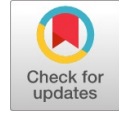# Metal Oxide Semiconductor: Future Material for Gas Sensors and it's Synthesis Techniques

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Abstract:-This paper provides a complete idea about metal oxide semiconductors ((MOSs) for gas sensing application. Metal oxide semiconductor nano-materials are showing much higher strength in many industries, research laboratories and public health and so on with their effective chemical, physical, and electronic properties. The morphology, band gap, porosity, conductivity properties, low cost and high surface area etc. are few of the properties of MOSs that are responsible for the enhancement of sensing properties in various applications. Besides these, now-a-days MOSs are grown in different nanostructures like nano rods, nano flowers, nano sheets, nano-wires etc. using the various growth techniques which are further responsible for their betterment as gas sensors. Therefore, this paper gives a complete idea about the different methods of synthesis of MOSs.

I. INTRODUCTION

Sensor seems to have come from the word 'sense' means to detect external stimulus. Hence, a sensor is a device that receives a signal of any form like physical or chemical or biological and converts it into an equivalent electric signal that should be compatible with electronic circuits [1]. Sensitivity is the ratio of magnitude of output signal to the magnitude of input signal. Sensor units with lower maintenance, higher reliability, lower cost, lower weight and less complex system architecture are highly needed. Till date different types of sensors have been developed by the researchers for different types of physical properties such as: speed [2], temperature [3], pressure [4], humidity [5], Infrared [6], gas [7] etc. for energy saving as well as for protection from different kinds of hazards. Amongst all, gas sensing technology has received increasing attention and has become more significant because of its widespread and common applications basing on their detecting and monitoring capability of flammable, toxic and exhaust gases both in domestic as well as in industrial environment. Apart from commercial use of gas sensors, indoor air quality monitoring is of great importance.

The detection of gas molecules such as triethyl amine [8], CO [9], formaldehyde [10], NO_x [11], H_2 gas [12] etc. are highly necessary due to their toxicity and associated risk to the ecosystem. Gas sensors with greater selectivity and higher sensitivity are on demand, for which many efforts are being made by the researchers for the selection of better gas sensing materials. In order to achieve an outstanding performance in gas sensing application a number of sensing materials such as metal oxide semiconductors (MOSs) [13], polymers [14], carbon nano tubes [15], graphene materials [16] have been taken a great interest. Among the different kinds of sensing materials MOSs are most investigated gas sensors having size in the range of 1-100 nm. These semiconducting materials show their uniqueness because of their mechanical, optical, electrical, magnetic and catalytic properties [17]. Apart from these properties, materials used for gas sensors need to show high surface area, so that significant resistant change may take place when exposed to target gases. Larger surface area increases the surface to volume ratio of the material leading to more adsorption of the target gas at the reaction sites and therefore a large resistance change takes place leading to better sensitivity [18]. In addition to high sensitivity, faster response-recovery, long term stability, excellent selectivity and most importantly cost effectiveness of MOSs places them at the top of the list as far as gas sensing applications are of concern. Apart from the surface area, other two most important factors responsible for sensing are i) morphology (size, shape and geometry) of the material ii) electron (e^-)/ hole (h^+) transportation in MOSs. Good crystalline structure, ability of doping noble metal and high production rate has increased the production of MOS based gas sensors [19].

To get proper structure and morphology of MOSs, synthesis plays an important role in material science. Among different synthesis methods thin film perform a significant part in sensing. The thicknesses of thin films are typically less than several microns and formed by atom to atom or molecule to molecule condensation [20]. In this article, we focused different synthetic procedure to develop thin film MOSs towards sensing.

II. METHOD OF SYNTHESIS

Metal oxide semiconductors for gas sensing application can be synthesized by various techniques like Spray pyrolysis technique, Physical vapor deposition (PVD) technique, Chemical vapor deposition (CVD) technique, Spin coating technique.

