TRACES DETECTION OF AMMONIA AND SOME AMINES IN THE AIR OF NEARBY THE DRAINAGE WATER OF SWARNREKHA RIVER IN GWALIOR REGION WITH THE HELP OF SEMICONDUCTING METAL OXIDE GAS SENSING TECHNOLOGY.

D. Thakur*,M. Jha,B. Sharma*****
*Asso.prof & HOD Engg.Chemistry/EEES/coordinator PG/ coordinator Renewable Energy Club at SRIIT,Banmore near Gwalior(M.P.).
** Asst. professor Biochemistry & Microbiology at IILM,Noida..
***Lecturer Engg.Chemistry at SRIIT,Banmore near Gwalior(M.P.)
E-Mail : youvisitdilip@gmail.com

Abstract

Semiconducting metal oxide sensors are one of the most widely studied technique of gas sensing. These sensors are designed to react with a class of gases by reduction and oxidation. This process causes the semiconductor oxide sensors to exchange electrons with the target molecule of gas at a certain characteristic rate, and in this way affects the sensor's resistance and generate a certain signal. The reaction of semiconductor oxide materials with gases and the result of the conductometric changes were introduced in 1950's by Brattein *et al.* and Heiland. After that Bielanski *et al* . and Seiyama *et al.* introduced applications of the semiconductor oxide sensors as catalysts and electric conductive detectors toward various gases . During few years past semiconductor oxide gas sensors is becoming a prime technology in the detection of pollutants with very low concentration in river, pond, reservoir, lake and municipal supply water.

There may be three types of sensors available which are based on electrochemical nature, catalytic combustion and resistance modulation of semiconductor oxides with metals.

Semiconductor oxide gas sensing devices have several unique advantages such as low cost, small size, measurement simplicity, durability, easy fabrication, and low concentration detection. To enhance the accuracy of these sensors we use some materials. These Semiconductor oxides mixed with different dopants, catalysts, adhesives, binders, volatile fillers, and electrodes. To mix we uses different deposition techniques like pyrolysis, oxidation of metallic films, reactive sputtering, chemical vapor deposition (CVD), laser ablation, and electron-beam evaporation techniques. Here we are using this gas sensing technology for detecting the pollutants (NH_3 & Amine) in the

atmosphere of Gwalior's industrial area and atmosphere of nearby area of swarnrekha river drainage.

Keywords: Semiconductor metal oxide, gas sensing through SMO, NH3 sensing.

Introduction

The wastage water of Gwalior region contains NH3 and other Amines in low or high concentration. Here we are detecting it with the help of semiconductor oxide base Gas sensing technology.

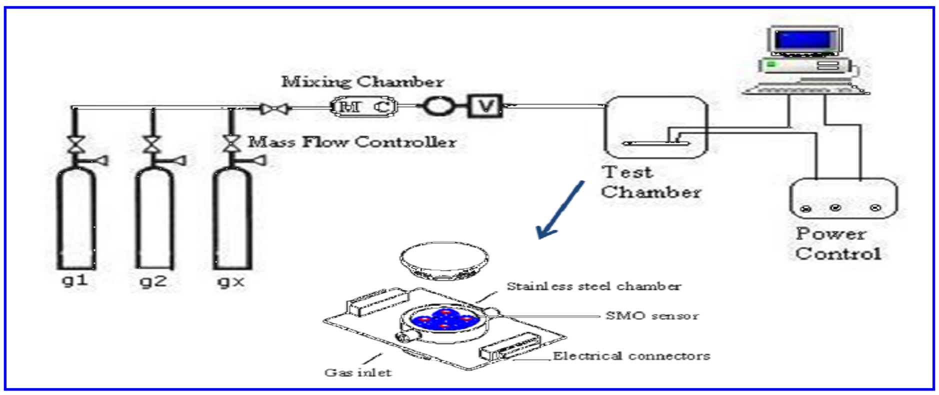
Though semiconductor technique is simple but the detection mechanism is complex and not yet fully understood. This complexity is due to the various parameters that affect the function of the solid state gas sensors. These include the adsorption ability, electro- physical and chemical properties, catalytic activity, thermodynamic stability, as well as the adsorption/desorption properties of the surface. However, it is believed that gas sensing by semiconductor devices involve the functioning itself as receptor and transducer.

