tetraethoxysilane (TEOS) as a silica matrix source and cetyl trimethylammonium bromide (CTAB) as a surfactant for porosity generation. The chemical nature of ZnO source (zinc acetate solid salt, zinc acetate alcoholic solution or ZnO nanopowder) used for the sol preparation was found to significantly affect the thermal decomposition of complex precursor and the microstructure and properties of the nanocomposite thin films (Musat, 2008). Thin SiO$_2$-NiO and SiO$_2$-Co$_x$O$_y$ nanocomposite films consisting of either NiO or Co$_x$O$_y$ nanocrystals in a porous SiO$_2$ matrix were also prepared by the sol-gel method, in which one solution containing the silica (mixture of tetraethoxysilane, methyltriethoxysilane, H$_2$O, HCl and EtOH) was mixed with another solution containing the metal oxide precursor (dissolving CoCl$_2$·6H$_2$O or NiCl$_2$·6H$_2$O in EtOH). Either 3-aminopropyl triethoxysilane or N-[3-(trimethoxysilyl)propyl]-ethylenediamine molecules was added to the solution to coordinate the Co$^{2+}$ or Ni$^{2+}$ cations (Cantalini, 2005). Other mixed metal oxides nanocomposite films prepared by the sol-gel process include SiO$_2$-NiO films ((100-X)SiO$_2$-XNiO with X = 10, 20, 40) (Martucci, 2003); MoO$_3$-TiO$_2$ films (Li, 2001); Fe$_2$O$_3$-SnO$_2$ films for detecting NO$_x$ and C$_2$H$_5$OH gas (Kotsikau, 2004); NiO-SiO$_2$ films for detection of H$_2$, CO and humidity (Martucci, 2004 & Martucci, 2003); In$_2$O$_3$-SnO$_2$ film for detecting H$_2$ at ppm-level at room temperature (Satyajit, 2005); and Li and Ti co-doped NiO nanocomposites (Li$_{0.1}$Ti$_{0.882}$Ni$_{0.882}$) for detecting toluene, ethanol and chloroform (Qureshi, 2009).

PVD process has also been used to deposit mixed metal oxide nanocomposite films. Wisitroaat et al. (Wisitroaat, 2007) used oxygen ion-assisted electron beam evaporation to prepare various TiO$_2$ based mixed oxide nanocomposite films such as TiO$_2$-WO$_3$, TiO$_2$-MoO$_3$, TiO$_2$-NiO$_x$ and TiO$_2$-ZnO. They first mixed TiO$_2$ powder with WO$_3$, MoO$_3$, NiO$_x$, or ZnO powders, and then pressed the mixed powder to form pellets. Electron beam evaporation of the pellets occurs in vacuum chamber to form mixed oxide films. After annealing the films in air at 500 °C, various TiO$_2$ composite films having nanocrystalline structure with fine grain size ranging from 10-50 nm were prepared. Flame spray pyrolysis was also used to prepare WO$_3$-doped ZnO nanoparticles (Siriwong, 2009).

Unique properties

Mixing metal oxides of complementary behaviours forms a new class of nanocomposite materials. This type of nanocomposite films show a significant improvement in gas sensing properties. For example, by embedding transition metal oxide nanoparticles such as NiO and Co$_x$O$_y$ in a porous silica glass matrix, the nanoporosity of such composite matrix provides a path for the gas molecules to reach the functional ultrafine NiO and Co$_x$O$_y$ particles. The sensor response of the NiO-SiO$_2$ and Co$_x$O$_y$-SiO$_2$ nanocomposite films to H$_2$ (20-850 ppm) and CO (10-500 ppm) in dry air and at different operating temperatures (50-300°C) has been investigated by Cantalini et al using both conductometric and optical transmittance transduction methods (Cantalini, 2005). Both the NiO and Co$_x$O$_y$ doped films exhibit a conductometric p-type response, with a resistance increase upon exposure to the reducing gas. The nanocomposite films also showed a reversible change in the optical transmittance in the vis-NIR range when exposed to CO (10-10,000 ppm) in dry air. SiO$_2$-
NiO films have shown the highest response to H₂ at 300°C operating temperature and good selectivity to H₂ when CO is the interfering gas. Selectivity tests shown in Fig. 5 comprise a first exposure (first section) to 200 ppm H₂ target gas in dry air, followed by a second exposure (second section) where the films are subjected to 200 ppm H₂ and to 200 ppm CO interfering gas. In the third section, films are exposed to the interfering gas alone (200 ppm CO). For the SiO₂-Co₃O₄ nanocomposite film, CO slightly increases the film resistance in addition to resistance increase due to H₂ saturation as depicted in the second section of Fig. 5. This effect is totally absent for the SiO₂-NiO film. The lack of CO interfering effects may be explained in terms of a stronger affinity of the H₂ molecules to adsorb on the metal oxide surface (Cantalini, 2005).

