

CHAPTER VI

Summary and Conclusions

A flourishing effort has been made to modify the conventional chemical spray pyrolysis technique into an advanced spray pyrolysis technique to by retaining all its advantages, to deposit the undoped and doped nanocrystalline ZnO thin films at much lower temperature. It is noteworthy that the films deposited by advanced spray pyrolysis at substrate temperatures 473K shows comparable structural, morphological, electrical and optical properties to that deposited previously by the conventional spray pyrolysis that employed substrate temperature $\geq 623\text{K}$. Further, the films were observed to be polycrystalline without any amorphous like phase. In the advanced spray pyrolysis setup, the pyrolytic chemical reaction is successfully completed in the reaction chamber with subsequent deposition of the final product on the substrates, which are kept at a low temperature. The lower substrate temperature changed micro structural properties of the deposits to some extent, especially the crystallite/grain size; which is smaller than that obtained using conventional spray pyrolysis. However, unexpectedly, the lower growth temperature hasn't modified the surface morphology of the film, and the films retained their compact surface structure without any porosity. The ZnO films are highly transparent in the visible region and exhibits a comparable direct band gap values reported previously. As compared to the conventional sprayed ZnO films, the present ZnO films show higher resistivity. This high resistivity may be due to nanocrystalline nature of the samples. Another possible reason for the high resistivity may also be the oxygen chemisorptions at grain boundaries since air was used as carrier gas during deposition and the decomposition reaction is about to complete in the ambient core of the reaction chamber. During deposition process it is somewhat expected that large numbers of oxygen molecules are chemisorbed at grain boundaries and also on the surface of the film. Because these molecules do not have time to leave the sample at the end of deposition, due to the rapid cooling effect.

Similar to most of thin film deposition techniques, particularly the spray pyrolysis, this novel advanced spray pyrolysis has its own process parameters that have profound effects on the physical and gas sensing properties of ZnO thin films and hence optimization of various system parameters have been done. Due to their crucial role in controlling many properties, the core temperature (reaction temperature), substrate temperature, thickness dependence and layer by layer (LBL) deposition dependence of structural, morphological, electrical, optical and gas sensing behavior of undoped ZnO thin films was studied and reported. Additionally, the doping effect of copper (Cu) and tin (Sn) on the ZnO thin film properties were evaluated. The different characterization techniques such as X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), spectrophotometry, and electrical resistivity measurement using two probe method were employed to study various properties of undoped and doped ZnO thin films. Moreover, the gas sensing performance of the films was also tested towards reducing atmospheres, using a home-made gas sensing testing unit.

a. Core Temperature or Reaction Chamber Temperature

Initially, keeping substrate temperature (473 K) and concentration (0.1 M) of zinc acetate solution (prepared in 100ml methanol) constant, zinc acetate solution is atomized towards the glass substrates maintained at different core temperatures from 548–648 K at steps of 25K; keeping other parameters same.

The crystallographic, morphological, optical and electrical properties of ZnO films were investigated with variation in core temperature. Film crystallinity is found to be strongly dependent on the core temperature. The films grown at low core temperature (<573K) are largely amorphous in nature incorporated with an undecomposed acetate group as expected from TGA-DTA analysis of zinc acetate, while the films grown at higher temperatures (≥ 598 K) are crystalline in nature. For ZnO thin film deposition, good crystalline properties were obtained at 598K. Thus, TGA-DTA analysis is recommended so as to determine the optimum core temperature for the quality deposition of the metal oxide films using advanced spray pyrolysis. The surface FESEM studies supports well to the XRD analysis and the film prepared at 598K shows highly compact surface. A noteworthy variation was observed in ZnO film thickness and

RMS roughness with variation in core temperature; which collectively determines their optical properties. The RMS roughness values of the polycrystalline ZnO films deposited by advanced spray pyrolysis technique were much smaller than that of the ZnO film deposited by conventional spray pyrolysis technique. The nanocrystalline nature of the samples and the oxygen chemisorptions at grain boundaries may be resulted into higher electrical resistivity to that compared with the conventionally sprayed ZnO films. The crystallographic properties and the film thickness influenced the electrical properties of the ZnO films deposited at different core temperatures.

