Nanostructured ZrO$_2$ thin films deposited by spray pyrolysis techniques for ammonia gas sensing application

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ABSTRACT. The spray pyrolysis deposition technique has number of advantages to produce advance nanostructured oxide films. The film surface morphology and structure depends on the precursor and doping solution and solvents used with their optimized parameters. The surface to volume ratio is achieved is beneficial to gas sensing. Therefore in this paper we report the nanostructured ZrO$_2$ thin films was prepared using spray pyrolysis technique for ammonia gas sensing. There is various precursors such as Zirconium acetylacetonate, Zirconium nitrate, Zirconium tetra chloride etc. In spite of them, the Zirconium oxychloride octohydrate (0.05 M) was chosen as precursor solution and was prepared by dissolving in pure distilled water (Solvent). The films were deposited on heated glass substrate at 350°C and were annealed at 500°C for 1 hrs. It was characterized using XRD, FESEM, and TEM technique to examine crystal structure, surface morphology and microstructure properties. The average crystallite and grain size observed to be nanostructured in nature. The different test target gas performances were tested with various concentrations at different operating temperature. The films sprayed for 20 min with optimized spray parameter were observed to be most sensitive (S=58.5) to NH$_3$ for 500 ppm at 150°C. The film thickness dependence parameters: FWHM (0.02678 radians) for peak 111, Inter-planer distance (d=0.2958 nm), lattice parameters Inter-atomic spacing (a=0.511 nm), atomic volume(a$^3$=133Å$^3$), micro strain (2.8 to 0.76 x 10$^{-2}$), crystallite size (4-5nm) average grain size (32nm), dislocation density (1.73 x10$^{15}$ lines/cm$^2$), texture coefficient (>1), specific surface area(31 m$^2$/g), activation energy and band gap were studied. The sensor shows quick response (4 s) and fast recovery (10 s). Reported results are discussed and interpreted.

1. INTRODUCTION

Recently nonmaterial and nanocrystals have attracted considerable scientific interest due to their improved properties resulting from grain size refinement in nanometer scale with enhanced surface area having controlled surface to volume ratio. [1] Spray pyrolysis is widely used in industry to produce fine nanocrystalline grained oxide powders and films. It is inexpensive and without vacuum continuous process that requires only ambient pressure and substrate condition. Therefore in this paper, the emphasis is laid on the spray pyrolysis deposition technique and the influence of the deposition parameters and post process condition like annealing on the dense solidification and nanostructures of ZrO$_2$ thin films were investigated and the results are reported. Doping is the necessary to obtain stabilized zirconium oxide but this work investigated very low molar concentration precursor solution below 0.05 Mol/lit gives stable zirconium oxide film during pyrolysis process with optimized parameters. The precursor drops undergoes five major steps during process: (1) Drop size depends on nozzle pore diameters, solvent and solution flow and controlled air carrier pressure,(2) The substrate and substrate temperature and the distance between substrate and nozzle,(3) drop size shrinkage due to evaporation,(4) conversion of precursor into oxides and (5) solid particle formation. The degree of crystalline- whether amorphous or biphasic amorphous-crystalline and fully crystalline sate as well m properties are dependent on post substrate temperature, molar concentration and post deposition process like annealing. [2-4]
Zirconium oxide (ZrO$_2$) has high refractive index, high melting point, high resistance to oxidation, high thermal and mechanical resistance, high thermal expansion coefficient, low thermal conductivity, good oxygen ion conductivity, high thermo chemical resistance, high corrosion resistance, high dielectric constant, photo thermal stability, etc [5-7]. High chemical and photochemical stability with low phonon energy makes it an optimized luminescent host [8, 10, and 11]. Therefore, it has extensive applications in photonics and other industries. It has three polymorphic phases, that is, monoclinic (below 1170°C), tetragonal (1170 to 2370 °C) and cubic (above 2370 °C)