![Fig. 5. Cross sensitivity test at 300 °C operating temperature of the SiO₂-NiO and the SiO₂-Co₃O₄ films to: (first section) 200 ppm H₂ in dry air; (second section) 200 ppm H₂ in dry air and 200 ppm CO; (third section) 200 ppm CO in dry air (Cantalini, 2005).](image)

Martucci et al. (Martucci, 2004 & Martucci, 2003) has also studied the gas response of SiO₂-NiO and SiO₂-SnO₂ nanocomposite films for H₂, CO and humidity at different operating temperatures ranging from 25 to 350°C and gas concentrations between 10 and 1000 ppm. SiO₂-NiO and SiO₂-SnO₂ nanocomposite films showed a p-type and n-type response, respectively, with greater sensitivity to H₂ gas than CO in the whole range of operating temperatures. The NiO- SiO₂ nanocomposite films also showed a reversible change in the optical transmittance in the VIS-NIR range when exposed to carbon monoxide gas.

Various TiO₂ based mixed oxide nanocomposite films, including TiO₂-WO₃, TiO₂-MoO₃, TiO₂-NiOₓ and TiO₂-ZnO, have been characterized for gas-sensing applications by Wisitsoraat et al. (Wisitsoraat, 2007). NiOₓ addition to TiO₂ with sufficiently high concentration has produced a p-type semiconducting thin film while WO₃, MoO₃, and ZnO inclusions result in typical n-type metal oxide semiconductors. The gas-sensing sensitivity, selectivity, and minimum detectable concentration toward different gases including acetone, CO, and NO₂ can be effectively controlled by different dopants and doping concentrations. The p-type NiOₓ doped TiO₂ showed high sensitivity towards ethanol and acetone with
distinct behaviours compared to other n-type TiO\textsubscript{2} thin films. Siriwong et al. (Siriwong, 2009) investigated WO\textsubscript{3}-doped ZnO composite containing 0.25, 0.50, and 0.75 mol\% of WO\textsubscript{3} for NO\textsubscript{2}, CO and H\textsubscript{2} gas sensing at different gas concentrations and operating temperatures ranging from 300-400°C in dry air. Their results showed that WO\textsubscript{3} doping significantly enhanced NO\textsubscript{2} gas sensing performance of ZnO nanoparticles. In addition, 0.5 mol\% is found to be an optimal WO\textsubscript{3} concentration which gives the highest sensitivity towards NO\textsubscript{2}. Other mixed oxides showing improved gas sensing properties include Cr\textsubscript{2}O\textsubscript{3}-WO\textsubscript{3} films for NO\textsubscript{2} in NO\textsubscript{X} mixtures (Cantalini, 2004), Fe\textsubscript{2}O\textsubscript{3}-ZnO films for NH\textsubscript{3} (Tang, 2006) and CuO-Cu\textsubscript{x}Fe\textsubscript{3-x}O\textsubscript{4} (with 0 < x < 1) for CO\textsubscript{2} (Chapelle, 2010).