The receptor involves the recognition of a target gas through a gas-solid interface which induces an electronic change of the oxide surface, while the latter is based on the transduction of the surface phenomenon into an electrical resistance change of the sensor. When a sensor is heated to a high temperature in the absence of oxygen, free electrons easily flow through the grain boundaries of the semiconductor oxide film. In an oxygen atmosphere, oxygen is adsorbed onto the semiconductor oxide surface, forming a potential barrier at the grain boundaries. The interaction of atmospheric oxygen with the semiconductor oxide surface forms charged oxygen

Species, which trap electrons from the bulk of the material. The layer of charged oxygen at the surface repels other electrons from interacting with the bulk of the film, creating a region depleted of electrons which results in an increased potential barrier at the grain boundaries. This impedes the flow of electrons and thus increases the resistance. When the sensor is exposed to an atmosphere containing a reducing gas, the SEMICONDUCTOR OXIDE surface adsorbs the gas molecules and lowers the potential barrier, allowing the electrons to flow easily and thus reducing the electrical resistance. In this manner, the sensors act as variable resistors whose value is a function of gas concentration. Metal oxides exhibit various electro-physical features, ranging from insulators to wide band-gap semiconductors. The non-transition metal oxides contain elements with one oxidation state because they require a large amount of energy to make other oxidation states that would bind to the oxygen ion ligand. In contrast, because of the various oxidation states that might form on transition metal oxides compared to non-transition metal oxides, the surface properties and the types of chemisorptions that occur on the surface are important and have been widely studied. This variation in the oxidation states causes significant changes in the surface chemistry response toward Sensors oxygen and other target gaseous molecules. Despite the fact that transition metals of dn oxides with $n > 0$ exhibit high potentials to perform oxidation and reduction processes, it has been noted that only transition metals with d0 configuration displayed real gas sensor application. For example, TiO_2, V_2O_5, WO_3 have d0 configurations and are the most widely used transition elements in sensor technology, along with non-transition elements with a d10 configuration like ZnO and SnO_2 based materials. The above choice of metal oxides were found to have a filled valence band of predominantly oxygen 2p character with band gap ranges between 3–4 eV. Since the mode of adsorption and/or reaction occur on a sensor's surface, several researchers have reported that the conductivity response is highly affected by the presence of an efficient catalyst that enhances the surface reactivity toward the target gaseous molecules. In specifics, catalytic reactions involving surface oxygen can change both the surface potential along with its defect level and thus control the electro-physical properties of the nanocrystalline modified metal oxide. Therefore, tuning the surface characteristics with specific catalysts has resulted in major advances in sensor technology where both reactivity and selectivity in a material's responses were improved .Both "spill over" and Fermi energy control mechanisms were applied to explain how catalysts affect the sensing strategy. In the "spill over" mechanism, the catalysts will dissociate the molecule and then

the atoms will spill over the surface while in the Fermi energy mechanism the adsorbed oxygen will remove electrons from the catalyst and then the catalyst will effectively dislodge from the surface catalyst film.

Basic principle will be same in all types and basic setup will be according the following figure.



Sensor array consists of a target gas, a multi-component gas mixer, a mass flow controller unit, a testing chamber, a power supplier and heaters, and an electrometer for resistance measurement. Lab VIEW based software is mainly used to control all testing parameters and measurements during the experiment. The testing chamber consists of semiconductor oxide sensor platforms with the ability to control and measure each sensor's temperature and resistance. The semiconductor oxide films are deposited on the sensing element as thin or thick film substrates. Thin film deposits are made via ultra high vacuum (UHV) or electron beam evaporation techniques, while thick films are deposited using spin coating methods or via direct deposition of the corresponding semiconductor oxide suspension. The sensor platform is bonded into a standard header and then placed in a test chamber and annealed at 400°C using a temperature controller prior to gas exposure where the testing experiments of the semiconductor oxide to the target gaseous molecules begins.

Detection of Ammonia and Amines :

To detect Ammonia and other amines in trace levels in Gwalior region is important since it is used extensively in many areas like food processing, fertilizers, chemical technology, medical diagnosis, and environmental protection, freezing etc.. Some of the well known materials for ammonia sensors are WO_3 , copper based materials, ZnO , SnO_2 , iron oxide , Cr_2O_3. WO_3 thin films were prepared via a sol-gel technique using WCl_6 as a precursor and then tested for its sensing properties toward Trimethylamine (TMA) gas at a low operating temperature of 70 °C. WO_3 films were deposited between interdigital gold electrodes on the outer wall of a ceramic tube. The gas sensitivities to TMA, C_2H_5OH gas, gasoline, CH_4, CO, and water vapor were measured. The sensitivity of the sensor was carried out in a range of temperatures and different TMA concentrations. For 100 and 500 ppm of TMA, the optimum operating temperature was found to be 70 °C. Even for 700 and 1,000 ppm concentrations of TMA, the sensitivity is highest at 70 °C.

Pure ZnO and RuO_2-doped ZnO were prepared by a screen printing technique on an alumina
Substrate in a desired pattern and their gas sensing performances were studied. The thick film samples were made by dipping pure ZnO thick films into an aqueous solution (0.01 M) of ruthenium chloride for different time intervals: 5, 15, 30, 45 and 60 minutes. The responses to 1,000 ppm NH_3 of pure ZnO sensors fired at 500–700 °C were measured

