

## INFLUENCE OF DIFFERENT PROCESS PARAMETERS UPON MICROSTRUCTURE OF ZnO FILMS PREPARED BY SPRAY PYROLYSIS

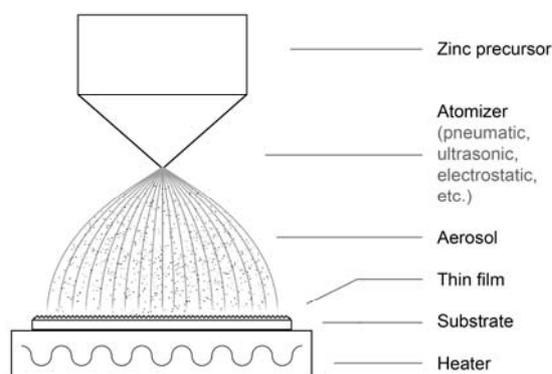
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Recently, there has been a significant amount of research and development related to spray pyrolysis (SP) preparation of nanosize ZnO films. This paper presents a review of the effects of the basic spray deposition parameters on the crystal and surface structure of ZnO films. The main parameters which impact on the films morphology and crystal structure are: substrate temperature (ST), chemical nature of the precursor etc. The choice of suitable synthesis parameters is also determinant for the final crystal orientation. Most of the authors have proved that the zinc oxide films preferentially growth along *c* axis at elevated ST, while below ST=300°C the films are randomly oriented. Switching the orientation from (002) to (100) or (101) can be achieved by changing both the substrate temperature and the solution concentration. Thus the spray pyrolysis method is suitable for preparation of ZnO thin films with wide range of potential applications in optoelectronic devices, sensors, catalysts etc.



### INTRODUCTION

Preparation and investigation of ZnO films has attracted an emphasized interest in the recent years. Zinc oxide (ZnO) has a wurtzite crystal structure having a number of alternating planes composed of fourfold coordinated O<sup>2-</sup> and Zn<sup>2+</sup> ions stacked alternatively along *c*-axis of hexagonal unit cell. The wide variety of the applications is also determined by its electronic structure. It is known that ZnO is a wide band gap semiconductor (E<sub>g</sub> = 3.37 eV) with a large excitation binding energy (60 eV) and exhibits near UV emission,

transparent conductivity and piezoelectricity, which make it particularly attractive e.g. for light emitting diode (LED),<sup>1</sup> varistors,<sup>2</sup> optical devices,<sup>3</sup> gas sensors,<sup>4</sup> solar cells,<sup>5</sup> acoustic devices<sup>6</sup> etc. Zinc oxide also is considered a possible alternative of TiO<sub>2</sub> (again a wide zone semiconductor) as photocatalyst, which can be used for purification of water and gases contaminated with organic substances.<sup>7</sup>

Preparation of ZnO films is realized by different methods: sol-gel,<sup>8</sup> wet chemical methods,<sup>9</sup> chemical vapor deposition,<sup>10</sup> evaporation,<sup>11</sup> sputtering<sup>12</sup> etc. Among these, the spray pyrolysis

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method has several advantages such as: low cost, relatively easy composition control, large area deposition and high growth rate.<sup>13</sup> The spray pyrolysis technique consists of spraying a soluble salt or complex solution with the aid of a carrier gas onto heated substrate. The process of spray pyrolysis is based on a chemical reaction – thermal decomposition of the initial material. The oxidation of the decomposition products ensures formation of layer or particles. To ensure that the pyrolysis process is the only one taking effect on the substrate surface, it is necessary that the initial material temperature is kept below the decomposition temperature. This is achieved first by dissolving the material in a solvent. The precursor solution is atomized to an aerosol state consisting of fine droplets, which are finally transported to the heated substrate by the means of the carrier gas. The formation of the aerosol stream is implemented in several different ways, which determines the type of the pyrolysis method. Different kinds of atomizers such as pneumatic, ultrasonic or electrostatic can be part of the spray pyrolysis equipment. The technique of atomization determines the droplet size and size distribution, the rate of atomization and the spray angle. It is necessary for the substrate temperature to be kept in a certain range in order to secure the complete decomposition of the precursor; at lower temperatures it is possible that some non decomposed products remain on the substrate, while at higher temperatures the droplets will evaporate before reaching the substrate and therefore there will not be any layer formation.