### 4.3 Polymer-metal or metal oxide

Gas sensors using metal oxide films always lack in selectivity and require high operating temperatures (300-500°C). High operating temperatures may lead to sensor instability and response variation. Sensing materials with low operating temperatures can inhibit structural changes, reduces the power consumption and enables safer detection of combustible gases. Conducting polymers such as polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh) and their derivatives typically can operate at low temperature in comparison to most of the metal oxide sensors. Conducting polymers can behave like semiconductors due to their heterocyclic compounds. As a result, reversible changes in the sensing polymer layer’s conductivity can be detected upon adsorption of polar gas molecules on the surfaces at low temperature. This effect is believed to be caused by the charge transfer between gas molecules and the polymer or the polymer film’s swelling. Conducting polymers are also easy to be synthesized through chemical or electrochemical processes, and their molecular chain structure can be modified conveniently by copolymerization or structural derivations. In addition, conducting polymers have good mechanical properties, which allow a facile fabrication of sensors. Conducting polymer matrices embedded with nano-scale metal or metal oxide particles forms a new class of nanocomposite materials that has shown better gas sensing features. The reasons for such an improvement can be attributed either to catalytic behaviours of metal particles or to the formation of metal oxide-polymer junction. For example, the n-type SnO\textsubscript{2} forms a hetero pn-junction to p-type conducting polymer with a depletion region. The gas adsorption causes a change in depletion region and thus modulates the conductivity of the junction. Other non-conductive polymers such as fluorocarbon films swell when exposed to the vapours of organic solvents having a net dipole moment or electron-rich moieties therefore can also be used as active materials for the gas sensing. Addition of metal or carbon to those polymers was found to improve their swell sensitivity.

**Fabrication**

Metal-polymer nanocomposites can easily be prepared by PVD processes such as sputter deposition and vacuum thermal evaporation, as well as wet chemical deposition. For example, Tiwari et al. (Tiwari, 2009, & 2010) used vacuum thermal evaporation of poly(o-phenylenediamine) (PoPD)/WO\textsubscript{3}.nH\textsubscript{2}O mixed powder pellet to fabricate nanocomposite films of PoPD-WO\textsubscript{3}.nH\textsubscript{2}O on an indium tin oxide (ITO) coated glass surface for NO\textsubscript{2} gas sensor applications. Using the same method; they also prepared aniline-formaldehyde condensate (AFC)-WO\textsubscript{3}.nH\textsubscript{2}O nanocomposite films. The mixed powder pellets were formed via hydraulically pressing of nanocomposite powders which was prepared by in situ condensation reaction of PoPD or AFC in the presence of sodium tungstate. The composite
thin films exhibited a crystalline surface morphology containing nanocrystals of $\text{WO}_3\cdot n\text{H}_2\text{O}$ with a diameter ranging from 5 to 20 nm. Cioffi et al. prepared gold-fluorocarbon (Au-CF$_x$) and palladium-fluoropolymer (Pd-CF$_x$) nanocomposites films on silicon substrates by co-sputtering a Teflon and a gold targets or a Teflon and a palladium targets, respectively, with $\text{Ar}^+$ ion beams (Cioffi, 2002 & 2004).

Wet-chemical deposition route can also be used to prepare polymer-metal oxide nanocomposite films, for example, tin oxide-intercalated polyaniline nanocomposite have been deposited at room temperature by Deshpande et al. (Deshpande, 2009) through the following procedure: $\text{SnCl}_2\cdot 5\text{H}_2\text{O}$ was first hydrolyzed at $\text{pH} \leq 4$ using dilute HCl. Hydrogen peroxide was added to the solution to oxidize tin ions to form tin oxide suspension. The suspension solution was mixed with aniline and (NH$_4$)$_2\text{S}_2\text{O}_8$. Pre-cleaned glass substrates were inserted vertically into the solution for the growth of the nanocomposite film on the substrate. Tin oxide exists as nanoparticles form in the polyaniline (PANI) matrix in the composite films. Intercalation reactions is another wet-chemical process used to prepare polymer-metal oxide nanocomposite, for example, polypyrrole (PPy)-MoO$_3$ nanocomposite thin films have been prepared by the intercalation reactions of highly oriented MoO$_3$ thin films with the following procedure: hydrated sodium ions were inserted into the CVD grown MoO$_3$ thin films on LaAlO$_3$ (100) single crystal substrates to give $\text{[Na(H}_2\text{O)}_2\text{]_yMoO}_3$ films. The obtained $\text{[Na(H}_2\text{O)}_2\text{]_yMoO}_3$ thin films then reacted with an excess amount of pyrrole and oxidizing agent (FeCl$_3$) to form the (PPy)$_x\text{MoO}_3$ thin films. Intercalation of hydrated sodium ions successfully proceeded without loosing the crystallographic orientation. The (PPy)$_x\text{MoO}_3$ thin films can detect formaldehyde gas by increasing their electrical resistance, whereas they showed no response to toluene (Hosono, 2004). Tai et al. (Tai, 2007 & 2008) reported using simultaneous polymerization of aniline monomer and oxidation of PANI molecules in an active solution contained colloidal TiO$_2$, aniline monomer, HCl and oxidizing agent ammonium persulfate ((NH$_4$)$_2\text{S}_2\text{O}_8$) to fabricate the polyaniline-titanium dioxide (PANI-TiO$_2$) nanocomposite films for NH$_3$ gas-sensing application.