Zirconia (ZrO$_2$) has emerged as an important material for wide range of applications such as gas sensors, high-temperature electrolysis, thermal barrier coatings, soli oxide fuel cells, catalytic supports in automotive exhaust system, oxygen sensors, bio-sensor, heat resistance in high temperature furnace etc.[8-9]

In this work it was shown ammonia sensing performance. Ammonia is produced and utilized in many sectors: food processing industries, fertilizer industries, refrigeration systems, medical diagnosis, instrumental and educational laboratory, fire power plants, chemical industries etc. leak in this system is problems to human health since it harmful and toxic. Despite of high sensitivity, selectivity, the main drawback of such ZrO$_2$ films is that they do not stable long term and not operated at room temperature. To fabricate sensors for detection of low as well high concentration ammonia at room temperature and accordingly leak alarm, security alarm is interest of numerous investigators, researchers and scientists. Investigation of low concentration room temperature operable thin film sensor is future priority work.

2. EXPERIMENTAL

2.1 Preparation of spraying precursour solution

The preferable precursor are zirconium hydroxyl acetate (ZHA), inorganic Zirconium tetra chlorate (ZrCl$_4$), Zr(NO$_3$)$_4$, and metalloorganic Zirconium acetylacetonate(Zr(C$_5$H$_7$O$_2$)$_4$, and Zr-tetra-but oxide(Zr[OC(CH$_3$)$_3$]$_4$. Every precursor has its own advantages and disadvantages with respect to surface morphology. They were dissolved in a wide variety of alcohol solution with some content of water. The precursor used in this study was Zirconium oxychloide octohydrate (ZrOCl$_2$.8H$_2$O). It consists chloride ions and 8 water molecules, therefore most common solvents seemed to be water. This slat was reagent agent (Sigma Adrich 99.99 pure) and it was dissolve in pure double distilled water so as prepare 0.05M solution. Sometimes few percentage of alcoholic solvents (TEG, EG, PVG or Ethanol) were preferred to maintain low surface tension and viscosity facilities. But in this case we used pure water and controlled spray parameters.[10]

2.2 Details of spray pyrolysis setup

The schematic experimental set up of the spray pyrolysis system which is built in our lab is shown in figure 1. It consists of spray gun with nozzle, substrate heater, automatic temperature control unit, air compressor, pressure regulator, thermocouple, stepper motor with controller and power supply. The heater is a stainless steel block furnace electrically controlled by an automatic temperature controller unit to attain the required substrate temperature to an accuracy of± 2°C. The resulting temperature on the surface of the substrate is measured with a chromel–alumel thermocouple. Hazardous fumes evolved during thermal decomposition of the precursor are driven out through an exhaust system attached to the spray pyrolysis unit. The spray nozzle is made up of borocil glass having different bore diameters (viz.0•1 mm, 0•3 mm, 0•5 mm). Due to air pressure of the carrier gas, a vacuum is created at the tip of the nozzle to suck the solution from the tube after which the spray starts.
The spray nozzle is fixed at an appropriate distance from the substrate. The precursor solution was sprayed on to the substrate in air as small drops and around a high temperature zone where thermal decomposition and possible reaction between solutions occur, through compressed air, which is used as carrier gas with a flow rate controlled through air compressor regulator. To achieve uniform deposition, the moving arrangement has been used. For this, substrate is kept stationary; while the nozzle is free for to and fro motion with mechanical moving arrangement as stepper motor has been advantageous, so we do not have to spend energy moving the table with the hotplate and all electrical connections. The nozzle system is very lightweight with easy slider trolley attached. The spraying system and heater are kept inside a metallic chamber of size $60 \times 60 \times 60$ cm$^3$. The inner surface of the box is painted by epoxy liquid, to reduce heat loss through the surface.[11-16]

2.3 Deposition of nanostructured thin films

As prepared precursor solution of ZrOCl$_2$.8H$_2$O(0.05M) was sprayed, through a galss nozzle of 0.1mm bore diameter on hot glass substrate at temperature $350^\circ$C $5^\circ$C at spray rate 5ml/min for different spray time 10min.,20min.,30min. The optimized spray parameters are tabulated as shown in table 1. The fine droplets react on heated substrate which provides thermal energy, owing to pyrolytic decomposition of solution. Droplets achieved small evaporate and splash strikes at high velocity after hitting surface and converted into solid densified oxide powder with fine spherical grain. The precursor drops undergoes five major steps during the course of spray process is already explained in introduction.