Thus, structural, morphological, optical and electrical characteristics suggest that the sample prepared at core temperature of 598K gives better results. Therefore core temperature 598K is optimized and constantly employed for further studies.

b. Substrate Temperature

With previously optimized core temperature (598 K) , the 0.1M zinc acetate solution (100ml) prepared in methanol is atomized towards the glass substrates maintained at different substrate temperatures from 423 to 523K at steps of 50K; keeping other parameters same.

The crystallographic, morphological, optical and electrical properties of ZnO films are investigated with variation in substrate temperature. Film crystallinity is found to be proportional to substrate temperature. The increase in mobility of the surface atoms and subsequent thermodynamic stability resulted into the improved crystallinity with increase in substrate temperature. Nevertheless, there is an insignificant change in their structural properties of the films deposited at 473K and 523K. Morphological studies confirms that film adheres well with the glass substrate without any pores within the film and revealed a columnar growth at higher temperatures, consistent to the better crystal quality at high temperature showed in XRD patterns. The ZnO film thickness and RMS surface roughness were influenced by the growth temperature and it decreases with an increase in substrate temperature. The decrease in roughness with increasing substrate temperature may be ascribed to the fact that the respective grains have increasingly similar growth rates at high temperature. The optical transmittance increases with the increasing growth

temperature and the average transmittance of the films including glass substrates in the visible range is over 82% at 550nm. This variation is mostly determined by the film thickness and RMS roughness. Further, the direct band gap is slightly decreased when the substrate temperature increased from 423K to 523K. The change in band gap may be attributed due to increased crystallinity of the films. The room temperature electrical resistivity was observed to decrease when substrate temperature varies from 423K to 523K with a step of 50K. However, the resistivity variation is insignificant for the films deposited at 473K and 523K.

Thus, though the advanced spray pyrolysis technique exploits comparatively low substrate temperature, a temperature change of 50 K has profound effects on properties of ZnO films when substrate temperature is $\leq 473\text{K}$. However, films deposited at 473K and 523K, shows almost similar structural, morphological, optical and electrical behavior. Accordingly, a substrate temperature 473K is chosen as an optimum growth temperature for further studies.

c. The ZnO film thickness

With the earlier optimized core and substrate temperature, the ZnO film thickness effect on the different properties of ZnO films were investigated by spraying various volumes (50ml to 200ml at a step of 50ml) of spraying solution; keeping other parameters same.

Structural, morphological, optical and electrical investigations were carried out upon ZnO thin films as a function of their thickness. The structural analysis indicated that the ZnO films were polycrystalline with highly orientated along (200) planes. The thicker film of ZnO develops well-defined microstructures. The crystallite sizes become larger as the thickness of the film increases. From FESEM micrographs the films appear smoother at low thickness while the surface smoothness appears to reduce with an increase in film thickness. It is also observed that the grain size increases when the thickness increases. A linear relationship was observed amongst the film thickness and RMS surface roughness attributable to the development of the larger grains by agglomeration of smaller grains. The optical transmittance decreases with increasing film thickness. The room temperature resistivity of sprayed ZnO films falls almost linearly with increasing thickness, in which the decreasing trend can

be attributed to the inverse linear dependence of film resistivity increase on grain size.

d. The ZnO layer by Layer deposition

For the ZnO layer by layer deposition, first layer was deposited by spraying 100ml solution onto glass at a constant substrate temperature (473K) and core temperature (598K) and then allowed to cool down at room temperature. For the second layer, as-deposited single layered zinc oxide thin films were used as substrates and same deposition procedure was carried out by maintaining same deposition conditions. For third and fourth layers, same process was repeated so that the previous zinc oxide under-layer will act as substrate for the subsequent over layer.