Unique properties

Polymer-metal or metal oxide nanocomposite is a new class of material that combines the advantages of both organic polymer material and inorganic metal or semiconductor oxide and shows improved optical, electrical and mechanical properties for gas sensor applications. Cioffi et al. (Cioffi, 2004) investigated -CF$_x$ polymer films embedded with Pd or Au nanoparticles (Pd-CFx and Au-CFx nanocomposites films) for detecting vapours of organic solvents. They found that Pd-CFx and Au-CFx nanocomposites films swell more significantly than pure -CF$_x$ film when exposed to the vapours of organic solvents having a net dipole moment or electron-rich moieties such as acetone, chloroform, 2-propanol. Ellipsometric evaluation of the thickness changes of -CF$_x$ and metal-CF$_x$ films when they exposed to an increasing concentration of acetone vapours was shown in Fig. 6(a). All the films show almost linear dependence of the thickness change upon the analyte concentration but -CF$_x$ swelling sensitivity is much less pronounced than that of the metal-CF$_x$ composites. Acetone-induced swelling of both Au-CF$_x$ and Pd-CF$_x$ materials increases as the metal loading increases and the swelling response of Pd-CF$_x$ films is higher than that of Au-CF$_x$ of the same metal loading. TEM surface morphology of the Pd-CFx film with a metal loading of 0.15 and 10 nm thick is shown in Fig. 6(b). TEM graphs revealed a regular, non-porous Pd-CFx film structure with homogeneous distribution of palladium.
nanoparticles. The mean diameter of the palladium nanoparticles is $2.9 \pm 0.6 \text{ nm}$. The morphological similarities exist between Pd-CF$_x$ and Au-CF$_x$ films of same metal volume fraction. Differences in the materials sensing performances are ascribed to different chemical reactivity and selectivity of Pd and Au. Swelling behaviour of poly(2-hydroxyethyl methacrylate) (PHEMA)-carbon black nanocomposites was also investigated by Mauro et al (Mauro, 2009) for volatile organic compounds (VOCs) detection using white light interferometry. They demonstrated that swelling in the range of only a few nanometers can be measured and the PHEMA-C nanocomposite undergoes a more pronounced swelling process than PHEMA itself.

Polyaniline (PANI) is a conducting polymer with high electrical conductivity. Due to its ease of synthesis, environmental stability, and response to acid/base doping, it was thoroughly studied for its application as an active material for gas sensors. Mixing semiconductive metal oxide with PANI to form nanocomposites was found to be an effective way to improve the gas sensing properties of PANI. Tai et al. (Tai, 2007) studied a polyaniline-titanium dioxide (PANI-TiO$_2$) nanocomposite films for the NH$_3$ gas sensor. They found that the nanocomposite exhibited higher sensitivity, faster response and recovery rates to NH$_3$ than those of pure PANI thin film sensors fabricated under identical conditions. They found that the TiO$_2$ components influenced the morphology of the nanocomposite film, which led to the variation of the sensor response-recovery behaviours. Deshpande et al (Deshpande, 2009) discovered that good sensitivity; reproducibility and faster response to NH$_3$ at room temperature can be achieved by using SnO$_2$-PANI nanocomposites films while under the same conditions pure SnO$_2$ films remain inert. They found that resistance of the nanocomposite (SnO$_2$-PANI) films decreases while pure PANI film resistance increases when exposed to NH$_3$ indicating SnO$_2$ doping totally changed the electrical property of PANI. PANi-In$_2$O$_3$ was another PANI-oxide nanocomposite films that was thoroughly investigated. The nanocomposite film based gas sensor was fabricated on AT-Cut quartz crystal microbalance (QCM) and its sensitive properties to CH$_4$ and CO were characterized.

