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LABORATORY OF THIN FILM CHEMICAL TECHNOLOGIES

Deposition of ZnO and ZnO:In thin films by chemical spray on glass and polymeric substrates

Master Thesis

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Materials and Processes of Sustainable Energetics

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Declaration

Hereby I declare that this master thesis, my original investigation and achievement, submitted for the master degree at Tallinn University of Technology has not been submitted for any degree or examination.

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ZnO ja ZnO:In kilede kasvatamine keemilise pihustamise meetodil klaas- ja polümeersetel alustel

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Table of contents

List of abbreviations and acronyms

Al – aluminium

at.% – atomic percent

B – boron

CVD – chemical vapour deposition

F – fluorine

FTO – fluorine doped tin oxide; SnO_2:F

Ga – gallium

In – indium

$InCl_3$ – indium chloride

IR – infrared

ITO – indium tin oxide (tin-doped indium oxide; In_2O_3:Sn)

LCD – liquid crystal display

n – charge carrier concentration, [cm^{-3}]

PV – photovoltaic

SEM – scanning electron microscopy

Zn – zinc

ZnO – zinc oxide

ZnO:In – indium doped zinc oxide

T_{Sn} – tin bath temperature, [°C]

T_{Sub} – growth temperature, [°C]

UV – ultraviolet

UV-VIS-NIR – ultraviolet visible near infrared spectroscopy

V – spray solution volume, [ml]

v – solution spraying rate, [ml/min]

XRD – X-ray diffraction

Zn – zinc

ZnO – zinc oxide

ZnO:In – indium doped zinc oxide

μ – charge carrier mobility, [cm^2/(V·s)]

ρ – resistivity, [Ω·cm]

1. Introduction

Nowadays, nearly ⅔ of the electricity produced on Earth comes from fossil fuels[1]. Since the fossil fuel sources are limited and the population on Earth increases rapidly, the need for new energy resources is needed.

Many consider nuclear power to be the solution for supplying the electricity needed. However, nuclear power has its advantages and disadvantages, some may say that nuclear power is not the answer to provide world energy on long term in sustainable way. Instead of using one particular resource for the production of energy, several different energy resources should be used by increasing the amount of energy produced from renewable sources year by year.

Renewable energy is energy that is produced from naturally replenishing resources. The renewable resources are geothermal heat, wind, biomass, rain, streaming water (e.g. tide) and the sun. Most of the renewably produced worldwide electricity is generated from hydropower (nearly 17% in 2010) and 1.6% was produced from wind[1]. In 2010, only 0.2% of the worldwide electricity was produced from solar power. Western Europe produced nearly 69% of the worldwide electricity obtained from solar sources where Germany produced 36.1% and Spain 21.2%[1].

Solar energy is the radiant energy produced by the sun. The sunlight can be collected and converted into electricity via photovoltaics. Photovoltaics (PV) is known for generating electric power by using solar cells to convert energy from the sun directly into electricity. At the moment, the crystalline silicon solar cells dominate the PV module production[2]. However, the production of these thick silicon solar cells in expensive due to the high cost of materials and high preparation process temperatures[2]. Thin film solar cells are 200 times thinner and thus bear a potential to reduce the cost of PV solar cells due to low material consumption, simple production methods and high productivity by depositing on large areas[2]. The energy payback time for thin film solar cells is shorter due to lower processing temperatures and low material consumption[2].

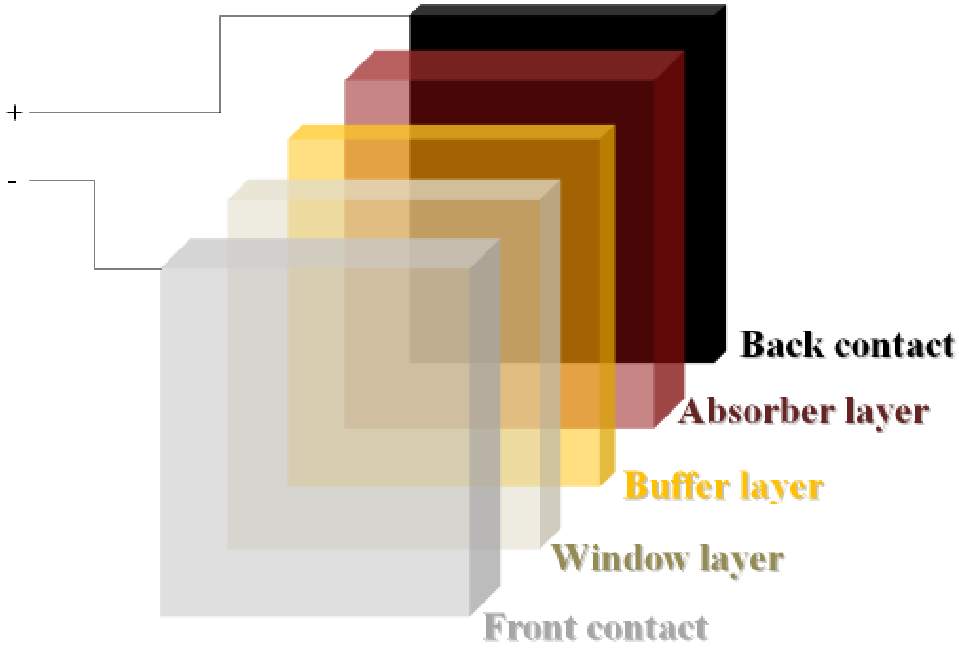

Figure 1 Layers of thin film solar cell.

A typical thin film solar cell is presented in Figure 1. Back contact (e.g. Mo) is at the end of the solar cell. Then an absorber layer ($CuInS_2$, $CuInGaSe_2$) is follows. The next layer is the buffer layer (e.g. In_2S_3). Then comes the window layer (e.g. ZnO). The final layer, transparent conductive oxide (ITO etc.) is pointed towards the sun.

In this thesis, research on depositing ZnO and indium doped ZnO on glass and polymeric substrates and studying their properties has been carried out. If doped ZnO is grown as transparent and as conductive as possible, it can substitute ITO and FTO as front contact and lower the price of solar cells and other devices where ZnO could be used.

At the moment, this study is an ongoing cooperation with Justus Liebig University in Giessen, Germany with prof. Derck Schlettwein and doctoral student Max Beu.

2. Literature overview

2.1. ZnO properties and applications

ZnO is a semiconducting compound of the group IIb element zinc and the group VI element oxygen. The natural crystal structure of ZnO is the hexagonal wurtzite structure[3, 4] (see Figure 2). ZnO occurs naturally as the rare mineral zincite but most zinc oxide is produced synthetically[2].

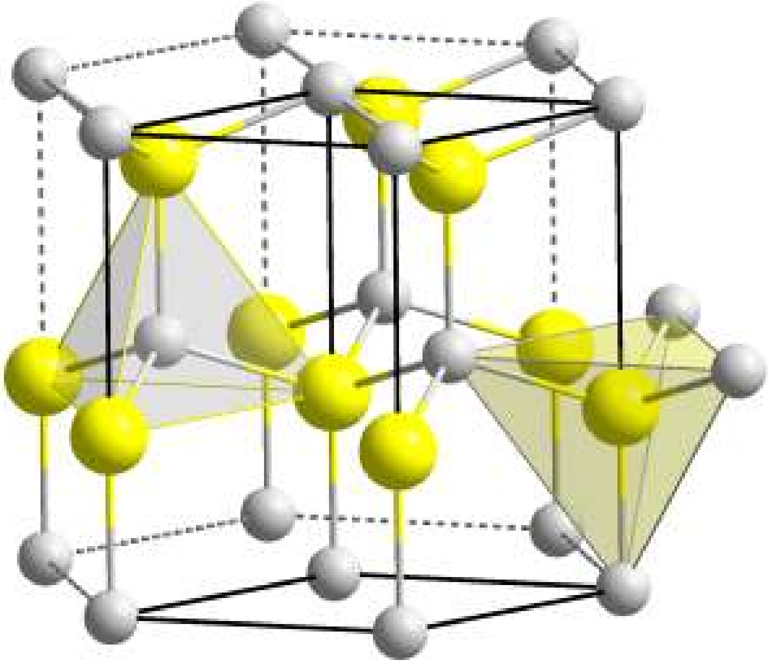

Figure 2 One possible ZnO hexagonal structure – wurtzite[5].

ZnO is a wide band gap semiconductor with n-type conductivity due to oxygen vacancies[2]. ZnO has been used in several applications due to its various properties[2, 3, 5] e.g. good optical transparency in visible (~90%) and near infrared part of the spectrum due to the direct band-gap of ~3.37 eV, high stability at room temperature, good piezoelectric properties. For instance, ZnO has been used as transparent electrodes in LCD's, in energy saving or heat-protecting windows and in thin films transistors, light-emitting diodes in electronics, etc[2, 4, 5]. ZnO is used also in paint pigments, as a flux in ceramic glazes, as a filler material for rubber products, coatings for paper, sunscreen and sun blocks for preventing sunburn due to its ability to absorb UV light[5]. Although the study of ZnO in depth started from the mid 1930's, it has drawn the attention as the future material with the development of the second generation solar cells.

The 2nd generation solar cells are most frequently associated with thin film solar cells. These types of solar cells are called thin films because they are several micrometers thick. The 2nd generation solar cells are designed using minimal materials and cheap manufacturing processes to lower the cost of solar cells[3]. ZnO can be used as a component of p-n junction and a window layer material or as a front contact in the 2nd generation solar cells. If ZnO is used as a front contact, it has to been as transparent and as conductive as possible. Due to the low cost, abundance and the simplicity of producing ZnO, this semiconductor can substitute expensive ITO and FTO that are currently used as front contacts in solar cells[2].

2.2. Techniques for preparing ZnO thin films

ZnO thin films with different morphology can be prepared by a number of physical and chemical methods. Some physical methods for the deposition of ZnO thin films are molecular beam epitaxy (MBE), electron beam evaporation, sputtering, pulsed laser deposition (PLD), aerosol spraying (evaporation from solution), ion beam deposition[2, 3, 5, 6, 7]. Chemical methods can also be divided according to the phase of the source: gas phase methods (chemical vapour deposition, atomic layer deposition, etc.) or liquid source methods (dip-coating, spin coating, sol-gel, spray pyrolysis, etc.)[2, 3, 5, 6, 7].

In this present work, spray pyrolysis was used to grow transparent and conductive ZnO thin films.

2.3. Deposition of ZnO thin films by spray pyrolysis

2.3.1. Spray pyrolysis in general

Spray pyrolysis is a process in which a thin film is grown by spraying a spray solution onto a heated surface. On the heated surface, the dissolved precursors in spray solution go through a thermal decomposition to form the needed chemical compound[8]. As an example, for ZnO the constituents can be zinc acetate, 2-propanol, deionized water, acetic acid and for ZnO:In, also indium chloride to prepare the spray solution. The reactants for spray pyrolysis are selected such that unwanted products are volatile at the deposition temperature leaving behind only desired compound[8]. Spray pyrolysis is especially useful for the deposition of oxides[8].

Spray pyrolysis system consists of an atomizing nozzle, substrate heater, temperature controller and liquid flow and gas flow meters[6, 7, 8]. The substrate heater is a metal block or a liquid metal bath[8]. A thermocouple connected to temperature controller is used to regulate the growth temperature[8]. As a carrier gas, air can be used or inert gas when oxidation of chemicals is a problem[8]. Due to the inevitability of uneven deposition thickness, a random motion of the spray head, the substrate or the movement of both is needed to obtain as uniform deposition thicknesses as possible[8].

The typical spray pyrolysis equipment is presented in Figure 3.

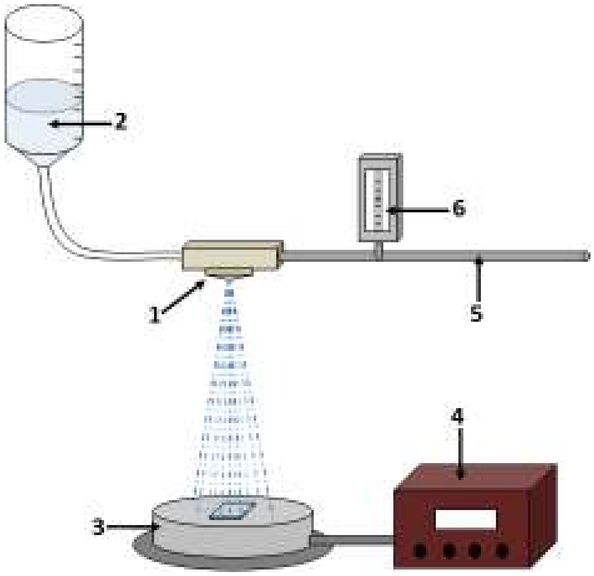

Figure 3 Typical spray pyrolysis equipment. 1 – atomizing nozzle; 2 – spray solution; 3 – hot plate; 4 – temperature controller; 5 – carrier gas flux tube; 6 – gas flow meter.