It is well established that the properties of the ZnO layers, synthesized by spray pyrolysis are greatly influenced by the synthesis conditions. That is why this review takes a closer look at the published literature, analysing the data for the influence of some process parameters (*i.e.* substrate temperature (ST), chemical nature of the precursor salt and solvent, molarity of the precursor solution, spray rate, solution acidity etc.) upon important features of the films. The ability to control morphology, microstructure and orientation of ZnO films is of particular interest for the broad variety of applications such as optoelectronic, sensing, laser etc. devices. Here we discuss the influence of these basic factors upon the morphology, grain size and crystallographic orientation of ZnO layers.

## INFLUENCE OF DIFFERENT DEPOSITION PARAMETERS

### 1. Substrate temperature (ST)

The substrate temperature is a critical factor that determines morphology, uniformity and properties of ZnO sprayed layers. It affects the processes on the substrate: droplet drying, decomposition or melting, crystallization and grain growth. An ideal deposition scenario is when the droplet approaches the substrate just as the solvent is completely removed. The process is characterized by relatively high substrate temperatures *e.g.* several hundred degrees. The lower limit of ST is dictated by the required chemical dissociation reaction. Higher substrate temperatures, as regard to the pyrolysis temperature of the precursor, generally favour the growth of large size crystallites.

Krunks *et al.* showed that at 200-300°C and initial solution of zinc acetate, a solid phase is formed from the precursor with a shape of dendrite like crystallites.<sup>14</sup> At ST = 300-400°C the solvent evaporates before the droplets reach the substrate, which causes a formation of a dense film, consisting of spherical crystallites, 50-100 nm in size. At higher temperatures (above 450°C) the  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  decomposes in the gas phase, and only hollow crusts are formed. In this case the film consists of spherical grains with two distinct sizes; (i) 50-100 nm, (ii) 300-500 nm approximately. The films produced at low temperatures have (100) orientation only. When the ST increases, a (002) orientation appears and becomes more dominant. The high transmittance of these films makes them suitable for applications in solar cells.

Lee C.H. *et al.* have also investigated morphology of ZnO layers, deposited on silicon substrates at different substrate temperatures.<sup>15</sup> They established that at temperatures below 300°C, layers with amorphous structure and smooth surface are formed, while above 300°C the crystalline phase has circular grains and (002) orientation. The transparency of these films is higher than 90% in the 380-850 nm region.

The effect of the substrate temperature upon the thin layer morphology was also investigated by Krunks *et al.*<sup>16</sup> The authors have obtained ZnO films using an aqueous solution of zinc chloride (0.1M/L) by conventional spray pyrolysis. It was proved that at ST = 400°C, the films consist of

dense packed grains, 50-100 nm in size. At  $ST = 450^{\circ}\text{C}$  the crystals transform to cylindrical shape with 300 nm diameter and at  $ST = 490^{\circ}\text{C}$  to prismatic crystals with 200-300 nm diameter and 700 nm length. The samples prepared at  $560^{\circ}\text{C}$  revealed preferred (002) orientation.

Ma *et al.* obtained ZnO layers on (0001) sapphire substrates from zinc acetate by ultrasonic spray pyrolysis with different morphology at different ST.<sup>17</sup> The authors showed that at  $ST = 200^{\circ}\text{C}$  there is a transition from amorphous to grain polycrystalline structure with (002) orientation and grain size of 40 nm. At  $ST = 250^{\circ}\text{C}$  the (101) peak was detected. At higher temperature ( $ST = 280^{\circ}\text{C}$ ), the surface produced was extremely rough.

Transparent and conductive ZnO layers by ultrasonic spray pyrolysis, using a mixture of nitrogen (carrier gas) and oxygen (reactor gas) and zinc acetate were obtained in.<sup>18</sup> Zinc oxide thin films showed preferred grain growth along the (002) plane. The layers morphology was studied at different ST ( $350\text{--}500^{\circ}\text{C}$ ). At temperatures up to  $450^{\circ}\text{C}$  the layers are dense, while at  $500^{\circ}\text{C}$  they are porous.