Fig. 6. (a) Acetone-induced thickness variations ($\Delta t$) of Pd-CF$_x$, Au-CF$_x$ and CF$_x$ layers (metal volume fractions are in brackets) upon exposure to increasing partial pressures of the organic solvent measured by ellipsometry; (b) TEM micrographs of Pd-CF$_x$ films with metal loading of 0.15 (Cioffi, 2004).
They found that PANi-In$_2$O$_3$ thin film has good linear sensitive property to CH$_4$ and CO, and it is more sensitive to CH$_4$ than CO (Yan, 2009). Misra et al. (Misra, 2004) studied the Fe-Al doped nanocomposite copolymer of aniline and formaldehyde and found that the nanocomposite exhibits high stability, sensitivity, selectivity and a fast response towards the HCl vapours in the air at room temperature. Optimization of doping (Fe-Al) level in nanocomposite copolymer during synthesis can improve the sensing properties. Other polymer nanocomposite films that were investigated for gas sensor applications include TiO$_2$-porphyrin film coated on a quartz crystal to detect volatile organic compounds such as ethanol, acetone, 2-propanol, cyclohexane, toluene and o-xylene (Arshad, 2008); poly(vinyl butyral)-carbon black films prepared for methanol, propanol and hexanol vapour (Arshak, 2006); sodium polystyrenesulfonate (NaPSS)-ZnO for humidity sensors (Yang, 2002); polypyrrole (PPy)-SnO$_2$, PEDT-SnO$_2$, PHTh-SnO$_2$ and copolymer (HTh-EDT)-SnO$_2$ films for NO$_2$ gas sensing applications (Ram, 2005); poly(3-hexylthiophene)-ZnO films for NO$_2$, NH$_3$, CO and ethanol detection (Baratto, 2006); PoPD-WO$_3$.nH$_2$O (Tiwari, 2009) and AFC-WO$_3$.nH$_2$O (Tiwari, 2010) films for NO$_2$ gas sensing.

4.4 Carbon nanotube based nanocomposite films

Carbon nanotubes (CNTs) are very useful materials for gas-sensing applications because of their high surface to volume ratio. The large surface area provided by the hollow cores and outside walls in nanotubes gives them very large capacity for gas absorption. Interaction of CNTs with certain gases can change the electrical properties of semiconducting CNTs even at room temperature. However, CNTs based sensor has a number of limitations including long recovery time, and weakness to humidity. In addition, the range of gas molecules that can be detected by CNTs sensors is limited to the molecules that have large binding energies and charge transfers with the CNTs. To improve the gas sensing properties of CNTs, catalytic metal nanoparticles, semiconductive metal oxides or conductive polymers were mixed with CNTs to form nanocomposites. The composite combines the advantages of CNTs and other gas-sensing materials and provide a new class of active materials with unique gas sensing property.