Table 1: Process parameters for the spray deposition for ZrO$_2$ thin films

<table>
<thead>
<tr>
<th>Spray parameters</th>
<th>Values</th>
<th>Annealing Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant parameters</td>
<td></td>
<td>550 $^\circ$C for one hrs.</td>
</tr>
<tr>
<td>Concentration of solution</td>
<td>0.05M</td>
<td></td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>$350^\circ$C</td>
<td></td>
</tr>
<tr>
<td>Distance between spary nozzle and substrate</td>
<td>28 cm</td>
<td></td>
</tr>
<tr>
<td>Spray rate</td>
<td>5ml/min</td>
<td></td>
</tr>
<tr>
<td>Compressed carrier gas</td>
<td>air</td>
<td></td>
</tr>
<tr>
<td>Deposition time</td>
<td>10.20,30Min.</td>
<td></td>
</tr>
<tr>
<td>Carrier pressure</td>
<td>8 kg/cm$^2$</td>
<td></td>
</tr>
</tbody>
</table>
3. MATERIAL CHARACTERIZATION

The structural, morphological, electrical and optical properties have been studied. The crystalline structure of the films, obtained at annealing temperature and it was examined by X-ray diffractometer pattern, FE-SEM and TEM micrograph SAED pattern.

3.1 Structural properties of the films

![XRD pattern of ZrO$_2$ thin film as deposited and 30 min. deposited film with annealed at 550$^\circ$C](image)

**Fig. 2.** XRD pattern of nanostructured ZrO$_2$ thin film as deposited and 30 min. deposited film with annealed at 550$^\circ$C

X-ray diffraction pattern of ZrO$_2$ thin films deposited with respect to annealing temperature is shown in fig.2. Generally with increase in spray deposition time and annealing temperature, structure of the film changes to fully crystalline and grain growth occurs increase in mobility with temperature. In this case it polycrystalline and nanostructured. The increase in intensity reflects the increase in content of oxide with enhanced thickness, also the increase in broadening of XRD peaks reflects the nanocrystalline nature. The effective broadening can be caused by lattice strain and small crystallite size. The peaks (111),(200),(220),(311),(222) and(400) well matched with standard JCPDS data card.(17-0923,36-020 and 34-1084).[17] They are tetragonal and monoclinic phase. The crystallite size is determined using Sherrer formula. The FWHM for peak 111 is 0.02678 radians and average FWHM was observed 0.028 radian. The calculated value for average crystallite size was within range (4-5 nm). The average grain size was observed 32 nm by FE-SEM.
\[ D = 0.9 \lambda / \beta \cos \theta \] (1)

Where, 

- \( D \) = Average crystallite size
- \( \lambda \) = X-ray wavelength (1.542 Å)
- \( \beta \) = FWHM of the peak
- \( \theta \) = Diffraction peak position.

Where \( D \) is the crystallite size (nm), \( \lambda \) is the wavelength of Cu-K\( \alpha \)-x-ray radiation (1.542 Å), \( \theta \) is the Bragg’s angle (in degree), \( \beta \) is the calibrated width of a diffraction peak at full width half maximum (radian). The lattice inter-planer distance \( d \) was determined using Bragg’s condition found to be 0.2958 nm. It was matched with estimated \( d \) value by TEM pattern. The inter-atomic spacing estimated \( (a=0.511 \text{nm}) \) and atomic volume of unit cell estimated as \( (133 \text{Å}^3) \).