Homogeneous layers of zinc oxide with crystallite size from 20 to 30 nm, (002) orientation and high optical transmission were produced by conventional spray pyrolysis.<sup>19</sup> It was proved that ST has an effect upon the microstructural features of the layers. Substrate temperature of  $320^{\circ}\text{C}$  was found critical and above which individual crystallites grow preferably in their crystallographic axis. Below this critical temperature the film losses orientation and the microstructure becomes more porous with crystalline aggregates.

Hwang *et al.* proved that the surface morphology is influenced by ST for zinc oxide transparent films produced by electrostatic spraying of zinc acetate dissolved in 2-methoxyethanol (0.6M/L).<sup>20</sup> The layers deposited at  $300^{\circ}\text{C}$  have more uneven surface with large crystallites, while at  $400^{\circ}\text{C}$  they are relatively smooth.

Zinc oxide films with different orientations were deposited from water-methanol solutions of zinc acetate (0.1M/L) at various ST in the range of  $300\text{--}500^{\circ}\text{C}$ .<sup>21</sup> It was established that at temperatures below  $420^{\circ}\text{C}$  the films are polycrystalline. At  $ST = 420^{\circ}\text{C}$  the films grow preferentially in (002) orientation, while at  $ST = 500^{\circ}\text{C}$  the orientation is changed to (100) direction.

Rao *et al.* have obtained ZnO photoluminescence films with polycrystalline, granular morphology by spraying of ethanol-water mixture of zinc acetate at  $ST = 350, 400$  and  $450^{\circ}\text{C}$ .<sup>22</sup> The grain size is found to increase as the substrate temperature increases. The samples prepared at  $400^{\circ}\text{C}$  exhibit uniform grains in comparison to the other two substrate temperatures. The increase in ST increases the atomic mobility and reduces the structural defects, thus a relaxation of the ZnO films is observed. The films deposited at lower temperatures exhibit strong compressive stress. The intensity of PL emission peaks is found to be varying with ST. The maximum intensity of the violet peak (420 nm) was observed for films, prepared at  $350^{\circ}\text{C}$  and can be attributed to the Zn vacancies. Electrical resistivity was found to decrease with the substrate temperature.

ZnO films were prepared by spray pyrolysis at different ST, selected from  $200^{\circ}\text{C}$  to  $500^{\circ}\text{C}$ .<sup>23</sup> The films were obtained from 0.3 M/L zinc acetate solutions. The XRD pattern for the  $200^{\circ}\text{C}$  deposited films corresponds to ZnO hexagonal polycrystalline structure. The films prepared at  $400^{\circ}\text{C}$  have a preferred growth orientation along the *c*-axis. ZnO usually grows in the (002) orientation due to the low surface free energy of the (002) plane. The (101) and (102) peaks also appear with increasing the ST above  $450^{\circ}\text{C}$ . All films are densely and uniformly covered. The surface of ZnO films deposited at  $200^{\circ}\text{C}$  and  $300^{\circ}\text{C}$  is covered by aggregates of small crystals. The ZnO layer consists of hexagonal-like microplates and nanoseeds when deposited at  $ST=400^{\circ}\text{C}$ . At this temperature, the solvent evaporates before the droplets reach the substrate and only solid precursor reaches the substrate where the decomposition occurs. Better crystallization and preferential (002) orientation of ZnO crystallites were observed. The ZnO films prepared at  $500^{\circ}\text{C}$  consist of seed and no plate was observed, because the zinc acetate decomposition occurs in the gas phase.

The effect of the substrate temperature on the crystallinity, band gap and crystallite size of ultrasonically sprayed ZnO thin films was also studied by Benramache *et al.*<sup>24</sup> The precursor solution was prepared by dissolving 0.1M  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  in ethanol with addition of monoethanolamine as a stabilizer. It was found that the intensity of the (002) orientation is weak for the films deposited at  $300^{\circ}\text{C}$ , but it increases with

increasing the ST to 350°C. However, the films deposited at 400°C showed weaker orientation in the *c*-axis plane. The crystallite sizes of the films prepared at the temperature range of 300–400°C were found similar.

A strong effect of ST on the crystallographic orientation, growth rate and morphology was observed in reference.<sup>25</sup> At very low ST (below 300°C), the films are not uniform and possess (101) preferred orientation. Between 300–400°C ST, the (002) orientation becomes more prominent, while the (101) and (100) peaks decrease. Dense and homogeneous (002) oriented ZnO films were prepared at ST=400–450°C.