The advantages of spray pyrolysis[6, 7, 8]:

- ◊ Low operational cost;
- ◊ Simple facilities;
- ◊ Ambient operation;
- ◊ Potential for mass production;

- Reproducibility of films;
- Large surface area coverage;
- The ease of doping with suitable element in a required ratio.

Doping can be possible if the precursors are soluble in solvent and the course of solubility is similar. Doping with suitable element in a required ratio is easy due to homogeneous solubility, therefore the film is homogeneously doped throughout the film.

The disadvantages of spray pyrolysis[7, 8]:

- Limited amount of suitable precursors;
- The three dimensional growth of the film;
- The properties of deposited thin films depend on many deposition parameters that can be hard to control.

The properties of spray deposited thin films depend on[6, 8]:

- Precursor and precursor concentration in spray solution;
- Solvent;
- Dopant and dopant concentration in spray solution;
- Growth temperature;
- Growth environment;
- Substrate properties
- Spray set-up etc.

2.3.2. The effect of zinc source on the properties of sprayed ZnO thin films

In spray pyrolysis technique, several sources for zinc can be used. The most frequently used zinc sources are zinc chloride ($ZnCl_2$), zinc acetylacetonate ($Zn(C_5H_7O_2)_2$), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and zinc acetate dihydrate ($Zn(C_2H_4O_2)_2 \cdot 2H_2O$).

Experimental details and obtained results of several studies of ZnO thin films are presented in Table 1 and Table 2.

Table 1 Experimental details and properties of sprayed undoped ZnO thin films.

Experimental details			**Film properties**			**Reference**
Zinc source, concentration	**Solvent,** ratio or ml	**Temperature**	**XRD** preferred growth	**Transmittance,** %	**Electrical properties –** ρ, Ω·cm μ, $cm^2/(V·s)$ n, cm^{-3}	
$Zn(C_2H_4O_2)_2·2H_2O$ 0.02 M	Ethanol	T_{Sub}=400°C	Not presented	Not presented	ρ: 0.8 μ: 0.5 - 1.5 n: 5 - $8·10^{18}$	9
$Zn(C_2H_4O_2)_2·2H_2O$ 0.2 M	2-propanol & deionised water (3:2)	T_{Sub}=400°C	(002)	<70%	ρ: 20 μ, n: not presented	10
$Zn(C_2H_4O_2)_2·2H_2O$ 0.01 M	Water	T_{Sub}=300°C – 500°C	(002)	Not presented	ρ: 321 μ, n: not presented	11
$ZnCl_2$ 0.01 M				80%	ρ: 78 μ, n: not presented	
$Zn(C_2H_4O_2)_2·2H_2O$ 0.1 M	Methanol	T_{Sub}=350°C	(002)	75%	ρ: 0.5 μ, n: not presented	12
$Zn(C_2H_4O_2)_2·2H_2O$ 0.7 M	Methanol & deionised water (3:1)	T_{Sub}=450°C	(100)	80%	ρ: 0.08 μ: 8 n: 10^{19}	13
$Zn(NO_3)_2·6H_2O$ 0.15 M	Water	T_{Sub}=500°C	(002)	85%	ρ: 140 μ, n: not presented	14
$Zn(NO_3)_2·6H_2O$ 0.2 M					ρ: 110 μ, n: not presented	

$Zn(C_2H_4O_2)_2\cdot 2H_2O$ 0.05 M	Methanol & deionised water (3:1)	T_{Sub}=300°C – 500°C	(002)	Not presented	ρ: 200 μ, n: not presented	[15]
$Zn(C_2H_4O_2)_2\cdot 2H_2O$ 0.2 M	Water & 2-propanol (2:3)	T_{Sn}=350°C – 590°C	Not presented	50% - 85%	ρ, μ, n: not presented	[16]
$Zn(C_2H_4O_2)_2\cdot 2H_2O$ 0.1 M	Deionised water & ethanol (9:1)	T_{Sub}=350°C	(100)	>75%	ρ: 527 μ: 0.20 n: $5.9\cdot 10^{15}$	[17]
		T_{Sub}=400°C			ρ: 320 μ: 0.26 n: $7.3\cdot 10^{15}$	
		T_{Sub}=450°C			ρ: 270 μ: 0.34 n: $6.8\cdot 10^{15}$	
$Zn(C_2H_4O_2)_2\cdot 2H_2O$ 0.1 – 0.4 M	Water	T_{Sub}=210°C – 435°C	(002)	85%	ρ, μ, n: not presented	[18]
$Zn(C_2H_4O_2)_2\cdot 2H_2O$ 0.1 – 0.4 M	Water & 2-propanol (2:3)	T_{Sn}=220°C – 430°C	(002)	<70%	ρ: >1 μ, n: not presented	[19]

Table 2 Experimental details and film properties of sprayed doped ZnO thin films.

Experimental details					**Film properties**			**Reference**
Zinc source, concentration	**Solvent,** ratio or ml	**Doping element, concentration**	**Dopant source**	**Temperature**	**XRD** preferred growth	**Transmittance,** %	**Electrical properties –** ρ, Ω·cm μ, $cm^2/(V·s)$ n, cm^{-3}	
$Zn(C_2H_4O_2)_2·2H_2O$ 0.02 M	Ethanol	Al 0.5 – 10 at.%	$Al(C_5H_7O_2)_3$	T_{Sub}=400°C	Not presented	85%	ρ: not presented μ: 30 n: $3·10^{20}$	9
$Zn(C_2H_4O_2)_2·2H_2O$ 0.2 M	Water & 2-propanol (2:3)	In 0 – 4 at.%	$In(NO_3)_3$ & $InCl_3$	T_{Sub}=400°C	(101)	80%	ρ: 10^{-3} μ, n: not presented	10
$Zn(C_2H_4O_2)_2·2H_2O$ 0.01 M	Water	Al 0 – 3 at.%	$AlCl_3·6H_2O$ or $Al(NO_3)_3$	T_{Sub}=400°C	(002)	Not presented	ρ: 1.3 μ, n: not presented	11
$ZnCl_2$ 0.01 M	Water	Al 0 – 3 at.%	$AlCl_3·6H_2O$; $Al(NO_3)_3$	T_{Sub}=400°C	(002); (101)	80%	ρ: 0.8 μ, n: not presented	11
$Zn(C_2H_4O_2)_2·2H_2O$ 0.1 M	Methanol	In 0 – 8 at.%	$InCl_3$	T_{Sub}=350°C	(002)	65 - 85%	ρ: 0.17 μ, n: not presented	12
$Zn(C_2H_4O_2)_2·2H_2O$ 0.7 M	Deionised water methanol & (1:3)	B 0 – 5 at.%	H_3BO_3	T_{Sub}=450°C	(002)	>90%	ρ: $2.54·10^{-3}$ μ: 28 n: $9·10^{19}$	13
$Zn(C_2H_4O_2)_2·2H_2O$ 0.05 M	Deionised water methanol & (1:3)	F 0 – 1 at.%	NH_4F	T_{Sub}=300°C – 500°C	(002)	90%	ρ: 10^{-1} μ: 7 n: $6·10^{19}$	15
$Zn(C_2H_4O_2)_2·2H_2O$ 0.2 M	Water & 2-propanol (2:3)	In 3 at.%	$InCl_3$	T_{Sn}=420°C – 510°C	(101)	70% - 85%	ρ: $6.9·10^{-3}$ μ: 15 n: $7.5·10^{19}$	16

$Zn(C_2H_4O_2)_2\cdot 2H_2O$ 0.2 M	Water & 2-propanol (2:3)	In 0 – 5 at.%	$InCl_3$	T_{Sn}=350°C	(101)	<70%	ρ: >1 μ, n: not presented	19
$Zn(C_2H_4O_2)_2\cdot 2H_2O$ 0.2 M	Methanol	In 0 – 4 at.%	$InCl_3$	T_{Sub}=285°C	(002)	80%	ρ: $6\cdot10^{-3}$ μ: 21 n: $4\cdot10^{19}$	20
$Zn(C_5H_7O_2)_2\cdot H_2O$ 0.1 M	Deionised water, methanol, acetic acid (30:55:15)	In 1 – 5 at.%	$InCl_3$	T_{Sub}=450°C – 525°C	(002)	85%	ρ: $3.2\cdot10^{-3}$ μ: 7.5 n: $2\cdot10^{20}$	21
	Deionised water, ethanol, acetic acid (30:55:15)				(002)		ρ: $3\cdot10^{-3}$ μ: 9.5 n: $1.5\cdot10^{20}$	
	Deionised water, 2-propanol, acetic acid (30:55:15)				(002)		ρ: $2.8\cdot10^{-3}$ μ: 8.5 n: $1.3\cdot10^{20}$	
$Zn(C_2H_4O_2)_2\cdot 2H_2O$ 0.2 M	Deionised water, methanol, acetic acid (300:675:25)	Al 0.5 – 8 at.%	$C_{17}H_{25}AlO_8$	T_{Sub}=500°C	(002)	85%	ρ: $1.3\cdot10^{-2}$ μ: 1 n: $6\cdot10^{20}$	22
	Deionised water, ethanol, acetic acid (300:675:25)						ρ, μ, n: not presented	
	Deionised water, 2-propanol, acetic acid (300:675:25)						ρ, μ, n: not presented	
$Zn(C_2H_4O_2)_2\cdot 2H_2O$ 0.02 M $ZnCl_2$ 0.02 M	Water	Al 0 – 5 at.%	$AlCl_3$	T_{Sub}=350°C	Not presented	80%	ρ: 10^{-2}	23
$Zn(C_2H_4O_2)_2\cdot 2H_2O$ 0.2 M	Deionised water, methanol, acetic acid (25:65:10)	Ga 3 at.%	$Ga(NO_3)_3$	T_{Sub}=475°C	(002)	80%	ρ: $1.5\cdot10^{-2}$ μ, n: not presented	24
		Al 3 at.%	$Al(C_5H_7O_2)_3$		(002)	90%	ρ: $4\cdot10^{-2}$ μ, n: not presented	
		In 3 at.%	$InCl_3$		(101)	80%	ρ: $8\cdot10^{-3}$ μ, n: not presented	

$Zn(C_2H_4O_2)_2\cdot 2H_2O$ 0.2 M	Deionised water, acetic acid, methanol (25:10:65)	Ga 0.5 – 3 at.%	$Ga(NO_3)_3$	T_{Sub}=400°C	(002)	90%	ρ: $9.37\cdot 10^{-3}$ μ, n: not presented	25
$Zn(C_5H_7O_2)_2\cdot H_2O$ 0.2 M	Deionised water, methanol, acetic acid (300:150:550)	In 1 – 8 at.%	$In(NO_3)_3$	T_{Sub}=450°C – 525°C	(101)	85%	ρ: $4.8\cdot 10^{-3}$ μ, n: not presented	26
	Deionised water, ethanol, acetic acid (300:150:550)				(101)	70%	ρ: $3.8\cdot 10^{-3}$ μ, n: not presented	
	Deionised water, 2-propanol, acetic acid (300:150:550)				(101)	80%	ρ: $4.7\cdot 10^{-3}$ μ, n: not presented	

Only few research groups have compared the use of different zinc sources. However, the results obtained in different studies are incomparable due to different deposition conditions and spray set-ups. Romero et al.[11] found that different zinc sources affected the morphology and crystallinity of the films; smoother films were grown when zinc acetate was used as a precursor which was also confirmed by Arca et al.[27]. The use of zinc chloride led to rough discontinued layers (nanorods, nanopillars, etc.) as studied by Arca et al.[27], Krunks et al.[28] and many more. Krunks et al.[28] concluded that high roughness of the films prepared by spray of $ZnCl_2$ solutions is due to the formation of ZnO nanopillars. While Arca et al.[27] tend to think that these layers could be attributed to the formation of oxychloride that ends with the formation of ZnO and coproduct HCl that induced a chemical etching of the surface[27]:

$$ZnCl_2 + H_2O \rightarrow ZnCl_2{\cdot}4Zn(OH)_2{\cdot}5H_2O \rightarrow ZnO + 2HCl \qquad (1)$$

According to Arca et al.[27], the chemical etching of the surface could be responsible for the roughness of the ZnO film grown from zinc nitrate precursor solutions. Arca et al.[27] also state that the TG-DTA studies showed that the thermal decomposition of the $Zn(NO_3)_2{\cdot}6H_2O$ is a complex process for which different pathways are available. In that case the overall reaction could be[27]

$$Zn(NO_3)_2{\cdot}6H_2O \rightarrow ZnO + NO_2 + NO + O_2 + 6H_2O \qquad (2)$$

The orientation of the crystallites in the films was also affected by the precursor used to prepare the spray solution. Bigger crystallites and strongly c-axis oriented thin films were grown when zinc chloride was used[11, 27, 28].