![Graph showing the co-relation between deposition time, microstrain, film thickness and annealing temperature.](image)

**Fig. 3.** Co-relation between deposition time, microstrain, film thickness and annealing temperature

The lattice micro strain can be calculated using standard Williamson-Hall plot \( \beta \cos \theta / \lambda \) versus \( 2 \sin \theta / \lambda \) or using relation \( \beta / 2 \tan \theta \). It was observed that as annealing temperature, spray deposition time and film thickness increases micro strain decreases resulting increase in grain size. Fine grains, moderate porosity and maximum nanostructured grains have maximum grain boundary, it enhances high sensing surface area with optimum surface to volume ratio. Brunauer-Emmett-Teller (BET) method was applied for specific surface area evaluation and calculated for spherical particles using the following equation,

\[ \text{SSA} = 6 \times 10^3 / \rho D \] (2)

Where \( D \) is size of grain/particle size and \( \rho \) is the density of the particle/material. It was estimated 31 m\(^2\)/g at annealing temperature 500°C. The preferred orientation of the sample was described by the texture coefficient (TC) evaluated by the equation as defined by Barret and Massalski,

\[ \text{TC(hkl)} = \frac{I_{(hkl)}}{I_{(hkl)}} \left[ \frac{1}{N \sum I_{(hkl)}} / I_{(hkl)} \right] \] (3)
Where TC is the texture coefficients of the (hkl) plane, I is the measured intensity and I₀ is the JCPDS standard intensity of the corresponding material powder peak. N is the reflection number. The higher deviation of the texture coefficient from unity indicates the higher preferred orientation of the film and crystalline nature, here it was found greater than one for peak (111). It indicate crystalline growth. The average grain size obtained from FE-SEM images is 32 nm. The TEM image reveals decrease in particle size up to nanolevel. It is not single crystalline. It is observed to be nanocrystalline and polycrystalline. It does not have bulk nature and not formation of large grains and growth of single large particle crystal. This shows the nanostructure polycrystalline nature of the small particles. This may be because of decomposition of small droplets of spraying solution and kinetic of deposition. The high resolution TEM image shown lattice form of small spherical particles. It shown matched value of interplaner spacing (d) determined using Bragg’s condition and with XRD peak data. Therefore the surface morphology changes with precursor solution and solvents, it does not only temperature dependent and the role of spray parameter as well as precursor solution, low and high cationic doping, proper solvents is important. Because surface morphology and sensing surface area are co-related.[15-16].

Fig. 4. (a) and (b) FE-SEM images of nanostructured ZrO₂ thin films at scale 500nm, 300nm, (c) HRTEM image at scale 5 nm and (d) SAED pattern
3.2 Electrical I-V characteristics

![I-V characteristics of nanostructured ZrO\textsubscript{2} thin film sensors.](image)

The contacts were made by silver paste on thin film surface. Fig. 5 shows the I–V characteristics of samples prepared by different spray deposition time. It was observed to be nearly symmetrical in nature indicating ohmic nature of contacts. The non-linear I–V characteristics may be due to n-type oxide semiconducting nature of the films.

3.3 Electrical conductivity profile

Fig. 6 shows the variation of log (conductivity) with reciprocal operating temperature. The electrical conductivity of the sensor element varied linearly with operating temperature. The increase in conductivity of the sensor with an increase in temperature could be attributed to the semiconducting nature and negative temperature coefficient of the sensor resistance. This can be attributed to the generation of electrons due to thermal excitation.