## 2. Chemical nature of the zinc precursor

The chemical nature and solubility are very important characteristics of the precursor, which determines the final film morphology. The relatively low solubility of the zinc acetate is of major importance in the formation of reticular, porous structures. In contrast, the precursor of very soluble zinc nitrate results in dense films. Various zinc precursors are applied: (i) inorganic zinc salts (zinc nitrate and zinc chloride), (ii) organic: zinc acetate, (iii) zinc-ammonia complexes.

It was proved that the type of zinc precursor affects the morphology of ZnO layers.<sup>26</sup> The films were deposited at ST = 300, 400 and 500°C. When ZnCl<sub>2</sub> is used at ST = 400°C, polycrystalline layers with homogeneous grain structure and grain size from 40 to 60 nm have grown in (002) direction. If organic zinc compound – Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O is used, a preferred (101) orientation and linearly ordered individual particles with very fine crystallite size (18 nm) are formed.

Such diminishing of crystallite size for zinc oxide layers with organic zinc precursor was also observed by Messaoudi *et al.*<sup>27</sup> Films with crystal grain size around 1 micrometer were obtained from inorganic precursor solution (ZnCl<sub>2</sub>), while when Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O was used, the grain size was 1-2 orders of magnitude smaller. It was found that all films were highly transparent in the visible range.

The influence of three types of zinc precursors dissolved in water upon the morphology and orientation of the obtained layers was also studied.<sup>28</sup> The ZnO thin films are all in hexagonal crystallographic phase. ZnO films obtained using zinc chloride precursor had a high degree of preferential orientation along the *c*-axis. Zinc oxide

films grown by zinc nitrate and zinc acetate were polycrystalline. It was found that each precursor has a specific influence. The use of zinc nitrate results in production of indefinite grain boundaries. When zinc acetate is used as precursor, on relatively flat layer are formed elongated hexagonal crystalline islands, consisting of arbitrary oriented crystals of ZnO. From ZnCl<sub>2</sub> solution, relatively equal, ordered hexagonal large rods with diameter of 1 μm, oriented in (002) direction were obtained. Lehraki *et al.* also prepared ZnO thin films using these three precursors.<sup>29</sup> All precursors are dissolved in water to obtain concentration 0.1M/L. The physico-chemical properties of these solutions and their influence upon films growth rate were investigated. The obtained results indicated that surface tension and dissociation enthalpy of the solution play an important role in the droplet dynamic and in its final impact shape. Films deposited from zinc acetate are characterized by a smooth dense surface and high transparency, due to the low dissociation enthalpy of the zinc acetate. In the case of zinc chloride as starting solution, due to the high dissociation enthalpy of the latter, the droplets are not easily dissociated, which leads to nucleation only along the (002) plane. The resulting porous films have better crystallinity, but lower optical transmittance. Zinc nitrate solution, which has an intermediate value of dissociation enthalpy and surface tension, leads to ZnO films with intermediate structure, composed of (002) oriented crystallites embedded in an amorphous phase.

Transparent amorphous and crystalline nanostructured zinc oxide films were prepared by electrospray deposition technique using zinc nitrate and ammonia as precursors.<sup>30</sup> It was found that the addition of small amounts of diluted HNO<sub>3</sub> can have a direct effect on the morphology and crystallinity of the thin films. The films obtained from acidified solutions were dense, high crystalline and possess very small grains. Optical studies indicated that all of the films have a near band edge emission at 374 nm and an emission at 393 nm corresponding to ultra violet (UV) transmittance.

Highly oriented ZnO thin films were obtained by ultrasonically sprayed solution of zinc oxide, dissolved in aqueous ammonia solution and acidified with CH<sub>3</sub>COOH.<sup>31</sup> The films were prepared from low molarity and deposited at low ST (200–350°C). According to the XRD analysis the films possess wurtzite structure with preferential (002) orientation.

The Scanning Electron Microscopy (SEM) has shown that the films are dense with secondary particles on the surface.

Zinc oxide films were deposited from 0.1 M/L solution of zinc nitrate at ST = 400°C.<sup>32</sup> The films are polycrystalline with hexagonal wurtzite structure, strong *c*-axis orientation and grain size nearly 13 nm. SEM images of the films revealed a porous film structure with beads of different shapes, scattered throughout the surface. The films exhibited maximum gas sensitivity of 82% towards liquid petroleum gas at 350°C with short response and recovery time.