It is proposed by Paraguay et al.[18] that the following reactions take place on the heated substrate when zinc acetate dihydrate is used like in the experiments presented in this study:

$$Zn(CH_3COO)_2 \rightarrow 4Zn(CH_3COO)_2 \rightarrow Zn_4O(CH_3COO)_6 \rightarrow 4ZnO + 6CH_3COOH\uparrow \qquad (3)$$

Arca et al.[27] stated that besides CH_3COOH other organic volatile compounds like CH_3COCH_3 and CO_2 form, while zinc ions react with the oxygen present in the atmosphere or in the water to form ZnO according to thermal gravimetric analysis coupled to the differential thermal analysis:

$$Zn(CH_3COO)_2\,{\cdot}H_2O \rightarrow ZnO + CH_3COOH,\ CH_3COCH_3,\ CO_2 \qquad (4)$$

2.3.3. The effect of solvent on sprayed ZnO thin films properties

Three types of solvents have been used to prepare spray solution: deionised water, pure alcohol (methanol, ethanol, 2-propanol) or a mixture of deionised water and alcohol (methanol, ethanol, 2-propanol). Usually some acid, e.g. acetic acid, is added to solvent to prohibit the hydrolysis of Zn salt, i.e. precipitation of $Zn(OH)_{2.}$ Most of the researchers performed experiments using only one type of solvent. The experimental details and results of used solvents are presented in Table 1 and Table 2. Among researchers, Maldonado et al.[21, 26], Mondragón-Suarez et al.[22] and Arca et al.[27] have studied the effect of alcohol on the properties of ZnO thin films while keeping other parameters constant.

Arca et al.[27] studied the role of solvent on undoped ZnO films (the zinc precursor was zinc acetate). A ZnO thin film was grown when water, methanol or a mixture of them was used as a solvent. Several films were grown when solvent composition (ratio between water and methanol) was changed as follows: 100/0, 75/25, 50/50, 25/75, 0/100. Despite the different precursors and used solvents with variation in volumetric composition, all of the samples consisted of hexagonal zincite although the used solvent changed the orientation of films. ZnO thin films, deposited from solution where methanol was a solvent, were smooth while the surface got rougher when water content is increased. Therefore, the transmittance of ZnO thin films decreased while increasing the water content as a solvent. While increasing the water content as a solvent, the film growth rate increased. Pure methanol solvent led to the preferred c-axis orientation – (002) plane parallel to the substrate. The increase of water content in solvent increased the relative intensity of the (100) reflection according to XRD[27].

Maldonado et al.[26] studied the effect of solvent on the structural properties of indium doped ZnO thin films. According to XRD, they deposited polycrystalline ZnO:In thin films. Highly (101) orientated ZnO:In thin films were grown from ethanolic and isopropylic solvents. The use of ethanol as a solvent led to a significant contribution of the (002) and (100) planes but the preferred growth was (101) plane parallel to the substrate.

Mondragón-Suarez et al.[22] found that the surface morphology is affected by the type of alcohol used as a solvent. The smoothest and the most uniform film surfaces were obtained from ethanolic solutions[22]. Maldonado et al.[26] observed that ZnO:In films deposited from methanolic solutions result in the growth of big grains mixed with smaller grains while with the use of 2-propanol alcoholic solutions, only small grains are found. When ethanol was used as a solvent, the grains were uniform[26]. The optical transmittance for ZnO:In thin films grown from ethanolic solution and for ZnO:Al thin films grown from methanolic solution was nearly 85%[21, 22]. Maldonado et al.[26] deposited ZnO:In films at the same conditions from methanolic and ethanolic solutions. They found that ZnO:In films from methanolic solution have optical transmittance of 85% while the optical transmittance of ZnO:In from ethanolic solution was nearly 10% lower[26].

Maldonado et al.[21, 26] and Mondragón-Suarez et al.[22] obtained results in which the resistivity was affected by the use of different solvents despite the different dopant. For ZnO:In, the lowest resistivity ($2.8\cdot10^{-3}$ Ω·cm) was achieved when ethanol was used as a solvent[21, 26]. A resistivity as low as $1.3\cdot10^{-2}$ Ω·cm was obtained for ZnO:Al with methanol as a solvent[22]. The higher mobility of ZnO:In films was obtained from ethanolic solution (6 cm/(Vs))[21] and for ZnO:Al from methanolic solution (1 cm/(Vs))[22]. The carrier concentration was independent of the used solvent and of the used dopant and remained between the values of $0.5\cdot10^{20}$ cm^{-3} and $6\cdot10^{20}$ cm^{-3} [21, 22].

Concerning the film thickness, Arca et al.[27] stated that the ZnO films grown from aqueous solutions were always rougher and hence showed a lower transmission. It was concluded that droplet size and the surface temperature played a crucial role in the growth of a good layer: the solvent with low density created droplets with smaller size that did not impinge on the surface and the vaporization of the solvent happened just above the surface leading to a heterogeneous film.

2.3.4. The effect of doping on sprayed ZnO thin films properties

Doping is intentionally introducing impurities into an intrinsic material, in this case ZnO, for modulating its electrical properties. The doping element substitutes Zn or O atoms in crystal lattice. III group elements, e.g. B, Al, Ga and In, substitute Zn^{2+} atoms that provide a free electron in to the lattice and therefore the conductivity of doped ZnO increases. VII group elements, e.g. F and Cl, substitute O^{2-} atoms. It has been found that besides modulating the electrical properties doping also increases the optical transmittance in visible part of spectrum[13]. All these elements used for doping ZnO have been successfully applied when using spray pyrolysis.

Undoped ZnO thin films generally show a strong (002) XRD peak, therefore the crystallites are oriented c-axis perpendicular to the substrate. When dopant is added, the preferred orientation can be changed. Also, the crystallite size can be altered by adding dopant. Dependent on the deposition conditions, the undoped ZnO thin films can be milky and foggy besides being transparent but the doped thin films are usually transparent. The use of high concentration dopants in spray solution results in smooth films with smaller crystallites[10].

2.3.4.1. Doping with boron (B)

Doping with boron was studied by Pawar et al.[13]. H_3BO_3 was used as dopant source and the $[B^{3+}]/[Zn^{2+}]$ atomic percent was varied from 0 to 8 at.%. They observed that the grown films were polycrystalline despite of the concentration of boron. Doping with boron increases the intensity of peak (002) and decreases the intensities of peaks (100), (101) and (110) on diffractogram. The average optical transmittance of undoped film was nearly 80% and the transmittance of boron doped ZnO film was higher than 90%. The electrical properties of the films were eminently dependent on the boron doping concentration. The mobility and carrier concentration increased sharply while resistivity decreased sharply when the boron concentration was increased to 1 at.%. Further increase in boron concentration decreased the mobility and carrier concentration and increased the resistivity. Therefore, the lowest resistivity of $2.54 \cdot 10^{-3}$ Ω·cm, the highest carrier concentration of $9 \cdot 10^{19}$ cm^{-3} and the highest mobility of 27 $cm^2/(Vs)$ were obtained for boron concentration of 1 at.%.

2.3.4.2. Doping with fluorine (F)

Sanchez-Juarez et al.[15] researched the effect of doping with fluorine on the properties of ZnO thin films. NH_4F was used as a dopant source and the $[F^{4+}]/[Zn^{2+}]$ atomic ratio was varied from 0 to 5 at.%. The increase in F/Zn atomic ratio did not affect the preferential growth of ZnO thin films – the preferential growth along c-axis. The crystallite size decreased with the increase in the F/Zn atomic ratio. The excess of F incorporation in ZnO thin films decreased the crystallite size and inhibited the growth of ZnO crystal. The authors wrote that the overdose of fluorine also decreased the mean transparency making the surface of the film textured. The fluorine incorporation reduced drastically the resistivity of the films up to four orders of magnitude compared to undoped ZnO films (from 10^3 to 10^{-1} Ω·cm). The mobility of the films decreased from 6 $cm^2/(Vs)$ to 1 $cm^2/(Vs)$ when the fluorine concentration was increased from 0 at.% up to 0.7 at.%, after what, an increment up to 7.5 $cm^2/(Vs)$ was observed. The carrier concentration acted inversely – an increase from 10^{17} cm^{-3} to 10^{20} cm^{-3}

was observed when fluorine concentration was increased from 0 at.% up to 0.7 at.% and from there on, a decrease down to 10^{18} cm^{-3} was observed.

2.3.4.3. *Doping with gallium (Ga)*

De La Luz Olvera et al.[24] and Babar et al.[25] have studied the effect of gallium incorporation on the properties of ZnO thin films. For both studies, $Ga(NO_3)_3$ was used as a dopant source to grow gallium doped ZnO films. The $[Ga^{3+}]/[Zn^{2+}]$ atomic ratio in spray solution is varied from 0 to 3 at.%. All the gallium doped films grown were polycrystalline and the Ga incorporation did not change the preferred orientation (along c-axis); the optical transmittance was ca. 90%[24, 25]. Compared to undoped ZnO thin films, the surfaces of gallium doped ZnO thin films were smoother consisting of less needle-like structures[24, 25]. Babar et al.[25] obtained resistivity as low as $9.4 \cdot 10^{-3}$ Ω·cm for gallium doped ZnO thin films.

2.3.4.4. *Doping with aluminium (Al)*

Many researchers have studied the effect of incorporation of aluminium on the properties of ZnO thin films. $Al(NO_3)_3$, $AlCl_3$, $Al(C_5H_7O_2)_3$ are only some of the dopant sources used. The preferred orientation of Al doped ZnO thin films is (002), but as the $[Al^{3+}]/[Zn^{2+}]$ atomic ratio surpasses a critical value, the orientation of crystallites changes to (101) oriention[11, 22, 24]. For Romero et al.[11] the critical value was 3 at.% while for Maldonado et al.[22] the critical value was 5 at.%. The optical transmittance was between 80% - 90% for all deposited aluminium doped ZnO thin films[9, 11, 22, 23, 25]. Romero et al.[11] deposited ZnO:Al thin film with resistivity 1.1 Ω·cm while Mondragón-Suarez et al.[22] and De La Luz Olvera et al.[24] deposited ZnO:Al thin film with resistivity as low as $1.3 \cdot 10^{-2}$ Ω·cm. Gledhill et al.[9] used ILGAR spray method to grow ZnO:Al thin films with mobility and charge carrier concentration values of 13 $cm^2/(Vs)$ and $4 \cdot 10^{20}$ cm^{-3}, respectively.

2.3.4.5. *Doping with indium (In)*

Indium chloride ($InCl_3$) and indium nitrate ($In(NO_3)_3$) are mostly used as the source for doping elements. Krunks et al.[10] observed that the orientation of crystallites depends on the dopant concentration rather than on the indium precursor. The preferred crystallite orientation of indium doped ZnO thin films was not mainly (002) anymore. The preferred growth of crystallites could be (100), (101), (102) and (103) planes parallel to the substrate besides (002). The preferred growth varied due to different spray set-ups, deposition conditions etc. (see Table 2). The optical transmittance varied from 60% for heavily doped ZnO films grown by Hafdallah et al.[12] to 85% for moderately doped ZnO films[10, 20, 21, 24, 26]. Maldonado et al.[21]

obtained the resistivity of ZnO:In thin films as low as $3\cdot10^{-3}$ Ω·cm, mobility was 10 $cm^2/(Vs)$ and carrier concentration was $2\cdot10^{20}$ cm^{-3} ($Zn(C_5H_7O_2)\cdot 2H_2O$ was used as a zinc source and $InCl_3$ was used as In source). Benouis et al.[20] used $ZnC_4H_6O_4{\cdot}2H_2O$ as zinc source and $InCl_3$ as indium source and obtained the following results: $\rho=6\cdot10^{-3}$ Ω·cm, $\mu=21$ $cm^2/(Vs)$ and $n=4\cdot10^{19}$ cm^{-3}. Despite the exceptions ($\rho=0.17$ Ω·cm)[12], the resistivity values for ZnO:In thin films deposited by researchers worldwide tend to be near the value of $\sim10^{-3}$ Ω·cm[10, 24, 26].

2.3.5. The effect of temperature on the properties of undoped and doped ZnO thin films

The effect of growth temperature on the properties of undoped and doped Zn O thin films has been studied by many researches. In this section, a brief overview of some selected results is presented.

Paraguay et al.[18] reported that the surface morphology and micro structural characteristics of the ZnO thin films depend highly on deposition temperature. Romero et al.[11] found that films deposited at lower temperatures were thicker and rougher than films grown at high temperatures, so with the increase in temperature, the films became thinner and smoother. Romero et al.[11] and Prasada Rao et al.[17] presented that optical transmittance was not greatly affected by the change in growth temperature while Klauson J.[16] and Krunks et al.[19] found that an increase in growth temperature decreases the optical transmittance of ZnO and ZnO:In thin films. ZnO and ZnO:In films deposited at high temperatures were more transparent than films deposited at lower temperatures due to a decrease in film thickness, an increase in crystallinity and structural homogeneity[16, 19].

Prasada Rao et al.[17] and Sanchez-Juarez et al.[15] found that an increase in the growth temperature increases the grain size of ZnO thin films while Paraguay et al.[18] observed a small decrease in crystallite size with an increase in growth temperature. Almost no change in the orientation of crystals in ZnO films was observed. For doped films, the growth temperature changed the preferred orientation[16]: e.g. the intensity of peak (101) increased with the increase in deposition temperature for ZnO:In thin films[16]. Paraguay et al.[18] found that there was a critical temperature (in their case 330°C) below which the films do not have a preferential growth direction and their microstructure is more porous. Above this critical temperature, the ZnO films grow preferentially on c-axis perpendicular to the substrate.