Fabrication of gas sensors by depositing the material like a thin film over any substrate using the above techniques are possible. Physical Vapor Deposition (Pvd) Technique

Sputtering is a physical vapour deposition (PVD) technique used to deposit the material in the form of a thin film onto a surface as shown in Fig 1 below. In this process first of all gaseous plasma is created which consists of ions, which are then accelerated from the plasma into the other source material. High velocity positive ions (argon plasma) are directed towards the target surface to bombard and due to their momentum transfer process between the sputter gas and target atoms ejection from the surface or source atoms takes place. The ejected atoms from the target condense on the substrate to form a film.
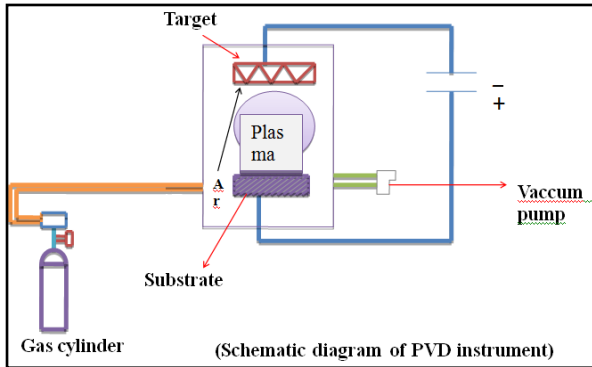

Fig 1. Schematic diagram of PVD technique

Besides neutral atoms, charged atoms and electrons are also emitted from the target surface and the number of atoms ejected per incident ion, which is termed as sputtering yield (S). Sputtering yield depends on various parameters like the composition of the material, binding energy, experimental geometry and the characteristics of the incident ion. Besides the mentioned parameters it is also dependent on the voltage and current at which sputtering takes place, which is because sputtering is done either using DC voltage (DC Sputtering) or using AC voltage (RF Sputtering). In case of DC sputtering, voltage is set from 3 to 5 KV, whereas for the RF sputtering a high voltage RF power supply is used set at 14 MHz. Sputtering is one of the preferred ways for deposition on a larger surface area not only due to high uniformity, density and lesser interface roughness of the deposited film, but also due to the higher kinetic energy of the sputtered particles which gives better adhesion to the substrate. A. Sanger and his co-workers have used the sputtering method to deposit a vertically aligned, highly ordered Pd decorated MnO_2 nanowall directly on a porous anodic alumina (AAO) and later used it as a gas sensor [21]. J. Zeng and his team used anodic oxidation method on DC magnetron sputtered metallic tungsten (W) film deposited on alumina substrate to synthesize high surface area porous WO_3. The gas sensing properties of porous WO_3 has been checked for NO_2 gas and found to be ranging from 100 ppb to 5 ppm for an operating temperature 100^0C to 200^0C. The SEM confirmed a coral like structure after annealing with the grain size of the 9 nm (WO_3 particle). High response has been reported towards sensing activities of NO_2 of different concentrations due to larger surface area, smaller grain size [22]. E. Turgut and his co-workers were grown NiO thin films by RF magnetron sputtering under different oxygen partial pressure by taking

pure Ni as target. Surface morphology and crystalline structure is hugely dependent upon the oxygen partial pressure effect. The granule size is 70 nm when the sample is grown on the moderate O_2 partial pressure whereas the granule size is reduced to 50 nm at higher partial pressure [23]. Behera et al. used sputtering technique to deposit a 100 nm thickness Tungsten metal film on SiO_2 coated Si substrate. Later to synthesize WO_3 nano-rods, the obtained film was oxidized in atmospheric condition inside a horizontal tube furnace at 500°C for 4 hours. A chemiresistive type gas sensor was fabricated by using these nano-rods. The sensor was tested for different types of gases and it showed high sensitivity towards NO_2 gases [24]. Vanadium pentoxidenano-needles for acetone sensor were synthesized by PVD method by Hakim et.al. Sensors sensitivity was tested by taking the acetone, ammonia, ethanol, propylamine at room temperature of concentration range 8.63-140 ppm and it showed better selectivity towards acetone gases [25]. Wei et.al have synthesized hollow porous flower like In_2O_3 for gas sensor application. The selectivity data of sensor reveals that at 500 ppb concentration NO_2 gas showed best result [26].