Homogeneous polycrystalline ZnO films with uniformly distributed oval particles (250-350 nm) are obtained by Goyal *et al.*<sup>33</sup> Aqueous solution of ZnCl<sub>2</sub> (0.4 M/L) was sprayed onto cleaned glass slides at 200°C, using home made spray equipment. The bandgap of ZnO and uniform electrical behavior are suitable for application in optical devices.

Stambolova *et al.* have proved that the films, prepared from polymer modified zinc nitrate solutions exhibit different morphology in comparison with the films obtained from modified zinc acetate sols.<sup>34</sup> The thin films consist of polycrystalline grains and no preferential growth is observed. The morphology of the acetate films prepared is relatively compact with crystallite size of about 15 nm. When zinc nitrate solution is used a typical film structure with aggregates of spherical shaped grains and very small crystallites is observed.

An interesting microstructure of ultrasonically sprayed ZnO films consisting of nanopetals was obtained in reference.<sup>35</sup> Zinc acetate dissolved in 2-methoxy ethanol and ethanolamine was sprayed using commercial ultrasonic nebulizer. The films were deposited at ST = 350°C for spraying periods of 30 and 60 minutes. The nanopetals dimensions increased drastically with spraying time. Film growth along the (002) crystallographic direction was observed, which is favoured for 30 min deposition time. All samples revealed remarkable photocatalytic activity, due to their good crystallinity and large surface area.

### 3. Concentration of the initial solution

The solution concentration influences important structural parameters such as: the films quality, the thickness, the porosity, the degree of crystallographic orientation, the grain size and some physical parameters like band gap etc.

The effect of solution concentration on the development of nanorod morphology was studied in reference.<sup>16</sup> Highly structured ZnO layers were deposited from zinc chloride aqueous solutions in the temperature range of 490–560°C. The Zn<sup>2+</sup> concentration of 0.02 M/L in the spray solution leads to the formation of separate crystals (200×200 nm). The use of more concentrated solutions of 0.05 mol/L results in elongated crystals (*d* = 100-300 nm). X-ray diffractograms also showed that solution concentration has an influence on the films orientation. The films obtained from low solution concentrations (0.05-0.1 M/L) have preferential (002) orientation, while higher concentration leads to a polycrystalline structure. Similar effects were obtained by J.L. van Heerden *et al.*<sup>21</sup> They have revealed that the films deposited from 0.05M/L zinc acetate solution have very definite (002) preferred orientation, while at higher molarity the (002) peak slightly decreases. Hosseinmardi *et al.* also revealed that low precursor concentrations could be used to obtain a uniform fine grained coating with low roughness.<sup>30</sup> The films were prepared from aqueous solution of zinc nitrate and ammonia (25%) with 3-4 drops of nitric acid.

Various microstructures of ZnO layers were obtained by ultrasound spray pyrolysis (frequency 920 kHz) using 0.1 and 0.2 M/L zinc nitrate solutions.<sup>36</sup> All films have shown preferential (002) orientation. The layers obtained from 0.1 M/L solutions are porous with crystallite size of 20 nm. At 0.2 M concentration the layers are dense and compact. The films possess good gas sensitivity characteristics to liquid petroleum gas (LPG), which depends upon their grain size.

Transparent zinc oxide thin films were deposited onto glass substrates at ST = 450°C from aqueous zinc acetate solution.<sup>37</sup> The solution concentration was varied from 0.1 to 0.4 M. The synthesized films were found to be polycrystalline, with preferential growth along the *c*-axis. A slight improvement in the texture coefficient is observed as the concentration of the solution is increased. The samples are hydrophobic with high transparency. These properties are of great importance in commercial applications such as transparent self-cleaning surfaces, anti-fog, anti-snow, fluid microchips and microreactors.