The electrical properties of doped ZnO depend strongly on the growth temperature as stated by Sanchez-Juarez et al.[15] and Maldonado et al.[21, 26]. It was found that, independent of doping agent, an optimum growth temperature value, at which the electrical resistivity has a minimum value, exists. Prasada Rao et al.[17] found that electrical resistivity decreased and carrier concentration and mobility increased with increasing the growth temperature.

2.4. Preparation of ZnO thin films on polymeric substrates

Polymeric substrates are considered as the future substrate. Polymers are substituting glass substrates in a variety of applications due to flexibility, lightweight and unbreakability[29]. Most of the research done in the field of ZnO on polymeric substrate has been done using radio frequency magnetron sputtering method[29,30] or ion-plating deposition[31] and substrates e.g. polyester[29], cyclo-olefin polymers[31] or polyimide[30,32] have been used. The polymeric substrate used in the experiments presented in this master thesis is a polyimide called Kapton®. Kapton® polyimide film is able to maintain its physical, electrical and mechanical properties over a wide temperature range (-273°C – 400°C)[32].

2.5. Summary of the literature overview

It is hard to compare the results presented in the literature overview with each other due to the different used spray set-ups and different deposition conditions every scientific group has. For example, ZnO thin films were grown from several zinc sources, e.g. $Zn(C_2H_4O_2)_2{\cdot}2H_2O$, $ZnCl_2$, $Zn(NO_3)_2{\cdot}6H_2O$, $Zn(C_5H_7O_2)_2{\cdot}H_2O$, while varying the concentration of Zn in the spray solution. Therefore, the optimal deposition conditions have not been clarified due to the different deposition conditions. In spite of the different deposition conditions, some general conclusions can be made:

- ◊ Spray pyrolysis is a convenient and simple method to grow ZnO thin films on glass substrates; to our best knowledge, the deposition of ZnO films by spray on polymeric substrates is not studied
- ◊ The structural, optical, morphological and electrical properties of ZnO thin films are easily varied by altering the deposition conditions: zinc source and its concentration in spray solution, growth temperature, dopant source and its concentration in spray solution, etc.

◊ Smooth and homogeneous films could be deposited when $Zn(C_2H_4O_2)_2{\cdot}2H_2O$ or $Zn(C_5H_7O_2)_2{\cdot}2H_2O$ was used as a Zn source, alcohol was used as a solvent and the dopant concentration in spray solution was in the proper amount. The use of $ZnCl_2$ resulted in rough films.

◊ The addition of dopant (F, B, Ga, In, Al) in the spray solution led to highly conductive ZnO thin films. According to XRD, the preferred orientation changed from c-axis perpendicular to the substrate ((002)) for undoped ZnO to (101) plane parallel to the substrate for indium doped ZnO. The use of F, B, Ga and Al did not change the preferred crystallite growth. Lowest resistivities were obtained when B and In were used as dopants.

◊ The deposition and characterization of ZnO thin films by spray pyrolysis has been widely studied. According to our knowledge, only Klauson J.[16] studied the effect of spraying rate on the properties of ZnO thin films by using pulse mode to spray the solution to the substrate. A paper of Klauson J. master thesis[16] was also published with the cooperation with Dedova et al.[33].

2.6. Aim of the thesis

There are three aims in this master thesis:

1) To study the effect of growth temperature on the properties of ZnO and ZnO:In thin films;
2) To study the effect of spraying rate on the properties of ZnO and ZnO:In thin films;
3) To study the growth of ZnO and ZnO:In thin films by spray pyrolysis on polymeric substrates.

3. Experimental

3.1. The deposition of ZnO thin films

3.1.1. The preparation of spray solution

For the deposition of zinc oxide and doped zinc oxide thin films, zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$, „pro analysi“, Merck) was used as a zinc source. To increase the ZnO thin film electrical conductivity, it was needed to introduce a dopant into ZnO crystal lattice. Indium chloride ($InCl_3$) was used as In source. Indium doped ZnO is designated as ZnO:In.

Indium chloride was prepared in person using metallic indium wire (99.99%, Alfa Aesar) and 37% HCl („pro analysi“, Merck). $InCl_3$ forms as presented:

$$2In + 6HCl \overset{°t}{\rightarrow} 2InCl_3 + 3H_2 \uparrow \qquad (5)$$

The mixture of deionized water (ρ=18.2 MΩ·cm, 25°C) and 2-propanol ($CH_3CH(OH)CH_3$, „pro analysi“, Merck) with ratio 2:3 (volume ratio) was used as a solvent. To prevent the precipitation of $Zn(OH)_2$, a few millilitres of acetic acid was added to the spray solution (CH_3COOH, „Pro synthesis“, Merck).

Spray solutions were prepared before every experiment. The zinc concentration in spray solution was kept constant at 0.2 M. To deposit highly transparent and conductive indium doped ZnO thin films, 3 atomic percent of In^{3+}, in reference to Zn^{2+}, was added to spray solution. For the deposition of ZnO and ZnO:In thin films on glass, the volume of spray solution was kept at 100 ml. To study the growth of ZnO on polymeric substrates, 30 ml or 50 ml of undoped spray solution and/or 50 ml of indium source containing spray solutions were used. The growth temperature to grow ZnO and ZnO:In thin films on glass was varied from 350°C to 500°C, while the growth of bilayer components on polyimide substrate was carried out in the growth temperature range of 350°C to 400°C. Due to the thermal properties of polyimide, the growth temperature of the deposition of ZnO and ZnO:In on Kapton® is similar to the tin bath temperature. The solution spraying rate was varied from 0.5 ml/min to 6.7 ml/min by altering the valve position on spray head.

3.1.2. Substrates and steps in substrate cleaning process

ZnO thin films were deposited onto glass and polyimide substrates. Microscopy glass slides ($20x20x1\ mm^3$) were used as glass substrates. Kapton® was used as polyimide substrate, obtained from company Katco Ltd.

All the substrates were passed through a cleaning process prior to the deposition process as follows:

Substrates were

1) washed using soapy water
2) rinsed with deionized water
3) rinsed with ethanol
4) dried using compressed air
5) ultrasonically cleaned in ethanol for 10 minutes
6) dried using compressed air

3.1.3. Spray set-up

ZnO and ZnO:In thin films were grown by spraying spray solution, containing zinc acetate, onto clean preheated substrate. Compressed air with flow rate of 8 l/min was used as a carrier gas. An injector head 1050-SS (*stainless steel*), from company Spraying Systems Co was used as a spray head working in continuous mode. The scheme of a spray set-up used in our laboratory is presented in Figure 4.

The spray solution is poured in to the separatory funnel and the air supply is opened. The spray solution is sprayed onto preheated substrate, which has been placed on molten tin to obtain good thermic contact. The heating sub-base is rotating to obtain homogeneous films. The temperature controller controls the temperature in tin bath, but the growth temperature is different from tin bath temperature.

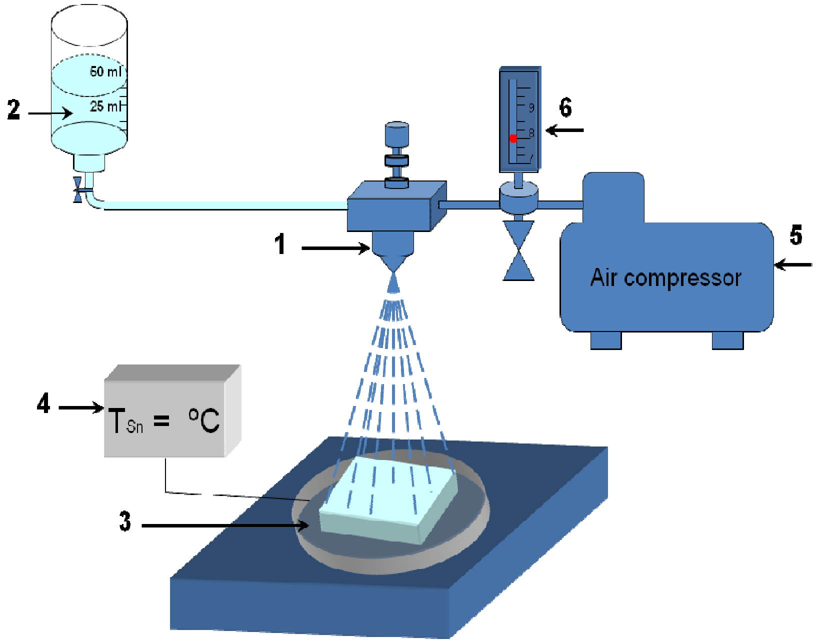

Figure 4 Spray set-up used in laboratory of thin film chemical technologies. 1 – nozzle; 2 – separatory funnel with spray solution; 3 – molten tin bath with substrate; 4 - temperature controller; 5 – air compressor; 6 – rotameter.

3.1.3.1. The determination of growth temperature

The growth temperature of films on glass substrates was determined at six different tin bath temperatures. The selected temperatures for tin bath were 250°C, 295°C, 340°C, 390°C, 435°C and 485°C, measured during the experiments with a thermocouple. A thermocouple was in contact with the glass substrate throughout the experiment through a little piece of indium that enabled to obtain good thermic contact between thermocouple and glass substrate. Spray solution with medium spraying rate of ca. 3 ml/min was sprayed onto cleaned glass substrates. The calibration curve of growth temperature versus tin bath temperature is presented in Figure 5. As can be seen from Figure 5, carrier gas is the main cooler of the surface. The use of spray solution has minor effect on the growth temperature. The growth temperature is approximately 50°C lower than tin bath temperature.

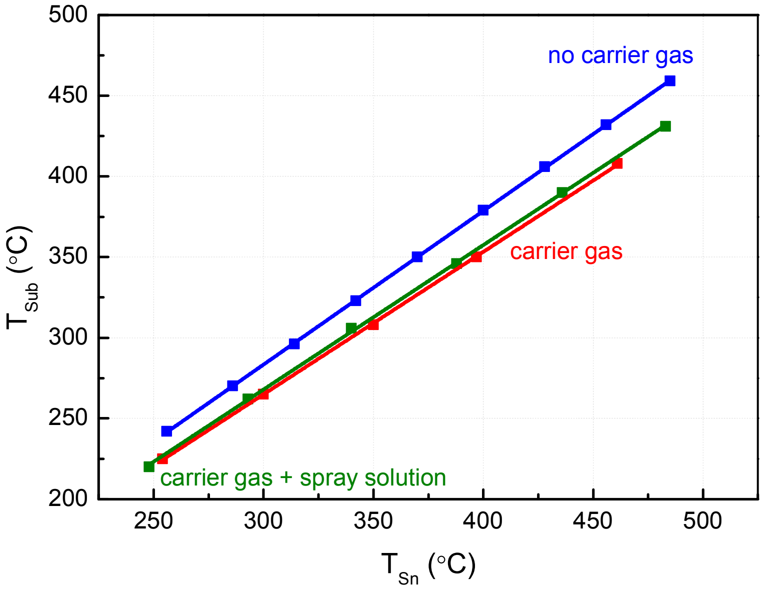

Figure 5 The dependence of growth temperature and tin bath temperature.

Starting from this moment, all the temperature values presented in this thesis represent the growth temperatures of thin films and are marked as T_{Sub}= .. °C.

3.1.3.2. The determination of specific spraying rate

Specific spraying rate is the amount of spray solution reaching to determined substrate area. Specific spraying rate was determined at room temperature by weighting a cylindrical vessel, where spray solution was sprayed, before and after spraying. ZnO:In spray solution was used as a spraying solution. It was found that with the increase in spraying rate, the specific spraying rate increases linearly as can be seen from Figure 6.

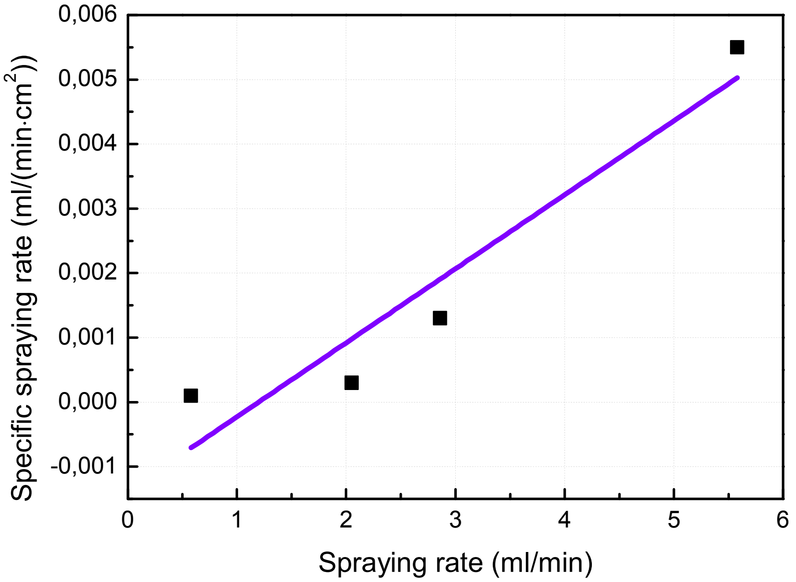

Figure 6 The dependence of specific spraying rate versus spraying rate. ZnO:In spray solution was used as spraying solution.