Chemical Vapor Deposition Technique

Coatings, powders, fibres and monolithic components can be fabricated by a versatile process called chemical vapour deposition (CVD). Using CVD technique it is possible to produce metals and nanometallic elements such as carbon and silicon as well as carbides, nitrides, oxides, inter metallics. Besides these CVD technique is also used in the manufacturing of semiconductors and other electronic components. The coating materials are mainly used in many optical, sensors, optoelectronic and corrosion applications. In chemical vapour deposition technique vapour transfer processes takes place at atomic level that is the deposition species are atoms or molecules or combination of all of these. It is not restricted to a line of slight deposition and has high throwing power. For three-dimensional configurations coating can be done with relative ease by this method at a higher deposition rate and thick coatings can be readily obtained. For CVD technique as shown in Fig. 2, ultrahigh vacuum is not necessarily required and the CVD equipments generally can adapt many process variations.
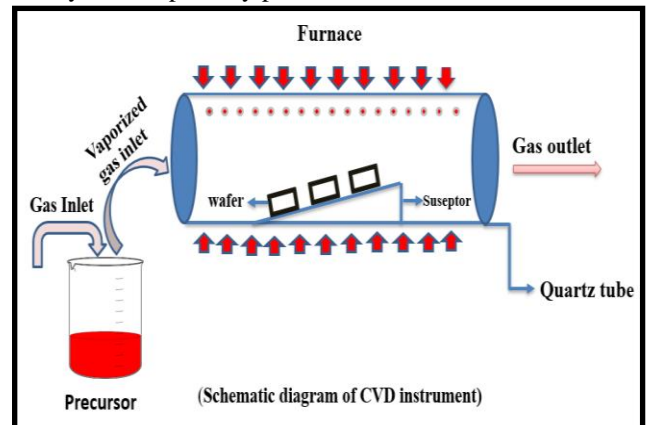

Fig 2. Schematic diagram of CVD technique

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It is flexible enough that during deposition and co-deposition of elements or compounds, many changes in composition is readily allowed and achieved too. T. Stoycheva and his co-workers prepared micromachined gas sensors by integrating tungsten oxide nanostructures (NSs) in the form of polycrystalline films, non-aligned and quasi-aligned nanoneedles (NNs) films with aerosol assisted chemical vapour deposition (AACVD). They have been evaluated basing on their performance when used for various types of sensors like NO_2, EtOH, H_2, H_2S, C_6H_6 and CO. For all the gasesnon-alligned NN sensors showed higher rate of response and high sensor activities compared to quasi-aligned NNs and polycrystalline films [27]. Januszko et al. established a thermoelastochromic sensor by preparing grapheme through chemical vapour deposition technique on copper and SiO_2 substrate. The device exhibited high resistivity at increased temperature and it can be widely used in military and civil monitoring process [28].Arun et.al. synthesizedNiO/graphenenanocomposites for electrochemical non-enzymatic biosensor by CVD technique. The sensor showed high sensitivity towards cholesterol concentration ranges from 2μM to 40μM and also able to detect in low concentration range [29]. Room temperature NO_2 gas sensor was fabricated by Shufen et.al. by taking MoS_2/porous silicon nanowires by different processes. The sensitivity of NO_2 gases in different composites was tested [30]

Flame Spray Pyrolysis Method (FSP)