Zinc oxide films were deposited from zinc acetate solutions with molar concentrations of 0.05 M, 0.10 M and 0.15 M.<sup>38</sup> The study confirms that all films are polycrystalline in nature with hexagonal wurtzite crystal structure. The band gap

energy increases with molar concentration and reaches a maximum value of 3.2 eV at concentration of 0.15 M. High resolution scanning electron microscopy shows a uniform distribution, densely packed grains with a plate like structure of 55 nm, when 0.05 M solutions are used. The texture coefficient for the (002) plane increases with the increasing of concentration. On the other hand, the texture coefficient for the (100) and (101) planes was found to be decreasing with increasing of molar concentration. The lattice parameters and crystallite sizes for the films, obtained from different solutions are constant. The room temperature PL spectrum of the films shows an emission in the blue spectral region. The films also exhibited good sensing properties for detection of low ammonia concentrations at 50°C, which makes them suitable for gas sensor devices. The similar effect of zinc acetate concentration on the films morphology and orientation was observed by Shinde *et al.*<sup>39</sup> The precursor was dissolved in double distilled water and the resulting solution was sprayed onto corning glass substrates with different concentrations ranging from 0.05 to 0.15 M. As the solution concentration increased, the intensity of the (002) plane increased and the (101) plane decreased evidently up to 0.1 M and vice versa. The films were uniform and compact with average grain size from 50 to 150 nm. The roughness and grain size increased with concentration up to 0.1 M and then decreased at higher concentrations. At higher than 0.1 M concentrations, hexagonal platelets grew as cluster of agglomerated grains. As solution concentration increased electrical and thermal conductivity have increased up to 0.1 M concentration and then decreased for higher concentrations. Goyal *et al.* explained the effect of increased solution molarity (0.02-0.2 M/L) on the improved (002) texture coefficient of ZnO films by incorporation of zinc in the interstitials of the crystal lattice.<sup>40</sup>

#### 4. Acidity of the initial zinc solution

The acidity of the initial solution of zinc precursor also plays a certain effect on the final microstructure and crystallite size of the layers. Investigators concluded that the selective absorption of acidic species inhibits the films growth along specific crystallographic surfaces. Rodriguez – Baez *et al.* proved that the increase of acetic acid content inhibits grain growth and leads to a switching from (002) to (101) preferential

orientation.<sup>41</sup> They used aqueous solution of zinc acetate with acetic acid as additive. The layers consisted of agglomerated grains (60 nm) and rodlike grains (about 250-300 nm). Moreover, when the concentration of the acetic acid in the initial solution is increased, the acidity level raises, which results in a finer grain structure.

Zinc oxide films with different porosity were obtained by ultrasound spray pyrolysis.<sup>42</sup> It was established that the specific surface area of the layers increases as pH changes from 2 to 5. At pH = 5 porous layers are formed and as a result they have high photocatalytic activity towards degradation of methyl orange dye. At low pH the films are more compact. The acidity of the solution has not significant influence on the crystal structure and films orientation. All films are well crystallized and randomly oriented.

#### 5. Type of solvent and polymer additions in the initial zinc solution

The type and concentration of the solvent affects strongly the films morphology and the preferential orientation. The high evaporation rate of the solvent in the spray cone while it transit from the spray nozzle to the substrate leads to a loss of material during the condensation. As a result the surface morphology of the deposited films highly uneven and powdery. The high boiling point of the solvents can keep the aerosol droplets wet until they impinge and spread out on the substrate surface, which leads to formation of porous structure. In order to lower the solvent evaporation various compounds as water,<sup>43-45</sup> propanol,<sup>46</sup> TEG<sup>47</sup> etc are applied.

It was demonstrated that the morphology and photocatalytic properties of ZnO layers depend on the water/ethanol ratio (R).<sup>43</sup> The morphology of the ZnO films obtained from R = 0-0.92 is dense with uniformly distributed agglomerates, whereas the films obtained from R = 0.03-0.31 are very rough. The films consist of zincite-like structure regardless of R. The size of crystallites also depends on the water/ethanol ratio in the solution. The films obtained from solutions with R = 0.12 are rough and possess the smallest crystallites and high photocatalytic activity.