3.2. The characterization of ZnO thin films

3.2.1. Structural properties

X-ray diffraction (XRD) patterns of sprayed thin films and bilayers were recorded using a Rigaku Ultima IV diffractometer with monochromatic Cu Kα radiation (λ=1.5406 Å, 40 kV at 40 mA). Data were gathered in the 2θ range of 30° – 80° with scan speed 4°/min and scan step 0.01° using the silicon strip detector D/teX Ultra. The X-ray diffractograms were identified using the software on the Rigaku system (PDXL 1.4.0.3). The crystallite size was calculated using the Debye-Scherrer method.

3.2.2. Optical properties

The specular transmittance of thin films was measured using Jasco V-670 UV-VIS-NIR spectrophotometer. The measurements were carried out in the range of wavelengths 350 nm – 2500 nm in reference to glass substrate. Through optical transmittance, the knowledge on one of the important parameter of ZnO thin film, the transparency was obtained. The measurements and processing were done using program Spectra Manager. The thickness of thin films was calculated based on the interference of thin film on transmittance spectrum by Spectra Manager program installed to the computer connected with UV-VIS-NIR spectrophotometer. The formula used for the thickness calculation is as follows:

$$d = \frac{m}{2(\upsilon_0-\upsilon_m)\sqrt{n^2-\sin^2\theta}}, \text{ where} \quad (5)$$

d – film thickness, m – maximum or minimum order, n – refractive index (n=2), Θ – angle of incidence, ν_0 and ν_m – wavenumbers (0 - beginning, m - end). The film thickness was used in the calculation for resistivity.

The thicknesses were measured from the most homogeneous place near the centre.

3.2.3. Morphological properties

Morphological properties of thin films were carried out using scanning electron microscopy EVO MA 15 Zeiss. The SEM photos of thin films and bilayers were taken by senior research scientist Dr. Valdek Mikli, Centre for Materials Research, Tallinn University of Technology. Through the cross-section images of undoped and doped ZnO and bilayer structure, the thickness of layers was determined. The difference of the thicknesses determined with UV-VIS-NIR and SEM remained in the acceptable value of ±10%.

3.2.4. Electrical properties – resistivity, charge carrier mobility and charge carrier concentration

Thin film resistivity, charge carrier mobility and charge carrier concentration were measured to characterize the electrical properties of ZnO and ZnO:In thin films. Electrical resistivity (also known as resistivity or specific electrical resistance) is a measure of how strongly a material opposes the flow of electric current. A low resistivity indicates a material readily allows the movement of electric charge. The unit of resistivity is Ω·m, SI. The resistivity (ρ) of a material is inversely proportional to the conductivity (σ) of a material (σ=1/ρ). The smaller the resistivity, the higher is the conductivity. The charge carrier mobility (μ) is the speed (cm/s) at which the charge carriers move in a material in a given direction in the presence of an applied electric field (V/cm). The unit of mobility is $m^2/(Vs)$, SI. The carrier concentration (n) is the number of electrons in the conduction band per unit volume. The unit of carrier concentration is m^{-3}, SI. The conductivity and charge carrier concentration can be increased by doping with suitable elements up to some point after what a decrease follows. The electrical properties of ZnO thin films were measured at room temperature by Hall & van der Pauw method using MMR's Variable Temperature Hall System (VTHS), which was controlled by Hall, van der Pauw Controller H-50. The contacts for van der Pauw and Hall measurements were made from carbon to obtain good ohmic contact with the film. The measurements were performed by doctoral student Erki Kärber and bachelor student Mart Kukk.

4. Results and discussion

4.1. The properties of undoped and doped ZnO thin films grown at different growth temperatures

ZnO and ZnO:In thin films were grown on glass substrates. The zinc concentration in spray solution was kept at 0.2 M and the volume of spray solution was kept at 100 ml. The indium to zinc concentration in ZnO:In spray solution was 3 at.%. During this part of the study, the solution spraying rate was kept constant at ca. 3 ml/min. The growth temperature was varied from (T_{Sub}) 350°C up to 500°C.

4.1.1. The structural properties of ZnO and ZnO:In thin films

Independent of growth temperature, all the grown ZnO thin films were c-axis oriented (figure not shown). According to XRD, the preferred orientation of ZnO:In thin films was changed from (002) to (101) plane parallel to the substrate independent of growth temperature (see Figure 7). All the peaks presented belong to zincite (PDF card nr. 01-079-0208, Quality: S). Also Klauson J.[16] and Maldonado et al.[26] deposited ZnO:In thin films with preferred orientation of (101) plane parallel to the substrate. It can be seen from Figure 7 that with the temperature increase the intensity of peak (112) in reference to peak (101) increases. With an increase in temperature, the crystallite size decreased from 40 nm to 25 nm. The similar tendency was observed by Paraguay et al.[18].

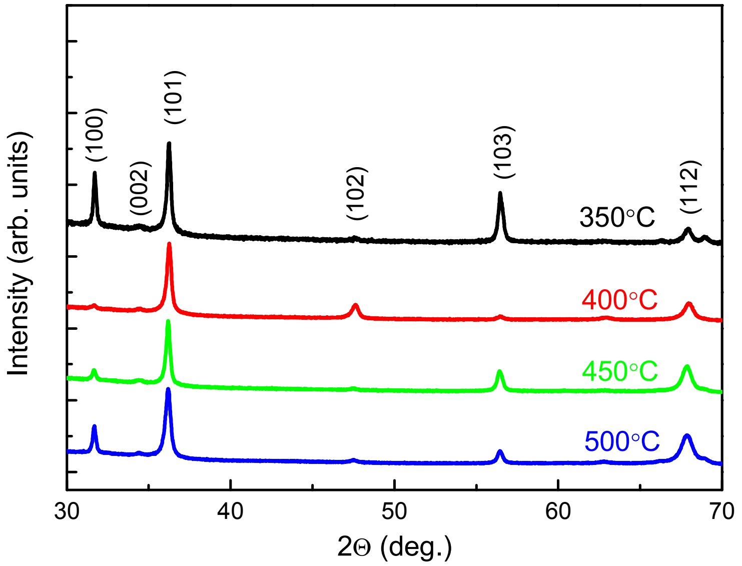

Figure 7 XRD patterns of sprayed ZnO:In thin films deposited at different growth temperatures 350°C, 400°C, 450°C and 500°C with constant solution spraying rate of ca. 3 ml/min.

4.1.2. The optical properties of ZnO and ZnO:In thin films

An exterior observation was done to ZnO and ZnO:In thin films grown by spray pyrolysis. All the films were transparent and relatively homogeneous. According to UV-VIS-NIR, the calculated film thickness for ZnO:In films varied from 1100 nm – 1500 nm while the thickness of undoped films was 950 nm – 1150 nm. The thickest ZnO:In films were grown on temperature 400°C. The specular transmittance spectra of ZnO thin films grown at temperatures 350°C and 400°C is presented in Figure 8 and the transmittance spectra of ZnO:In thin films grown at 350°C, 400°C, 450°C and 500°C are presented in Figure 9.

The specular transmittance of ZnO and ZnO:In thin films in visible part of spectrum was nearly 85%. The similar value of specular transmittance for ZnO and ZnO:In grown at the same temperature was observed by Dedova et al.[33]. For all the films, a small decrease in transmittance with an increase in growth temperature was observed. This tendency has been previously presented also by Klauson J.[16], Krunks et al.[19] and Dedova et al.[33]. As seen from Figure 8 and Figure 9, the specular transmittance of ZnO:In thin films in near infrared part of the spectrum is considerably lower than for ZnO thin films. The low transmittance in near infrared spectrum region can be caused by the high value of charge carriers as suggested by

Gledhill et al.[9]. Thus, the lower the transmittance of ZnO:In thin film in near infrared region, the more charge carriers the ZnO:In thin film could have (will be shown in paragraph 4.1.4).

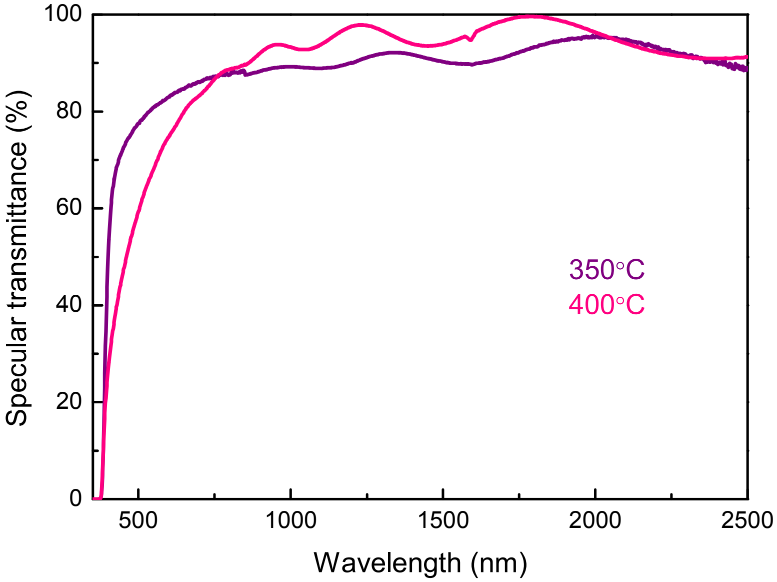

Figure 8 Specular transmittance spectra of ZnO thin films deposited at different growth temperatures (350°C and 400°C) with constant solution spraying rate ca. 3 ml/min.

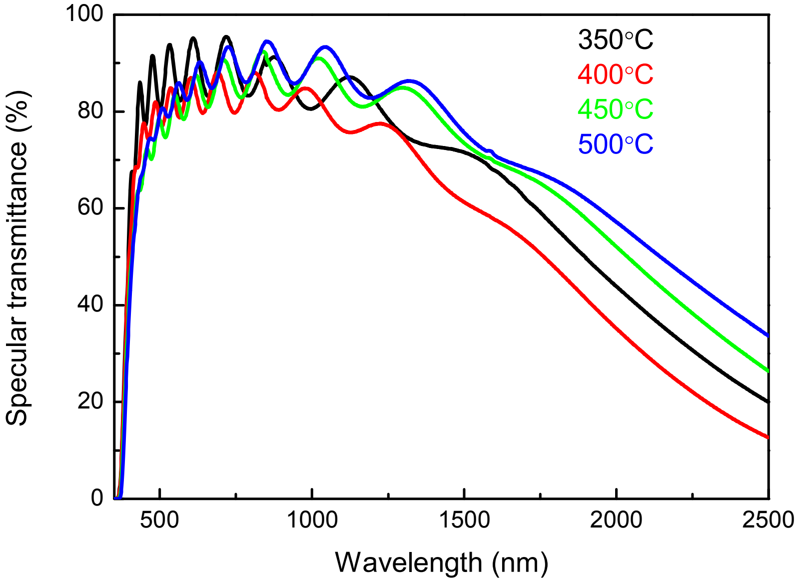

Figure 9 Specular transmittance spectra of ZnO:In thin films deposited at growth temperatures (350°C, 400°C, 450°C and 500°C) with constant solution spraying rate of ca. 3 ml/min.

The ZnO:In thin films with the highest optical transmittance were grown at T_{Sub}=350°C.

4.1.3. The morphological properties of ZnO and ZnO:In thin films

The surface of ZnO thin films was rough independent of the growth temperature. According to SEM study, an increase in growth temperature decreased the grain size of thin film (see Figure 10 and Figure 11). With the decrease of grain size of ZnO thin film, specific structures, needle- and cauliflower-likes, formed on the surface of ZnO thin films. Due to the formation of needle- and cauliflower-likes, ZnO thin film deposited at 400°C scatters light in visible light region more than ZnO thin film deposited 350°C (see Figure 8). The observations of the formation of needle- and cauliflower-like structures were also done by Klauson J.[16] and Dedova et al.[33].

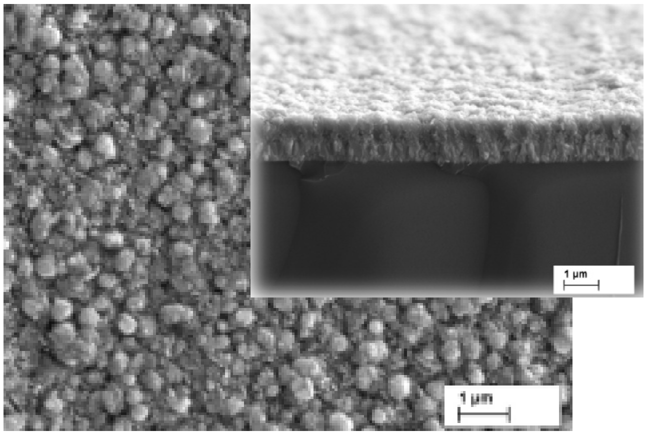

Figure 10 SEM image of ZnO thin films grown on glass substrates at temperature and 350C° with solution spraying rate of ca. 3 ml/min. Cross-sectional image is shown as inset.