Fabrication

CNTs nanocomposite films can be prepared by combining CVD and PVD processes. For example, Pt-, Ru- and Ag-nanoclusters embedded CNTs nanocomposites were prepared by RF magnetron sputtering and RF-discharge plasma enhanced chemical vapour deposition (PECVD) processes in the following steps: First, iron catalyst film of 2.5 nm thick was deposited by RF magnetron sputtering on alumina substrates using Ar flux of 43 sccm, process pressure of 1.2 $\times$ 10$^{-2}$ Torr and RF power of 150 W. The PECVD iron film was used for the subsequent CNTs growth at a substrate temperature of 600°C with 20/80 sccm C$_2$H$_2$/H$_2$ flow and total pressure of 1.5 Torr. The carbon nanotubes obtained were “forest-like” with ropes vertically-aligned to the substrate surface. CNTs surface has been subsequently modified by depositing 5 nm thick Pt-, Ru- and Ag nanoclusters. The Field emission SEM images of the metal-coated CNTs are shown in Fig. 7(a), (b), and (c), respectively. The metal-catalysts deposited onto the surface of the forest-like CNTs network existed as dispersed islands with non-uniform distribution. To drive metal nanoparticles diffuse into the inside of the CNT-forest, thermal treatment was used. The diameters of metal cluster are ranging from 3 nm for platinum and ruthenium (Fig. 7(a) (c)), to 50 nm for Ag (Fig.7 (b)), which depend on the reactivity between metal and graphite surface (Penza,
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Fig. 7. FE–SEM images of the CNT films surface-functionalized with (a) platinum (Pt), (b) silver (Ag) and (c) ruthenium (Ru) nanoclusters (Penza, 2009). Wisitsoraat et al. (Wisitsoraat, 2006) used electron beam evaporation of cylindrical pellets consisting of pressed multi-wall CNTs (MWCNTs) mixed with SnO$_2$ powder to form CNTs–SnO$_2$ nanocomposite films. The CNTs were synthesized by chemical vapor deposition using acetylene and argon gases with iron catalyst at 600 °C. The substrates for thin film coating were standard BK7 glass slides. Sol-gel process can also be used to prepare CNTs nanocomposites. For example, antimony-CNTs-tin oxide nanocomposite films were prepared with the following procedure: tin(IV) chloride pentahydrate (SnCl$_4$·5H$_2$O) was dissolved in ethanol as the precursor solution for the sol. After being mixed with antimony (III) chloride (SbCl$_3$), a certain amount of CNTs with weight percentage of 1-10 wt % to SnO$_2$ was dispersed into the former solution by ultrasonic dispersing. The CNTs with diameter from 6 to 8 nm were obtained via catalytic CVD process. The final sol was dip-coated onto a substrate. The as-fabricated sensor samples were dried for the formation of crack-free thin films. Subsequently, the samples were calcined in air at 500°C, the dip-coating and drying operation steps were carried out repeatedly to increase the film thickness (Liu, 2008). Duy el al. (Duy, 2008) also used the sol-gel process to prepare CNTs-SnO$_2$–TiO$_2$ nanocomposite films. The precursors used to fabricate the SnO$_2$–TiO$_2$ sol were tetrapropylorthotitanate Ti(OC$_3$H$_7$)$_4$, tinethylhexanoate Sn(OOC$_7$H$_15$)$_2$ and isopropanol C$_3$H$_7$OH. To synthesize the CNTs-SnO$_2$–TiO$_2$ composite material, the single-walled CNTs (SWCNTs) with a diameter less than 2 nm and MWCNTs with diameters ranging from 20 to 40 nm were introduced and dispersed into the SnO$_2$–TiO$_2$ sol solution by an ultrasonic shaker. The film was deposited by spin coating on silica substrate with Pt-interdigitated electrode and was dried at 60 °C and annealed at 500°C. The inclusion of CNTs did not affect the particle size as well as the morphology of the oxides. The sensing properties of those CNTs-oxides sensors towards different ethanol concentrations and operating temperatures were investigated (Duy, 2008). Other sol-gel fabricated CNTs nanocomposite films include SWNTs-SnO$_2$ film for hydrogen detection (Gong, 2004); and MWNTs-SiO$_2$ for methane, hydrogen and acetylene sensing (Xin, 2005).