The preferential orientation of the plane (100), as well as the films crystallinity, were found to be sensitive to ethanol concentration.<sup>44</sup> Zinc acetate was dissolved in a mixture of ethanol and

deionized water. A switching in the preferential growth from the random orientation to the (100) plane was observed with increasing of ethanol concentration from 10% to 50%. The crystallites size increased from 18 nm to 25 nm with the initial addition of 10% ethanol and was found to have a decreasing trend with further enhancement of the ethanol concentration. Bushiri *et al.* have used a water-ethanol mixture as solvent in order to enhance the evaporation rate, because of the poor solubility of zinc acetate in pure ethanol.<sup>45</sup> It was proved that the ethanol-water ratio of 4:1 is a good option for fast evaporation and homogeneity of the precursor solution. The films consisted of fine nanostructures with almost granular morphology. Most of the granules were less than 20 nm. The cathodoluminescence (CL) properties of the films were also investigated. The CL spectrum showed a broad band with intense contribution at around 385 nm due to NBE emission, which is usually related to oxygen deficiency.

ZnO thin films were deposited from aqueous acetate solution, mixed with different volumes of ethanol (ZE) or 2-propanol (ZP).<sup>46</sup> The grain size enhanced from 22 nm to 45 nm with increasing the ethanol concentration, while the variation of propanol did not affect the grain size much. The increase in grain size with the variation of the precursor solution concentration may be due to the difference in the boiling points of the two alcohols, resulting in the different 'residence time' of the drop on the hot substrate. The authors also reported that the ZnO samples prepared with ZP solution have lower resistivity, better crystallinity and higher optical transmission. According to the PL spectra of ZE and ZP films two emission peaks centred at 377 nm ('Near Band Edge' (NBE) emission) and at 500 nm ("blue-green emission") were registered. The intensity of NBE emission changed with the variations of concentrations of the alcohols in the precursor solutions. The films prepared from solutions with 70% propanol showed maximum height of NBE peak.

Nehru *et al.* have added triethylene glycol (TEG) into the zinc acetate solution, which results in reducing of both premature evaporation of the solvent in the spray cone while it transit from the nozzle to the substrate and the resultant loss of material during the condensation.<sup>47</sup> This made the surface morphology of the deposited films highly uneven and powdery. The morphology of the as-deposited ZnO thin films was amorphous and

made up of very small grains, which were packed closely and well distributed on the glass substrate. After annealing at 400°C–450°C, the grains became larger in size compared to the as-deposited ZnO which may be due to the crystallite growth by heat treatment. The luminescence spectrum of all samples revealed two main peaks located at about violet (418 nm) and green (525 nm). The films have shown about 80% optical transmittance in the visible region.

## 6. Spray rate

The carrier gas flow rate ( $f$ ) affects the size and velocity distribution of the droplets, which in turn affects the dynamics of the impingement.

T. V. Vimalkumar *et al.* observed that the spray rate played a decisive role in controlling the uniformity, the adhesion of the films, the grain size and crystallographic orientation – the experiments were carried out at various spray rates in the range of 3 mL/min–12 mL/min.<sup>48</sup> At low spray rates the films are randomly oriented, while the increased spray rate leads to a (002) preferred orientation. The transition in orientation was observed for the rates of 6 ml/min and onwards. When the spray rate is increased the grain size increases and the grains possess uniform orientation. The maximum intensity for the green emission of PL spectra has obtained for the samples deposited at  $f = 7$  mL/min. The structural and luminescence properties of ZnO thin films were also investigated by varying the flow rate in the region 2.5–7.5 mL/min.<sup>49</sup> An aqueous solution of  $\text{ZnCl}_2$  was used as precursor. The grain size of the films increased when the  $f$  increased from 2.5 to 5 mL/min, then decreased. The decrease in grain size with the flow rate beyond rate 5 mL/min appears to be mainly the effect of the non-incorporation of Zn particles on the material surface. The best crystallinity and luminescence were achieved with samples grown at flow rate 5 mL/min. At high flow rate (above 6 ml/min) a degradation of crystallinity was observed. The thin films exhibit three emissions in the PL spectra: near ultra-violet (UV) - band gap peak (382 nm), a blue-green emission (520 nm) and a red emission (672 nm).

A representative summary of the discussed properties of the ZnO thin films, sprayed at different deposition parameters is presented in Table 1.