at operating temperatures between 100–350 °C. The response value increased with increasing operating temperature, and the sensor fired at 650 °C was the most sensitive. Variations in gas response to 1,000 ppm NH_3 of ZnO films doped with different amounts of RuO_2 and different operating temperatures were also measured. In addition, ZnO thin films activated by chromic acid dipped for different time intervals and then fired at 500 °C for 24 hours in ambient air where CrO_3 is not thermally stable above 197 °C and thus oxygen was lost, forming Cr_2O_3 which is a stable compound. Cr_2O_3-activated sensors showed a good response to NH_3 even at room temperature and were highly selective towards NH_3 gas (300 ppm) even in the presence of other toxic gases of higher concentrations. The sensor also showed very rapid response and recovery times to NH_3 gas. In contrast, Cr_2O_3 thick films modified by 0.55-0.60 mass % Fe_2O_3 proved to be the most sensitive to not only NH_3 gas but also LPG, C_2H_5OH and Cl_2 gases. The operating temperatures for NH_3, C_2H_5OH, LPG, and Cl_2 were found to be 250 °C, 300 °C, 400 °C, and 450 °C, respectively. It showed good selectivity to a particular gas at a particular temperature against other reducing gases. The sensor also showed very rapid response and recovery rates to reducing gases.Gas sensitive sol-gel SiO_2-SnO_x-AgO_y films were fabricated where silver nitrate ($AgNO_3$), 0.01 l.%, was added to Tetraethoxysilane [$(C_2H_5O)_4Si$] solutions mixed with stannic chloride

($SnCl_4 \cdot H_2O$), in a 5:1 ratio, in order to prepare an alcohol precursor. The 150-nm thick films were deposited by spin-coating on a silicon substrate. These obtained films were dried at 120 °C for 2 hours and then annealed at higher temperatures (from 350–600 °C) in air. The gas-sensitive properties of the films were tested to NH_3 inputs which varied in the concentration range of 10–250 ppm in air. The films were shown to consist of Ag_2O_3, Ag_4SiO_4, Ag_2SiO_3, SnO, Sn_3O_4 and SnO_2. It was confirmed that the response and recovery times depend on the Sn/Ag ratio. Further, an AFM study showed that the only films which were porous had a minimum Sn to Ag ratio of 0.5 and were annealed at 600 °C for eight hours, thus showing the best sensing characteristics. The films also showed good sensitivity to ammonia gas even at low temperatures (>50 °C).

Finally, a different preparation technique for copper (I) bromide and their effects on its properties were investigated. The two different techniques of preparation used were (1) magnetron sputtering (sensor A) and (2) electrochemical (sensor B1) or chemical (sensor B2) oxidation of copper in the presence of bromide ions. The detection of ammonia on CuBr sensors can be described as a two-step mechanism, involving the formation of a chemisorptions layer during the ammonia treatment and dipolar effects due to physisorbed ammonia molecules during ammonia detection. All these results confirm that CuBr based sensors are of great interest for ammonia detection.

Conclusion :

It's quick responding techniques and also requires very low amount of sensing semiconductor oxide with doping and other material .This technique can detect NH3 or amines in very low or high concentration. We can make a portable and easy carrying instrument for detection of NH3 at different location with accuracy.

All analysis shows that in Gwalior region the atmosphere contains high concentration of ammonia (approx >=180ppm) while the area situated near by the Swarnrekha river specially bridge side areas exhibits more than 500ppm of NH3 and other Amines and the percentage of ammonia increases in morning and at night time. The air and vapors mix from drained water towards swarnrekha contains >= 1000 ppm of ammonia. All these data also confirmed by GC with only 2% result deviation makes this technique perfect tool for pollutant detection.

Refrences:

Samsonov, G.V. (1973). *The Oxide Handbook*; IFI/Plenum: New York, NY, USA.

Kumar, V.; Sharma, S.K.; Sharma, and T.P.; Singh. (1999). V. Band gap determination in thick films from reflectance measurements. *Opt. Mater.*, *12*.

Gupta, L.; Mansingh, A.; Srivastava, P.K. (1989) Band gap narrowing and the band structure of tindoped indium oxide films. *Thin Solid Films 176*, 33–44.

Xia, H.J.; Wang, Y.; Kong, F.H.; Wang, S.R.; Zhu, B.L.; Guo, X.Z.; Zhang, J.; and Wang, Y.M. ; (2008). Wu, S.H. Au-doped WO3-based sensor for NO2 detection at low operating temperature. *Sens. Actuat. B: Chem*, *134*, 133–139.

Kaur, J.; Roy, S.C.; and Bhatnagar, M.C. 2007. Highly sensitive SnO2 thin film NO2 gas sensor operating at low temperature. *Sens. Actuat. B: Chem.*.

Arya, S.P.; D'Amico, and A.; Verona, (1988). E. Study of sputtered ZnO–Pd thin films as solid state H2 and NH3 gas sensors. *Thin Solid Films* .

Nanto, H.; Sokooshi, H.; Usuda, and T. Smell, (1993). sensor using aluminum-doped zinc oxide thin film prepared by sputtering technique. *Sens. Actuat. B. Che.. Gas Sensors-Principles Operation and Developmens*; Sberveglieri, G., (1992). Ed.; Kluwer AcademicPublishers: Dordrecht, The Netherlands.