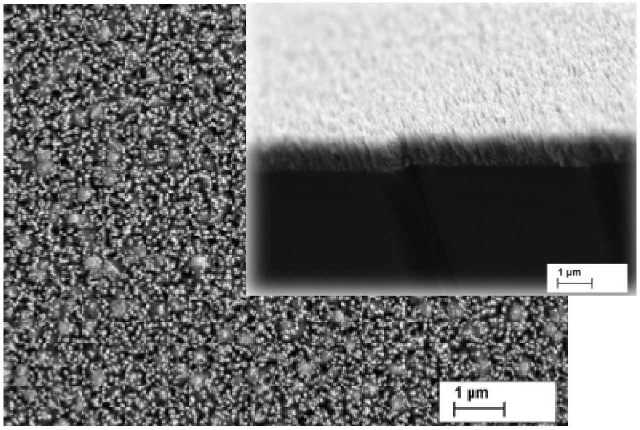

Figure 11 SEM image of ZnO thin film on glass substrate by spray pyrolysis grown at T_{Sub}=400°C with solution spraying rate of ca. 3 ml/min. Cross-sectional image is shown as inset.

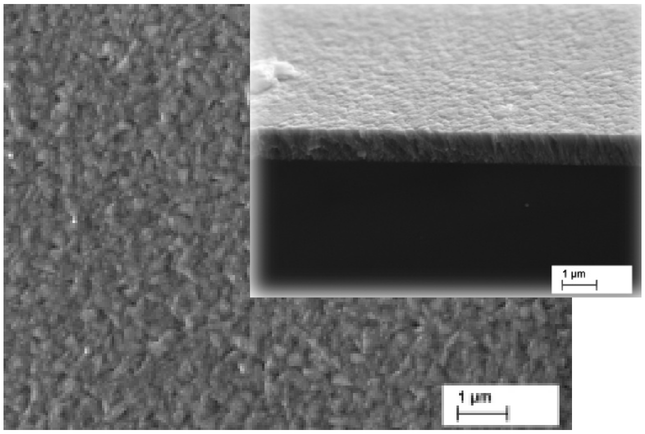

Figure 12 SEM image of ZnO:In thin film on glass substrate by spray pyrolysis grown at T_{Sub}=400°C with solution spraying rate of ca. 3 ml/min. Cross-sectional image is shown as inset.

Compared to the undoped ZnO thin film, the surface of indium doped ZnO film (SEM image presented in Figure 12) was smoother with no protrusive structures.

4.1.4. The electrical properties of ZnO and ZnO:In thin films

Independent of the growth temperature, the electrical resistivity of ZnO thin films was in the order of 10 Ω·cm or more (not shown). The dependences of electrical properties of ZnO:In thin films on growth temperature is shown in Figure 13. It can be seen that all the electrical properties depend on the growth temperature. The resistivity of sprayed ZnO:In films has a parabolic dependency on the growth temperature. The resistivity of ZnO:In thin film grown at T_{Sub}=400°C ($\rho=3\cdot10^{-3}$ Ω·cm) is more than 10 times lower compared to the highest obtained resistivity for film grown at temperature 500°C, therefore an optimum temperature exists as found also by Sanchez-Juarez et al.[15] and Maldonado et al.[21, 26]. The charge carrier mobility increases with the increase in temperature from 10 $cm^2/(Vs)$ up to 14 $cm^2/(Vs)$ due to larger crystallite sizes at 400°C (32 nm) compared to the crystallites of ZnO film grown at 350°C (25 nm). While increasing the growth temperature, the charge carrier concentration decreases slightly from $1.6\cdot10^{20}$ cm^{-3} to $9.4\cdot10^{19}$ cm^{-3}. The lowered carrier concentration at elevated temperatures could be due to the oxidation of dopant.

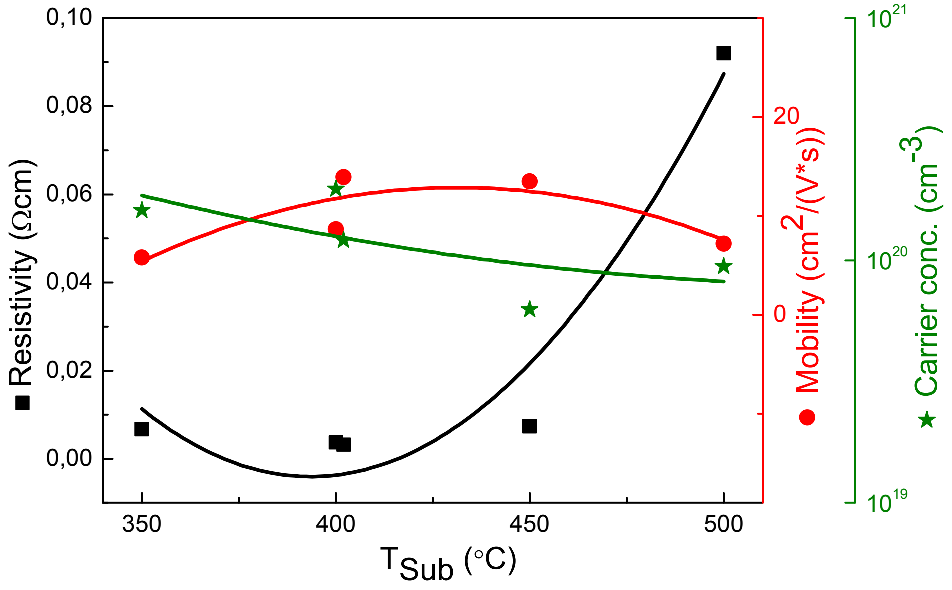

Figure 13 Resistivity, charge carrier mobility and charge carrier concentration of ZnO:In thin films deposited at 350°C, 400°C, 450°C and 500°C with constant solution spraying rate of ca. 3 ml/min.

4.2. The properties of undoped and doped ZnO thin films with different spraying rates

ZnO and ZnO:In thin films were grown on glass substrates. The zinc acetate concentration in spray solution was kept constant at 0.2 M and the volume of spray solution was kept constant at 100 ml. The indium to zinc concentration in ZnO:In spray solution was 3 at.% throughout the experiments. During this part of the study, the growth temperature was kept constant at ca. 400°C (selected after a study presented in 4.1). The solution spraying rate (v) was varied from 0.5 ml/min up to 6.7 ml/min. Spraying rate varying from 0.5 ml/min up to 2 ml/min is considered as slow spraying rate, spraying rate ca. 3 ml/min is medium spraying rate and spraying rates above 4 ml/min are designated as fast spraying rates.

4.2.1. The structural properties of ZnO and ZnO:In thin films

Sprayed ZnO thin film crystals are highly c-axis oriented perpendicular to the substrate, independent of spraying rate (see Figure 14). The preferred orientation of ZnO:In thin films remained (101) plane parallel to the substrate (see Figure 15) independent of spraying rate. All the peaks presented belong to zincite (PDF card nr. 01-079-0208, Quality: S). The unchanged preferred orientation was also observed by Klauson J.[16] and Dedova et al.[33]. Thus, the orientation of ZnO and ZnO:In crystallites is not affected by solution spraying rate.

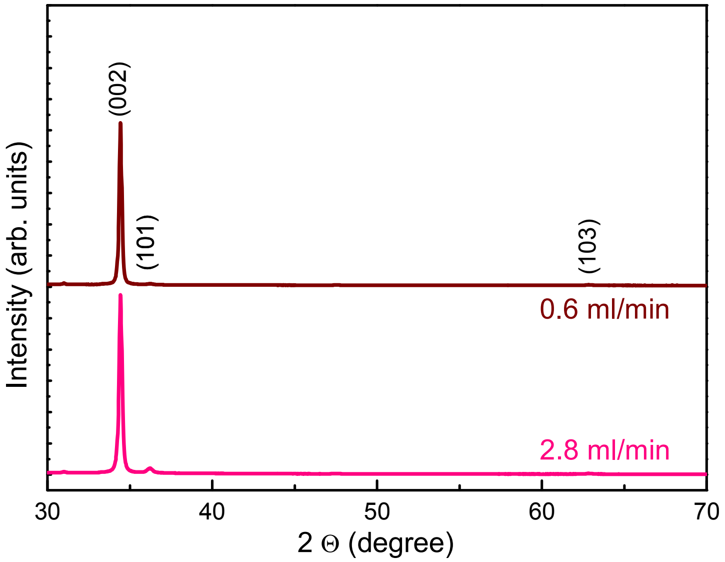

Figure 14 XRD pattern of ZnO thin films grown at T_{Sub}=400°C with solution spraying rates of 0.6 ml/min and 2.8 ml/min.

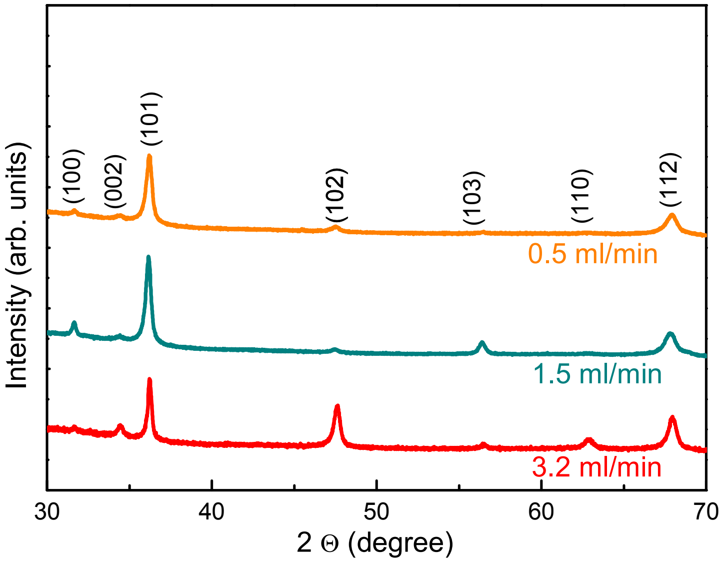

Figure 15 XRD patterns of ZnO:In thin films deposited at T_{Sub}=400°C with solution spraying rates of 0.5 ml/min, 1.5 ml/min and 3.2 ml/min.

As spraying rate increased from 0.6 ml/min to 2.8 ml/min, the crystallite size of ZnO thin film increased by 5 nm from 25 nm to 30 nm. The crystallite size for ZnO:In thin films increased from 15 nm up to 40 nm when spraying rate was increased from 0.5 ml/min up to 3.2 ml/min. Further increase in spraying rate up to 5.7 ml/min decreased the crystallite size by 5 nm down to 35 nm. The crystallite size changes with altering the spraying rate is presented in Table 3. Higher spraying rates resulted in thicker films (see Table 3). The lower film thickness at slow spraying rates can be due to the repelling of the solution droplets. The smaller crystallites of ZnO:In thin films can be due to the oxidation of In that prohibits the growth of ZnO crystals. This speculation is supported by the results of electrical characterization (see paragraph 4.2.4) where the lower concentration of free carriers is measured for films with slow spraying rates.

Table 3 ZnO and ZnO:In film thicknesses and crystallite sizes at different solution spraying rates. Films were grown at constant growth temperature of 400°C.

Spraying rate, ml/min	ZnO		ZnO:In	
	Crystallite size, nm	Film thickness, nm	Crystallite size, nm	Film thickness, nm
0.5	25	815	15	805
1.5	-	-	20	940
3	30	995	40	1360
4.7, 5.7, 6.7	-	-	~35	~1460

4.2.2. The optical properties of ZnO and ZnO:In thin films

All the films deposited at T_{Sub}≈400°C were transparent and homogeneous when examined with bare eye. The specular transmittance spectra of ZnO thin films grown with different spraying rates is presented in Figure 16 and the specular transmittance spectra of ZnO:In thin films grown with different spraying rates is presented in Figure 17. As can be seen on Figure 16 and Figure 17, the specular transmittance of ZnO thin films compared to ZnO:In thin films in visible light region is lower (75%) independent of spraying rate. Furthermore, ZnO thin film deposited with slow spraying rate is less transparent in visible light part of the spectrum than ZnO film deposited with medium spraying rate. Independent of spraying rate, the transmittance of ZnO:In thin films in visible light is similar, approximately 80%. As the growth temperature had little influence on the transmittance of ZnO:In thin films in near infrared region (see Figure 9 in paragraph 4.1.2), the spraying rate affects it noticeably, especially in near IR region. With an increase in spraying rate, the transmittance in the near infrared region decreases which could be due to the high number of charge carriers in the film. Gledhill et al.[9] deposited ZnO:Al thin films by ILGAR spray and noticed absorption and reflection in the near IR region which was explained by the high number of conduction band electrons. The effect of spraying rate to charge carrier concentration is presented in paragraph 4.2.4.