**Unique properties**

CNTs mixed with catalytic metal nanoparticles have been found to significantly improve gas sensing properties of CNTs. The Pt-, Ru- and Ag-CNT nanocomposites prepared by RF magnetron sputtering and PECVD as described previously in Fig. 7 was investigated for NO$_2$ gas by Penza et al. and the results are shown in Fig. 8. Fig. 8(a) and (b) shows the response curves of those nanocomposite films at a sensing temperature of 25°C and 150°C, respectively.
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Fig. 8. (a) Response of CNTs-metal nanocomposite chemiresistors towards NO\textsubscript{2} gas. The thickness of metal-catalyst and CNT layer is 5 nm and 10 μm, respectively. (b) Time response towards NO\textsubscript{2} gas of the CNT-metal nanocomposite chemiresistors at sensor temperature of 150 °C. (c) Calibration curves, at 150 °C (Penza, 2009). With comparison to unmodified CNTs, the enhanced response of Pt-, Ru- and Ag nanocluster coated vertically-aligned CNTs layer towards the NO\textsubscript{2} gas was clearly observed at both temperatures as shown in Fig.8 (a) and (b). The minimum gas detection of 0.1 ppm NO\textsubscript{2} was achieved at 150°C for metal coated CNTs. The calibration curves at 150 °C for unmodified and coated CNTs films are shown in Fig. 8(c). The maximum NO\textsubscript{2} gas response was achieved by Ag-coated CNTs. The metal coated CNTs films also significantly enhanced gas detection of H\textsubscript{2}, ethanol and toluene up to sub-ppm level that makes metal-CNTs nanocomposites highly promising candidates for environmental air monitoring applications (Penza, 2009). Brahim et al. has also investigated metal-carbon nanotubes (CNTs) nanocomposite materials as the active sensing layer for ethanol vapour detection at room temperature. They found that pure CNTs material was virtually non-responsive at low ethanol concentrations (< 50 ppm), while the metal-CNT composite films (Ti-, Mn-, Fe-, Co-, Pd- or Pt-CNTs) showed extremely high sensitivity to trace ethanol levels with 100-fold or more gains in sensitivity relative to the pure SWNTs (Brahim, 2009). By mixing semiconductive metal oxides such as SnO\textsubscript{2} with CNTs, the gas sensing properties of the oxides can also be improved. For example, Sb-CNTs-SnO\textsubscript{2} thin film shows higher sensitivity and shorter response time than pure SnO\textsubscript{2} and Sb-SnO\textsubscript{2} thin films for sensing polar gases, such as formaldehyde, ammonia, and toluene as shown in Fig. 9. The figure shows the response of pure oxides and CNTs-oxide nanocomposite films when they were exposed to target gases or dry air alternately. The voltage increased when the target gas was injected and decreased as dry air was introduced. The sensitivity of the Sb-CNTs-SnO\textsubscript{2} thin film is higher among the three films. The response time of the Sb-CNTs-SnO\textsubscript{2} thin film is also significantly shorter. CNTs addition was believed to affect the grain growth and surface area of SnO\textsubscript{2} as well as create CNTs-Oxide interfacial region which improves the gas sensing properties (Liu, 2008). CNTs doped SnO\textsubscript{2} film was also investigated by Wisitsoraat et al. (Wisitsoraat, 2006) for ethanol sensing and they found that SnO\textsubscript{2}-CNTs nanocomposite can operate with good sensitivity and stability at a relatively low temperature of 250-300 °C.
Fig. 9. Gas sensing response of SnO$_2$, Sb-SnO$_2$, and Sb-CNTs-SnO$_2$ thin films to (a) formaldehyde, (b) ammonia, (c) benzene, and (d) toluene (Liu, 2008).

The improved gas-sensing properties were attributed to the increasing in surface area of metal oxide induced by CNTs protrusion. The sensitivity to ethanol of CNTs incorporated SnO$_2$ thin film was found to increase by the factors of 3 to 7 with CNTs inclusion up to 2%. In addition, the response time and recovery time were found to reduce by the factors of 2 or more. However, they also found that if the CNTs concentration is too high, the sensitivity is decreased. Bhuiyan et al. (Bhuiyan, 2008) also observed higher sensitivity and lower operating temperature for SnO$_2$-SWCNTs nanocomposite films than the pure CNTs or SnO$_2$ films for the detection of NO and NO$_2$ gas in the carrier gas nitrogen (N$_2$) or air. CNTs-SnO$_2$ films were also investigated by Wisitsoraat et al. (Wisitsoraat, 2007) for sensing ethanol, CO and NO$_2$, and by Gong et al. for sensing H$_2$. Wisitsoraat found that 1% CNT-SnO$_2$ exhibit maximized response to NO$_2$ with sensitivity of ~10 at NO$_2$ concentration as low as 250 ppb at 200°C, while Gong found that nanocomposite films have greater sensitivity (a factor of 3), faster response time and recovery time, and less drift in resistance measurement for H$_2$ sensing. Small amount of CNTs incorporation into SnO$_2$ proved to be an effective means to enhance gas-sensing sensitivity of semiconductive metal oxide sensors. The improved sensitivity is credited to the large surface to volume ratio of gas sensing film with nano
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passes created by CNTs. Other metal oxides that were used to composite with CNTs include \( \text{SiO}_2 \) and \( \text{ZnO} \). Xin et al. (Xin, 2005) found that MWNTs-\( \text{SiO}_2 \) composite film was sensitive to methane, hydrogen and acetylene while the pure MWNTs was not. They believed that MWNTs and silicon dioxide formed the Schottky junctions. Adsorption of the gas molecules on the surface of the MWNTs affects the space discharge area of the Schottky junction, so that the dielectric constant of nanocomposite films changes with the gas adsorption. ZnO-SWNTs fabricated by oxidizing metallic zinc deposited on a SWNTs template also showed higher sensitivity and lower operating temperature than the zinc oxide film for hydrogen gas sensing (Jung, 2008).