Activation energy was calculated using formula:

\[
\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{kT}\right)
\]

Where, \(\sigma\) = conductivity
\(\sigma_0\) = conductivity constant
\(k\) = Boltzmann constant
\(T\) = Temperature

It is dependant. It was found at low temperature range 0.76 eV and at high temperature range 0.268 eV.
4. RESULTS AND DISCUSSION

4.1 Gas sensing performance of the sprayed ZrO$_2$ thin films

Gas response (S) of the sensor is defined as the ratio of change in conductance in presence of exposure of target gas to the conductance of the sensor in air atmosphere.

$$ S = \frac{G_g - G_a}{G_a} $$ (5)

Where $G_a$ = the conductance of the sensor in air

$G_g$ = the conductance on exposure of a target gas

Fig. 7 shows variation of gas response with operating temperature of samples on exposure of 500 ppm ammonia. It is clear from Fig. 6 that the ammonia response of sample prepared sample S2 shows maximum gas response ($S_2 = 58.5$) at 150 °C.
4.2 Selectivity of ammonia against various gases at different operating temperature

Fig. 8. Selectivity of nanostructured ZrO$_2$ thin films for different gases

It is clear from fig.8 that the responses of all samples to, H$_2$, C$_2$H$_5$OH, Cl$_2$, NO$_2$ and H$_2$S gases are lower as compared to their response to ammonia.

4.3 Response and recovery time

The time taken for the sensor to attain 90 % of the maximum decrease in resistance on exposure to the target gas is the response time. The time taken for the sensor to get back 90 % of original resistance is the recovery time.

Fig. 9. Response and recovery of the sensor (most sensitive sample = S2).

5. GAS SENSING MECHANISM

It is well known that the electrical conductivity in ZrO$_2$ oxide is due to a non-stiochiometric composition as a result of oxygen deficiency. The conductivity is n-type, when the sensor surface is placed in air ambient, the oxygen molecules are adsorbed at the surface resulting in the formation of O$_2^-$, O$^-$, O$_2^+$ ions, thus decreasing the concentration the number of charge carriers near the surface giving rise to a depletion region. When exposed to reducing gas ammonia mutual...
interaction between the reactant i.e. reducing gas and oxygen species, results in oxidation of reducing gas at the surface. This oxygen phenomenon helps in removal of oxygen ion from ZrO$_2$ resulting in decrease barrier height, thus increasing conductivity. During the chemisorptions at higher temperature 125$^\circ$C, oxygen is adsorbed in ionic form as shown in the following reactions.

$$\text{O}_2 + e^- \rightarrow \text{O}_2^- \quad (6)$$

$$\text{O}_2^- + e^- \rightarrow 2\text{O}^- \quad (7)$$

Above 175$^\circ$C, the reactivity of O$^{2-}$ species is high. The formation of O$^{2-}$ species is also possible as follows

$$\text{O ads}^- + e^- \rightarrow \text{O}^{2-} \quad (8)$$

O$^{2-}$ are not adsorbed because these species are not stable and are usually trapped by oxygen vacancies. In case of ZrO$_2$, the carriers are believed to be due to excess ions at the interstitial position, due to oxygen vacancies, acts as electron donors. Reducing gas like NH$_3$ reacts with adsorbed oxygen ions. The possible reaction is

$$2\text{NH}_3 + 3\text{O}^- \rightarrow 3\text{H}_2\text{O} + \text{N}_2 + 3e^- \quad (9)$$

$$2\text{NH}_3 + 3\text{O}^{2-} \rightarrow 3\text{H}_2\text{O} + \text{N}_2 + 6e^- \quad (10)$$

$$\text{NH}_3(g) + \text{H}_2\text{O} \text{(surface)} \rightarrow \text{NH}_4\text{OH} \text{(g)} \quad (11)$$

Ammonia hydroxide NH$_4$OH produced during the surface reaction is volatile in nature. The high volatility of NH$_4$OH influences the quick response and fast recovery of the sensor. [18-24]

6. CONCLUSION

Following conclusion cab be drawn from the experimental results:

(1) Surface morphology depends on precursor solution, optimum spray parameters and substrate temperature.

(2) Annealing is necessary to the grain growth of the films

(3) As spray time increases, micro strain decreases and film thickness as well as grain size increases.

(4) Surface mechanism is based on adsorption-desorption with oxygen vacancies role.

(5) Quick response and fast recovery time was recorded. It was observed 4 s and 10s.

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References

[17] JCPDS Data Card(36-020) and JCPD data, (17-0923) and (34-1084)