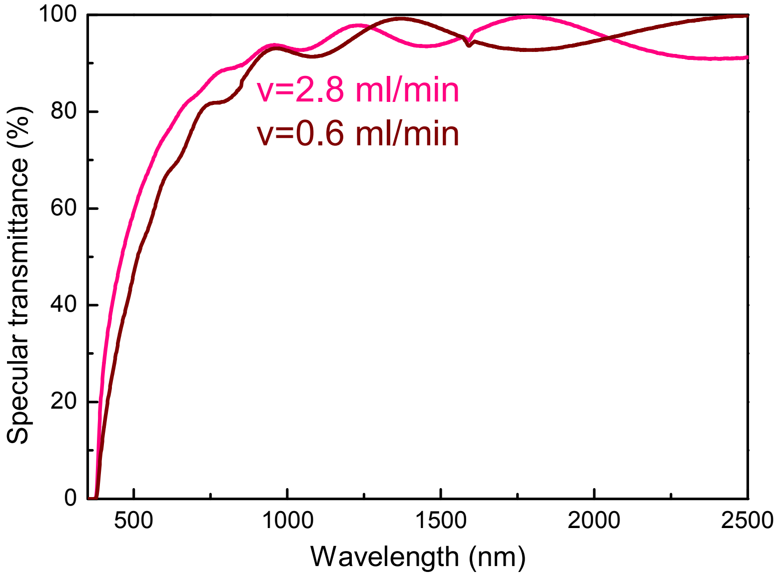

Figure 16 Specular transmittance spectra of ZnO thin films deposited at T_{Sub}=400°C with different solution spraying rates of 0.6 ml/min and 2.8 ml/min.

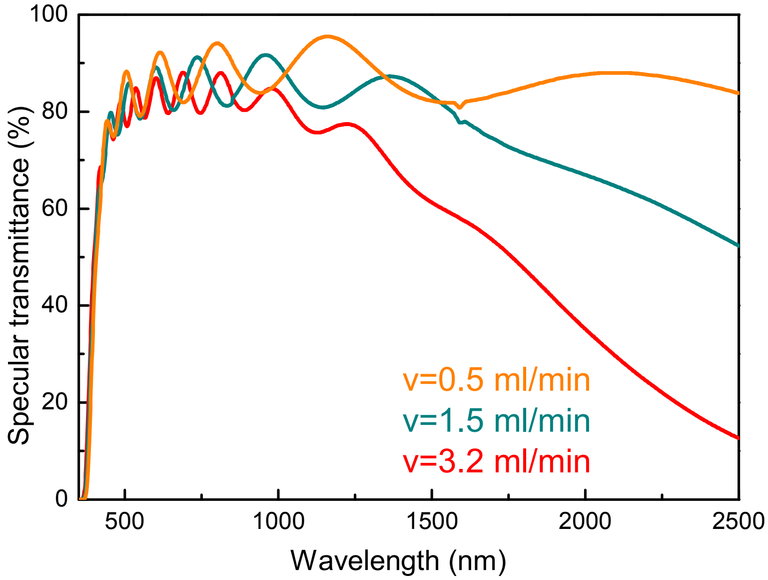

Figure 17 Specular transmittance spectra of ZnO:In thin films deposited at T_{Sub}=400°C with different solution spraying rates of 0.5 ml/min, 1.5 ml/min and 3.2 ml/min.

4.2.3. The morphological properties of ZnO and ZnO:In thin films

To study the surface morphology that is responsible for the thin film transmittance, SEM study was performed (see Figure 18 and Figure 19). According to SEM study, the surface of ZnO thin films consisted of needle- and cauliflower-like structures independent of spraying rate. Though, the amount of cauliflower-like structures was higher while the amount of needle-like structures was lower for ZnO thin film grown with spraying rate of ca. 3 ml/min. These results are in good accordance with results obtained in our laboratory in 2008 and presented by Dedova et al.[33]. It can be seen from Figure 18, that so-called 'spruce fir'-like structures which are the thickest near the substrate and thinnest near the tip are on the surface of ZnO films with slow spraying rate. With the increase in spraying rate, the 'spruce fir'-like structures resemble needle-like structures. Therefore, the ZnO thin films are not dense and the specific area is greater for film deposited using slow spraying rate not to mention the ZnO:In thin films.

The surface of ZnO:In thin films is the smoothest when spraying rate is ca. 3 ml/min. It can be seen from SEM images that independent of spraying rate, no needle- or cauliflower-like structures are present on ZnO:In thin film surface. The tetragonal surface structure of ZnO:In thin film decreases with increasing the spraying rate resulting in more homogeneous surface. Thus, it can be said that independent of solution spraying rate, doping with indium decrease the roughness of ZnO thin film, increases the mean grain size and therefore increases the intensity of interference in ZnO:In thin films in visible light region (see Figure 16 and Figure 17). The optical transmittance is higher and the scattering is lower due to the smoother surface and more denser structure of ZnO:In. Similar observation was also done for boron doped ZnO by Pawar et al.[13].

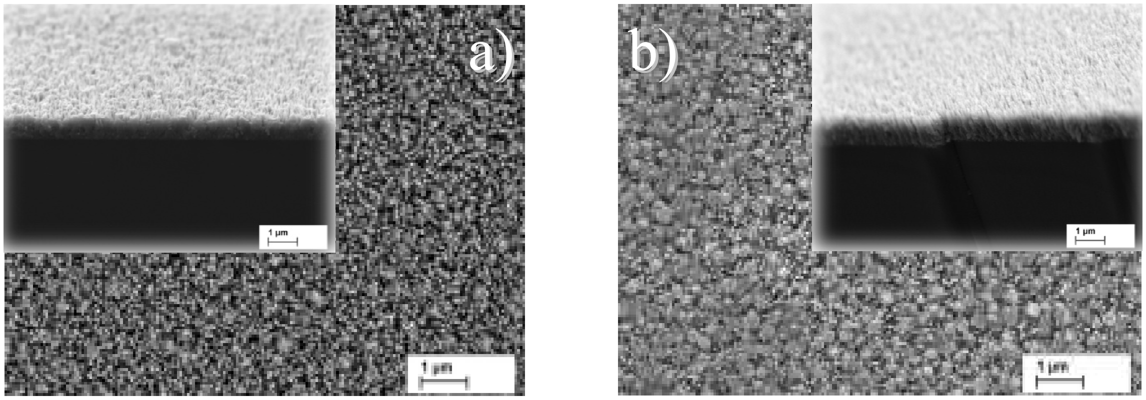

Figure 18 SEM images of ZnO thin films grown on glass substrates at T_{Sub}=400C° with solution spraying rates: a) 0.6 ml/min; b) ca. 3 ml/min.
Cross-sectional images are shown as insets.

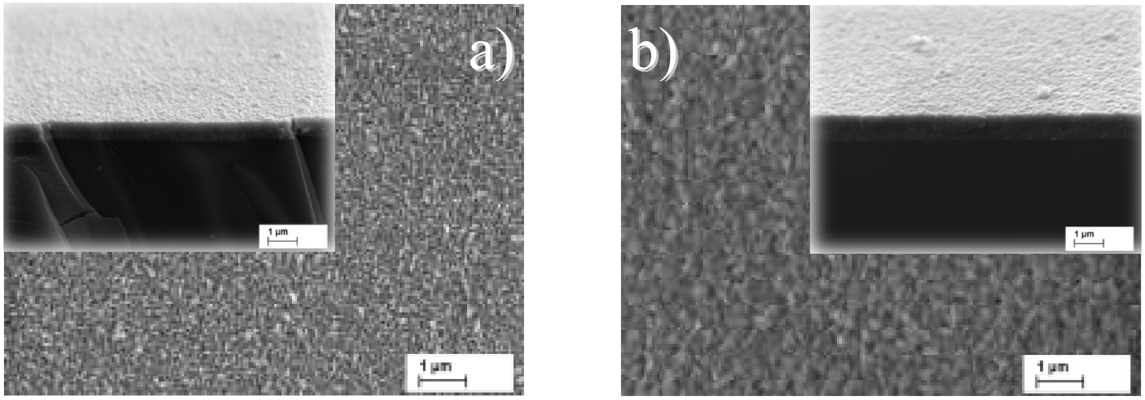

Figure 19 SEM images of ZnO:In thin films grown on glass substrates at T_{Sub}=400C° with solution spraying rates: a) 0.5 ml/min; b) ca. 3 ml/min.
Cross-sectional images are shown as insets.

4.2.4. The electrical properties of ZnO and ZnO:In thin films

Independent of spraying rate, the electrical resistivity of ZnO thin film was greater than 10 Ω·cm, therefore no data about ZnO thin films electrical properties is presented. Figure 20 presents the dependence of electrical properties (resistivity, mobility and carrier concentration) versus the spraying rate of ZnO:In thin films grown at T_{Sub}=400°C. The resistivity of ZnO:In thin films decreases rapidly from ca. $6 \cdot 10^{-2}$ Ω·cm as low as $3 \cdot 10^{-3}$ Ω·cm while spraying rate is varied from 0.5 ml/min up to 4.7 ml/min. An increase in spraying rate led to an increase in mobility and carrier concentration. It can be seen from Figure 20 that there are two main regions for mobility: spraying rates below 3 ml/min lead to mobility values below 10 $cm^2/(Vs)$ while spraying rates above 3 ml/min lead to mobility values above 10 $cm^2/(Vs)$. The increase in mobility can be due to an increase in mean grain size (see paragraph 4.2.3). An increase in carrier concentration from $1.5 \cdot 10^{19}$ cm^{-3} (for ZnO:In film deposited with spraying rate of 0.5 ml/min) up to $1.4 \cdot 10^{20}$ cm^{-3} (for ZnO:In film deposited with spraying rate of 4.7 ml/min) is shown on Figure 20. The low carrier concentration for ZnO:In thin films with slow spraying rates can be due to the oxidation of indium. The high number of carriers is accompanied by higher optical reflectivity in the near IR region (see Figure 17). The higher optical reflectivity in near IR region is explained by free carrier absorption[9]. For the deposition of ZnO:In as TCO, a comparison of optical and electrical properties lead to a preferred spraying rate ≥3 ml/min. The obtained optical and electrical properties of ZnO:In thin film deposited with spraying rates above 3 ml/min are: optical transmittance ~80%, resistivity as low as $3 \cdot 10^{-3}$ Ω·cm, charge carrier mobility nearly 15.5 $cm^2/(Vs)$, charge carrier concentration as high as $1.4 \cdot 10^{20}$ cm^{-3}.

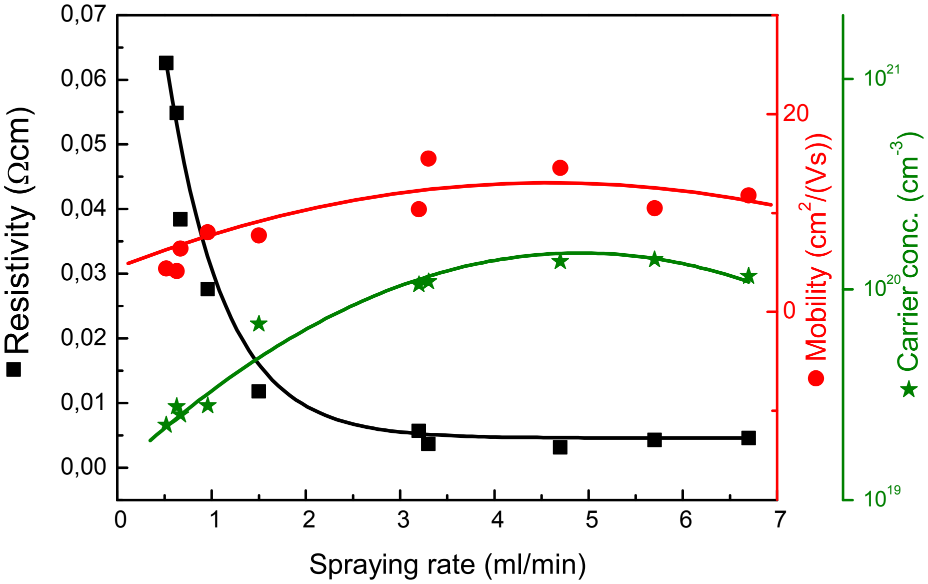

Figure 20 Resistivity, charge carrier mobility and charge carrier concentration of ZnO:In thin films deposited 400°C with various solution spraying rates from 0.5 ml/min up to 6.7 ml/min.

The results presented in paragraphs 4.1 and 4.2 have been presented in the 16th Semiconducting and Insulating Materials Conference in 2011, Stockholm. A published paper concerning paragraphs 4.1 and 4.2 has been added into this thesis in the appendix paragraph as APPENDIX 1.

4.3. The deposition of ZnO and ZnO:In thin films on polymeric substrates

The deposition parameters were selected based on study and result presented in paragraphs 4.1 and 4.2. Prior to the deposition, cleaned polyimide substrates were placed on molten tin bath.