Polymers can also be used to modify CNTs to improve its sensing properties. For example, PMMA-MWCNTs nanocomposite shows fast response and change in resistance upon exposure to different organic vapours. The room temperature gas sensing property of MWCNTs-PMMA nanocomposite makes it very attractive for miniature wireless gas sensor applications. The sensing mechanism of MWCNTs-PMMA films to organic solvents was attributed to the swelling of the polymer matrix due to the absorption of organic vapours which increases the volume and the distance between the nanotubes. The contact resistance between adjacent CNTs thus increases as their distance increase. The extent of swelling and hence the electrical response depends on the solubility of the polymer in the solvent. In addition, CNT surface that contains polar functional groups can also adsorb organic solvent molecules (Abraham, 2004). Hieu et al. investigated the effects of film thickness, annealing temperature, and SWCNTs content on gas-sensing response of PPY-SWCNTs nanocomposite for detection of \( \text{NH}_3 \) gas at room temperature. They found that the nanocomposite sensor had a response of 26-276% upon exposure to \( \text{NH}_3 \) gas concentration from 10 to 800 ppm, and their response and recovery times were around 22 and 38 s, respectively (Hieu, 2009). All the above results clearly indicate that by properly mixing metal or metal oxide with CNTs to form nanocomposites, higher sensitivity and lower operating temperature than that of pure metal oxide or CNTs films for gas sensing can be achieved.

5. Conclusion and future directions

Nanocomposite thin film-based gas sensors have been developed and demonstrate huge potential for a variety of applications such as drug, food and environmental monitoring. Different types of nanocomposite thin films can be fabricated by various deposition processes such as PVD, CVD, sol-gel, and other wet-chemical synthesis. It has been proved that the electrical resistance, sensitivity, selectivity, response time and operating temperature of gas sensors can be significantly improved by using nanocomposite films as the active sensing materials. This can be attributed to the complementary behaviours of the consisting materials, the unique interface characteristics and large surface areas, as well as nano-scale dimensional effects. Chemoresistors that measure the resistance change of nanocomposite films as the transducer is the most commonly used sensor structures. Compared to chemoresistors sensors, optical sensors present a number of advantages such as enabling multi-parametric detection, no need for electrical contacts, do not suffer from electromagnetic noise, allow optoelectronic integration and have the potential of multi-gas detection. Optical sensors using SPR response of nanocomposite films that consist of
metallic nanoparticles embedded in metal oxide or polymer matrix are of great interest and should be further explored. Acoustic wave sensors are most suitable for polymer based nanocomposites as they can precisely measure the thickness variation when polymers swell after their exposure to the vapours of organic solvents.

Although nanocomposite films have demonstrated their great potential for gas sensor applications, several challenges still remain. Synthesis of nanocomposite films with precisely controlling their chemical composition ratio, micro/nanostructures, phases, surface area and interfacial characteristics is still a challenging task. Depending on the preparation technique and process parameters, the property and behaviours of the nanocomposite sensors can vary significantly; therefore, the ability to reproduce nanocomposite films with consistent properties is very important for their wide use as active sensing materials. Degradation of the nanocomposite films stemming from aggregation of the nanosized components due to relatively strong inter-particle forces between them, micro/nanostructure changes due to high operating temperatures and surface contaminations due to impurity etc. has to be resolved before their large-scale adoption by the industry. With the increased interests and intensive research and development in the field, it is expected that, nanocomposite thin film gas sensors will have a promising future and will make a major impact on the gas sensor industry.

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Nanocomposite Films for Gas Sensing


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Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications was conceived as a comprehensive reference volume on various aspects of functional nanocomposites for engineering technologies. The term functional nanocomposites signifies a wide area of polymer/material science and engineering, involving the design, synthesis and study of nanocomposites of increasing structural sophistication and complexity useful for a wide range of chemical, physicochemical and biological/biomedical processes. “Emerging technologies” are also broadly understood to include new technological developments, beginning at the forefront of conventional industrial practices and extending into anticipated and speculative industries of the future. The scope of the present book on nanocomposites and applications extends far beyond emerging technologies. This book presents 40 chapters organized in four parts systematically providing a wealth of new ideas in design, synthesis and study of sophisticated nanocomposite structures.

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