Structural, morphological, optical and electrical investigations were carried out upon ZnO thin films as a function of number of layers. The structural analysis suggests that all the prepared ZnO thin film layers have a hexagonal wurtzite structure and are preferentially oriented along the c-axis perpendicular to the substrate surface. A slight shift in (002) peak position for first and second layer towards lower angle was observed. This may be understood as follows: for the ZnO monolayer the amorphous glass is used as the substrate whereas this monolayer itself used as a substrate for depositing the second layer to for the double layer structure. Thus, there stays the difference between the thermal expansion coefficients between the ZnO film and the substrate onto which it is grown. Further, similar to the thickness effect, the crystallinity improves with the increasing number of ZnO layers. The beneath layer provides the nucleation sites for the upper layer and thus modifies the morphology accordingly. The film surface roughness increases with increasing number of ZnO layers due to increasing thickness and subsequent the larger grain formation and agglomeration. The optical properties were merely determined by the film thickness and RMS roughness which strongly depend on the number of ZnO thin film layers. The room temperature resistivity for all samples falls almost linearly with increasing number of layers, in which the decreasing trend can be attributed to the inverse linear dependence of film resistivity increase on grain size.

Thus, in conclusion the layer by layer deposition of ZnO films shows almost similar properties to that obtained while variation in ZnO thin film thickness.

e. Effect of copper (Cu) doping in ZnO thin films

To investigate the effect of copper (Cu) doping on different properties of ZnO thin films, the ZnO thin films were deposited by varying the Cu doping concentration as 1, 2, 3 and 4 at% with previously optimized preparative parameters. The 150ml zinc acetate solution containing different copper concentrations was sprayed onto hot glass substrate for depositing ZnO: Cu films.

Structural, morphological and optical investigations were carried out upon ZnO thin films as a function of Cu doping concentration. XRD analysis shows an improvement in the c-orientation of ZnO films as an effect of Cu doping. The crystallinity and degree of orientation of the ZnO: Cu films were closely associated to the Cu doping concentration. The 3 at% Cu doped ZnO film exhibits highest crystallinity. The micrographs show that the 3 at% sample exhibits comparatively compact surface well covered with the granular structures. The columnar growth has improved crystalline structure with Cu doping and morphology observations clear the crystalline behavior understood from the XRD patterns. The evaluated RMS surface roughness is 4.89, 5.74, 6.32 and 4.97 nm for 1, 2, 3 and 4 at% Cu doped ZnO samples, respectively. The film thickness has decreased significantly with the Cu doping concentration. The transmittance of all copper doped ZnO films stays over 80% at 550nm. The optical transmittance is observed to increasing with Cu doping concentration up to 3 at%; however it again decreases slightly for 4 at% sample. The observed change in transmittance may be the effect of change in film thickness and consequent surface scattering of incident photons with variation in Cu doping concentration in ZnO.

f. Effect of tin (Sn) doping in ZnO thin films

To investigate the effect of tin (Sn) doping on different properties of ZnO thin films, the ZnO thin films were deposited by varying the Sn doping concentration as 1, 3 and 4 at% with previously optimized preparative

parameters. The 150ml zinc acetate solution containing different tin concentrations was sprayed onto hot glass substrate for depositing ZnO: Sn films.

Structural, morphological, optical and gas sensing investigations were carried out upon ZnO thin films as a function of Sn doping concentration. The XRD pattern of the films shows hexagonal wurtzite structure with a polycrystalline nature. No other peaks corresponding to tin oxide or tin are observed. The lattice distortion incorporated in the film with Sn doping. The incorporation of Sn into ZnO films caused the crystallinity to somewhat degenerate. The discrepancy in the ion radius between (0.074 nm) and Sn^{4+} (0.069 nm) might have caused a small lattice distortion and hence for that reason reduced the XRD Bragg peak intensity with the crystallite size. From micrographs, the surface morphology of the ZnO: Sn films observed to exhibit some modification with Sn doping concentration increase. The average particle size on the surface of ZnO: Sn decreased slightly with increase in Sn doping level. This is in a good agreement with X-ray diffraction results. The root-mean square (RMS) roughness decreased with Sn concentrations. The optical transmittance is observed to increase from ~84% to ~87% as the Sn concentration increases from 1 to 4 at%. This increase in transmittance may be attributed to the decrease in film thickness and RMS roughness with increase in Sn doping level. The optical band gaps are increased from ~3.28 to 3.29 eV as the Sn doping concentration increases from 1 at% to 4 at%. The increase in band gap is attributed deterioration of crystallinity.