Nanostructured powdered material of a broad range with specific surface area and definite particle size in the range of few nanometers can be produced by a gas phase combustion synthesis method called Flame spray pyrolysis (FSP). FSP involves an exothermic combustion reaction of a metal organic liquid precursor. For the flame synthesis process, the metal organic liquid precursor in its homogenous phase is injected into the flame either through an evaporation system working under controlled temperature, or in liquid phase it is injected through a spray system. The main advantage of FSP is the use of a wide variety of possible low-cost precursors for obtaining nanostructured powdered material as a final product with high purity, relatively narrow size distribution and of particular morphology. N. Tammanoon et al. used the FSP method to synthesize La_2O_3-doped SnO_2nano particulate thick films for acetone sensor. La-SnO_2nano belts were synthesized by thermal evaporation method. It exhibited optimal sensor responses to 100 ppm acetone, 100 ppm ethanol and 100 ppm ethanediol of 2.28, 3.75 and 8.76, respectively at 230°C. La_2O_3 doping has primarily enhanced the acetone response due to the formation of La_2O_3-SnO_2heterojunction. Therefore, for acetone detection the FSP-made La_2O_3-doped SnO_2 sensors are one of the potential devices with fast responsivity feature [31]. V. V. Ganbavleet. al. synthesized Zn_2SnO_4 thin films by FSP for NO_2 gas sensors at moderate operating temperature. To obtain the Zn_2SnO_4 thin films, $ZnCl_2$ and $SnCl_4$ of required quantity were dissolved in 50 ml of 2-propanol to form 0.1 M solution so that Zn/Sn ratio can be maintained to 2:1. The precursor solution formed is then sprayed onto the preheated glass substrates at different temperatures ranging from 325 to 400°C. The ternary oxide Zn_2SnO_4films deposited on glass substrate was then used for NO_2 sensor. The films were very highly sensitive and selective towards NO_2 gas. This indicates the sensitivity, fast response, stability and durability of the spray deposited Zn_2SnO_4films [32].Nisha et.al. have synthesized ZnO thin films by spray pyrolys is technique using zinc acetate as the precursor dissolved in propanol and water. The sensor was tested for NO_2 and H_2S gas and it showed better selectivity and response towards NO_2 gas. At 200°C the sensors response for 7 ppm NO_2 and 18 ppm H_2S gas were found to be 3.32 and 1.4 respectively [33]. Kim et. al. synthesized $CoCr_2O_4$-Cr_2O_3heterojunctions by spray pyrolysis technique for xylene sensor. The sensors response to p-xylene was studied by compairing the sensitivity of individual oxides with mixed hetero oxides and better resultswere found for hetero based mixed oxides [34]. Dan et. al. synthesized ZnOnanorods decorated with NiOnanosheets on FTO substrates by spray pyrolysis technique and observed the gas response of ethanol gas. The results showed 80% sensitivity towards 100 ppm ethanol at operating temperature 200°C [35].

Spin Coating Technique

In case of a spin coating technique, there exist a solvent dispense system which dispenses the coating material onto the substrate surface and then a drying step which removes excess solvent from the substrate by controlling the spin speed and spin time. The thickness of the film depends not only on the spin speed and spin time but also on the viscosity and concentration of the solution and the solvent. Thus, to fabricate functional oxide layers on glass or single crystal substrates a small amount of coating material is dropped at the centre of a substrate which is either spinning at low speed or not spinning at all. Then the substrate is rotated at a higher speed so that due to the centrifugal force the coating material spreads throughout the substrate to form uniform thin films with nanoscale thickness. Samiksha et.al.have synthesized MnO_2-CoO for humidity sensor using metal carboxylates as the precursors. For uniform deposition of MnO_2-CoO thin film on flat borosilicate substrates spin coating technique is applied and then annealed at 650°C. The humidity sensor was fabricated by using the film and the average sensitivity was found to be 2.225 μW/ % RH along with the response and recovery times 47 s and 59 s respectively [36]. Kim et. al. fabricated gas sensor for H_2S gas sensor by synthesizing Fe_2O_3nanoparticles-decorated carbon nanotubes. The sensor showed high sensitivity and selectivity to H_2S gas at room temperature and found to be a promising material in environmental monitoring. Low ppm concentration of gases can also be detected by the sensor device [37].

III. CONCLUSION

The detection and monitoring of harmful toxic gases liberated from industries like power generation, automotive, ceramics, glass, petroleum is necessary for environmental concern. In this regard, gas sensors have taken greater

demand in environmental monitoring, automotive emission monitoring, domestic monitoring and food safety testing because of their low operating cost, cheap, reliable, low power consuming, improved energy efficiency and reduced emission. It is an attempt to study the MOSs for different gas sensors in the review. Two overall research trends are used in sensing mechanism are 1) there should be good correlation between sensing elements and sensing properties. 2) The new and improved material synthesis, novel synthetic procedure and combination of sensing technologies and advanced device fabrication are essential to improve the sensitivity and selectivity of gas sensors.

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