Table 1

Representative summary of some properties of ZnO thin films, sprayed at different deposition parameters

\* ZA – Zn(CH<sub>3</sub>COOH).2H<sub>2</sub>O; ZN – Zn(NO<sub>3</sub>).6H<sub>2</sub>O; ZC – ZnCl<sub>2</sub>

Precursor*	Molarity	Solvent	ST (°C)	Morphology	Grain size (nm) {crystallites size}	Orientation	Reference
ZA	0.05 0.1 0.15	Water	400	Smooth, dense, non-uniform Flake net-like structure Nanorod structure	{76} {77} {76}	Random Random (002)	38
ZA	0.05-0.15	Water	450	Uniform and compact	50-150	(002) > 0.1M/L	39
ZA	0.1	Ethanol-water (R = 0 - 0.92)	–	Dense (R = 0-0.92) Rough (R = 0.12-0.3)	30-50	Random	43
ZA	0.1	Ethanol-water (0-10):100 (20-50):100	450	–	18-25 < 18	Random (100)	44
ZA	0.1	Water-methanol (1:3)	300-400 420 500	–	–	Random (002) (100)	21
ZA	0.1 0.2 0.3	Water	450	Non-uniform distributed spherical grains Uniform and compact Rough with agglomerates	{41-44}	(002)	37
ZA	0.3	Water-methanol (1:3)	200-300 400 450-500	Grained structure Hexagonal-like microplates Nanoseeds	32 39 48-41	Random (002) Random	23
ZA	0.3	Water-ethanol (ZE = 0:100) Water-propanol (ZP = 0:100)	450	Changes from ‘spindel-like’ structure to uniform with increasing of ethanol concentration	22-45	Random (002) peak increases with increasing ZE or ZP ratio	46
ZA	0.4	Water-acetic acid (S = 7:100 ~ 40:100)	450-500	Agglomerated grains Rod-like grains	60 250-300	(002) up to S = 10:100 (101) for S > 20:100	41
ZA	0.75	Water	450	Nanopetals	25 (thickness) 100-150 (length)	(002)	35
ZA	–	Water-isopropanol (2:3)	250-400 >450	Dense film Spherical grains	{50-100} two distinct sizes: 50-100 / 300-500	(100) (002)	14

Table 1 (continued)

ZA ZC	0.01	Water	300-500	Grained structure	18 40-60	(101) (002)	26
ZA ZC ZN	0.1	Water	200-500	Smooth and dense Porous structure Grained structure	15 245 200	Random, low crystallized (002) (002) embedded in amorphous phase	29
ZA ZC ZN	0.1	Water	550	Hexagonal crystal islands Hexagonal rods Non-uniform surface with indefinite grain boundaries	>1000 1000	Random (002) Random	28
ZA ZN	0.2	Water-ethanol (1:3)	300-400	Porous structure Fine grained structure	{15} {8-12}	Random	34
ZN	0.1	Water	400	Porous structure with beads on the surface	13	(002)	32
ZN	0.1 0.2	Water	350	Porous structure Dense film	{20} {29}	(002)	36
ZnO	0.025	Water-ammonia	200-300	Compact grained structure with secondary particles	{30}	(002)	31

## CONCLUSIONS

Spray pyrolysis is a largely applied chemical method for deposition of nanosize ZnO films with various properties. Zinc acetate is preferred for spray pyrolysis preparation due to its high dissolution in water or ethanol-water mixture as well as the decomposition of the salt at relatively low temperature.

Different factors play decisive role upon the morphology and crystallite size of the films, such as substrate temperature, type of precursor, solvent etc. It is possible to obtain ZnO films with various morphologies: dense, porous, nanopetals, spherical grains, ganglia-like, dendrite-like, hexagonal-like microplates, columnar-like, grained etc. The choice of suitable synthesis parameters is also important for the crystal structure and orientation. Most of the authors have proved that the zinc oxide films preferentially growth along *c* axis at elevated ST (in the range 300-450°C). As a rule below ST=300°C the films are randomly oriented. Switching the orientation from (002) to (100) or (101) can be achieved by changing both substrate temperature and solution concentration. Thus the spray pyrolysis method is suitable for preparation of ZnO thin films with wide range of potential applications e.g. (i) optical and optoelectronic devices; (ii) gas sensors; (iii) catalysts and photocatalysts.

Great attention is paid to the effects of substrate temperature, precursor, solution molarity and type of solvent on the morphology and crystal structure. On the other hand, the articles devoted to the influence of flow rate and acidic species on the films growth and surface structure are relatively scarce. Moreover, the investigations concerning the effect of polymer additions on physicochemical properties of ZnO films are not sufficient.

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