g. The H_2S gas sensing properties of undoped and doped ZnO films

The H_2S sensing results of advanced sprayed ZnO films are tabulated in the following table:

Core Temperature	H_2S gas concentration = 20 ppm			Operating Temperature = 573K	
Sample	548K	573K	598K	623K	648K
Sensitivity	14	9	19	23	28
Response time	41	34	5	14	19
Recovery time	20	19	19	28	38

Substrate Temperature	H ₂ S gas concentration = 20 ppm		Operating Temperature = 573K		
Sample	548K	598K	623K		
Sensitivity	13	19	76		
Response time	64	5	45		
Recovery time	40	19	35		
ZnO Film Thickness	H ₂ S gas concentration = 20 ppm		Operating Temperature = 573K		
Sample	135 nm	216 nm	298 nm	392 nm	
Sensitivity	66	19	12	9.6	
Response time	108	5	15	7	
Recovery time	38	19	14	8	
Layer by Layer (LBL) deposition	H ₂ S gas concentration = 20 ppm		Operating Temperature = 573K		
Sample	1 layer	2 Layer	4 Layer		
Sensitivity	19	15	17		
Response time	5	10	29		
Recovery time	19	20	34		
ZnO: Cu Thin Films	H ₂ S gas concentration = 20 ppm		Operating Temperature =523K		
Sample	1 at% Cu doped ZnO	2 at% Cu doped ZnO	3 at% Cu doped ZnO	4 at% Cu doped ZnO	
Sensitivity	11	14	21	28	
Response time	4	17	8	9	
Recovery time	7	29	29	24	
	4 at% Cu doped ZnO				
Operating temperature (K)	423	473	523	548	573
Sensitivity	12	14	28	18	5

ZnO: Sn Thin Films	H ₂ S gas concentration = 20 ppm		Operating Temperature = 523K	
Sample	1 at% Sn doped ZnO	2 at% Sn doped ZnO	3 at% Sn doped ZnO	4 at% Sn doped ZnO
Sensitivity	19	20	22	27
Response time	6	12	16	46
Recovery time	18	20	22	15
	4 at% Sn doped ZnO			
Operating temperature (K)	423	473	523	573
Sensitivity	17	27	25	23

In summary, resistive sensors were fabricated from nanocrystalline undoped and doped ZnO thin films which were prepared by an advanced spray pyrolysis method and their H₂S gas-sensing properties were measured. The H₂S gas-sensing properties were measured towards relatively low gas concentration i. e. 20 ppm (fix) at moderate operating temperature i. e. $\leq 573\text{K}$. The results demonstrated that the response to H₂S gas was dependent on the crystalline properties and the operating temperature was influenced by the dopants, namely copper and tin. The undoped ZnO films showed a good response at 573K and best preparative conditions for ZnO film to detect H₂S are: 598K core temperature; 523K substrate temperature; low thickness with spray solution quantity 100ml. Especially, the sensors could detect 20ppm H₂S. The copper doping has reduced the operating temperature to 523K; while the tin doping has lowered that to the 473K to get optimum gas response. Though, both 4 at% Cu and Sn doped ZnO films have a good response even at 523K towards 20 ppm H₂S gas. Thus, the nanocrystalline Cu and Sn doped ZnO films prepared by advanced spray pyrolysis technique are promising for practical use for detecting low concentrations of H₂S.