4.3.1. The deposition of ZnO and ZnO:In at T_{Sub}=400°C

Figure 21 shows sprayed ZnO and ZnO:In thin films on polyimide substrate. 50 ml of ZnO spray solution and 50 ml of ZnO:In spray solution were used and spraying rate was varied from 2 ml/min up to 3 ml/min. Independent of spraying rate, the ZnO thin film was smooth while ZnO:In thin film had cracks. Within few minutes, the ZnO:In thin film peeled off from the substrate independent of growth temperature and spraying rate. The reason for the peeling of ZnO:In thin films could be film orientation (see Figure 14 and Figure 15 in paragraph 4.2.1 for the XRD patterns of ZnO and ZnO:In thin on glass substrates). It was found that ZnO:In thin films could be grown on polyimide substrate if a seed layer was used. In this thesis, ZnO was used as the seed layer.

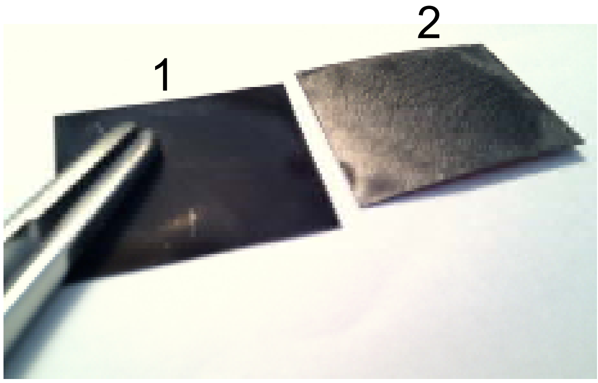

Figure 21 Spray deposited ZnO (1) and ZnO:In (2) thin films on polyimide substrate grown at temperature T_{Sub}=400°C with solution spraying rate of ca. 3 ml/min.

Bilayers, consisting of ZnO and ZnO:In films, grown from 50 ml of ZnO spray solution and 50 ml of ZnO:In spray solution (designated as 50 ml + 50 ml), were deposited on polyimide substrate at growth temperature of 400°C. Two different spraying rates were used: 2 ml/min and 3 ml/min. It was found that independent of spraying rate the surface of bilayer was extremely rough consisting of aggregated structures called ‘twisted belts’ (see Figure 22). It was found that with an increase in spraying rate, the number of ‘twisted belts’ increased while the overall size of a ’twisted belt’ decrease and the surface was not so rough.

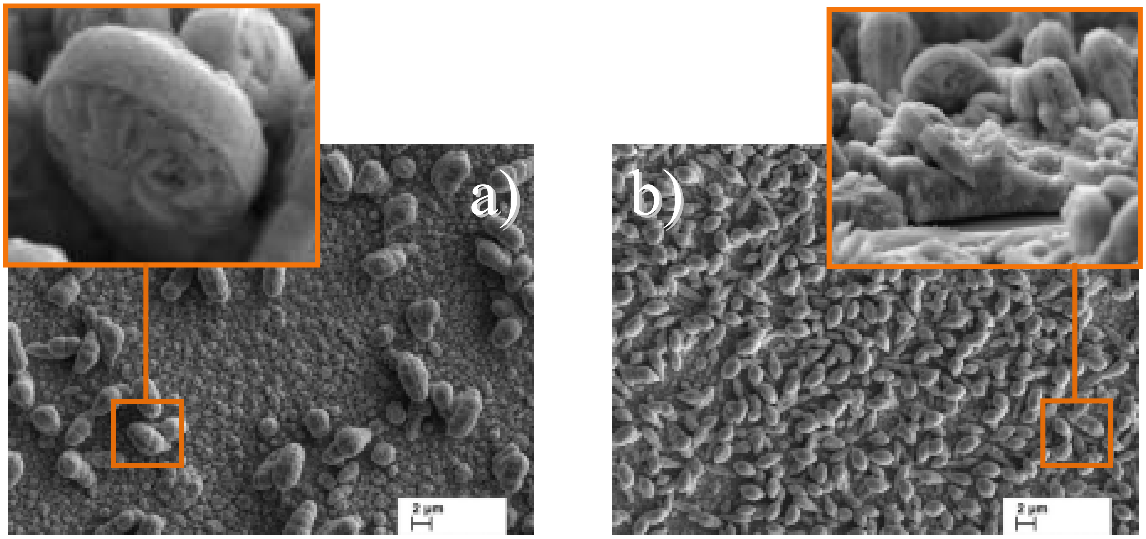

Figure 22 SEM micrographs of ZnO/ZnO:In bilayer on polyimide substrate grown at T_{Sub}=400°C with different solution spraying rates: a) 2 ml/min; b) 3 ml/min. Insets of ’twisted belts’.

To study the origin of ’twisted belts’, SEM micrographs of ZnO as seed layer on polyimide substrates were done (shown on Figure 23). It can be seen that spraying rate affects the morphology of ZnO thin films on polyimide substrate. For seed layer deposited with v=2 ml/min, the nucleation centres for the formation of ’twisted belts’ are bigger and more sparsely distributed on the surface. The nucleation centres on the surface of seed layer deposited with v=3 ml/min are smaller, yet with sharper tips.

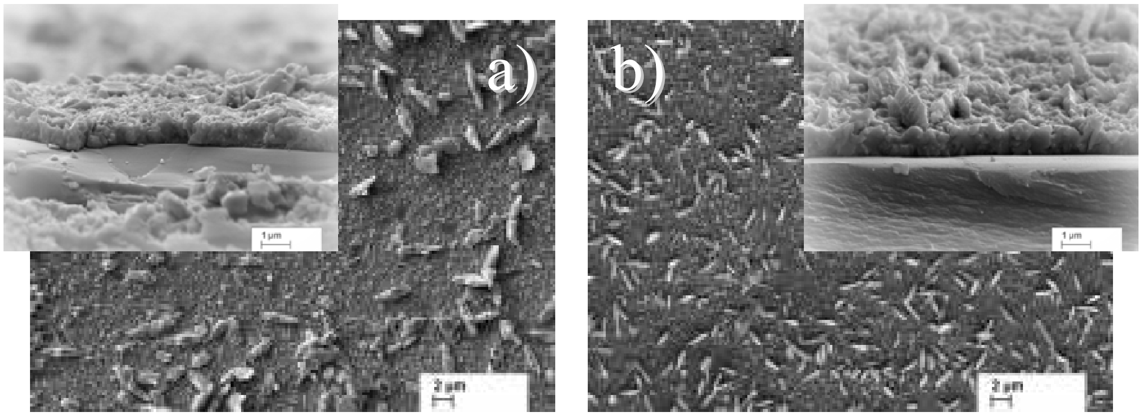

Figure 23 SEM micrographs of ZnO seed layers on polyimide substrate deposited at 400°C with different solution spraying rates: a) 2 ml/min; b) 3 ml/min. Cross-sectional images are shown as insets.

To reduce the roughness of ZnO seed layer and therefore the formation of ’twisted belts’, smaller amount of ZnO spray solution was used (30 ml) to deposit ZnO seed layer. Bilayers, consisting of ZnO and ZnO:In films, grown from 30 ml of ZnO spray solution and 50 ml of ZnO:In spray solution (designated as 30 ml + 50 ml), were deposited at growth temperature of 400°C. Two different spraying rates were used: 2 ml/min and 3 ml/min (see Figure 24).

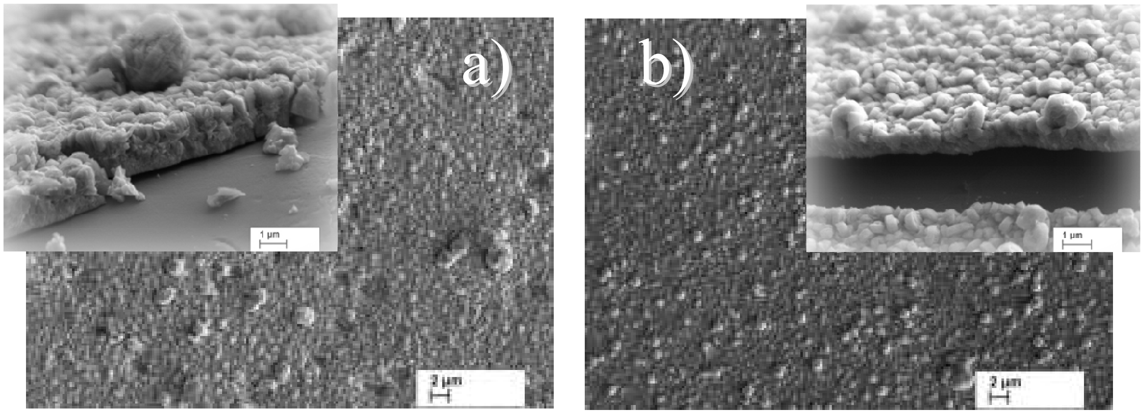

Figure 24 SEM micrographs of ZnO seed layers on polyimide substrate deposited at 400°C with different solution spraying rates: a) 2 ml/min; b) 3 ml/min. Cross-sectional images are shown as insets.

It is obvious from SEM images (compare Figure 23 and Figure 24), that the surface roughness of 30 ml + 50 ml bilayer is considerably lower that the roughness of 50 ml + 50 ml bilayer independent of spraying rate. Yet, compared to ZnO:In films obtained on glass surface, the surface is still rough (see Figure 12 in paragraph 4.1.3 and Figure 19 in paragraph 4.2.3). Thus, it can be said that the volume of ZnO spray solution and therefore the thickness of ZnO thin film influences the roughness of the final bilayer.

4.3.2. The deposition at T_{Sub}=350°C

ZnO/ZnO:In (50 ml + 50 ml) bilayer was grown at temperature of 350°C with spraying rate of 3 ml/min. The SEM image of grown seed layer is presented in Figure 25 a) and bilayer grown on mentioned seed layer is presented in Figure 25 b). The comparison between the ZnO seed layers grown at 400°C with v=3 ml/min (see Figure 24 b)) and ZnO seed layer grown at 350°C with v=3 ml/min (see Figure 25 b)), reveals that the surface of seed layer presented in Figure 25 b) is more homogeneous than seed layer presented in Figure 24 b). It is visible, that the surface of bilayer grown at 350°C with v=3 ml/min is smoother than for 50 ml + 50 ml bilayer grown at 400°C with v=3 ml/min (see Figure 22), yet it has cracks on the surface. Hence, the growth temperature of 350°C is not suitable to grow ZnO:In film on the ZnO seed layer. Therefore, besides the volume of seed layer spray solution, the morphology of ZnO/ZnO:In bilayers, especially ZnO seed layer is influenced by the growth temperature.

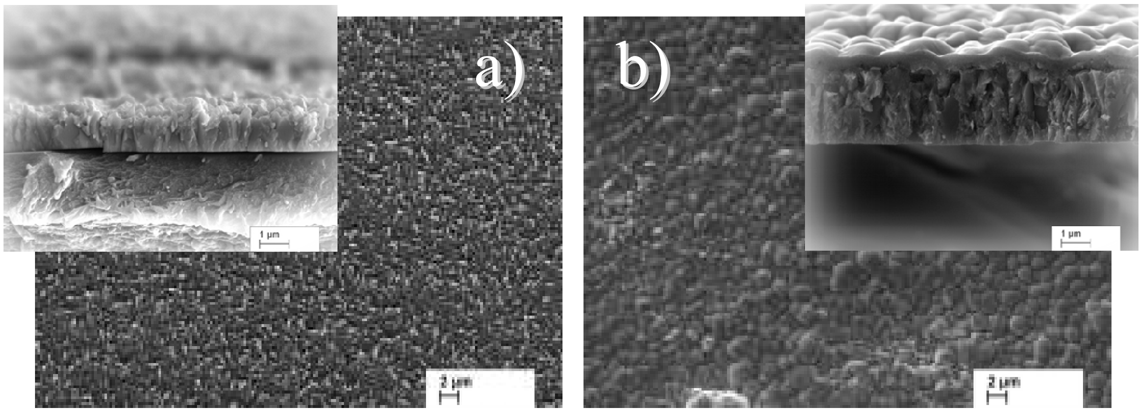

Figure 25 SEM images of ZnO (image a)) and ZnO/ZnO:In bilayer (image b)) on polyimide substrate grown at T_{Sub}=350°C with solution spraying rates of 3 ml/min. Cross-sectional images are shown as insets.

4.3.3. The deposition of bilayer at combined deposition parameters

For the next experiment, 30 ml of ZnO spray solution and 50 ml of ZnO:In spray solutions were used. For the seed layer (ZnO), the growth temperature was T_{Sub}=350°C and the spraying rate was 2 ml/min to grow smoother and crack-free film based on results presented in 4.3.1 and 4.3.2. For ZnO:In layer, the growth temperature was T_{Sub}=400°C and the spraying rate was 3 ml/min. As a result, the most homogeneous and continuous bilayer on polymeric substrate in this experiment was grown (see Figure 26).

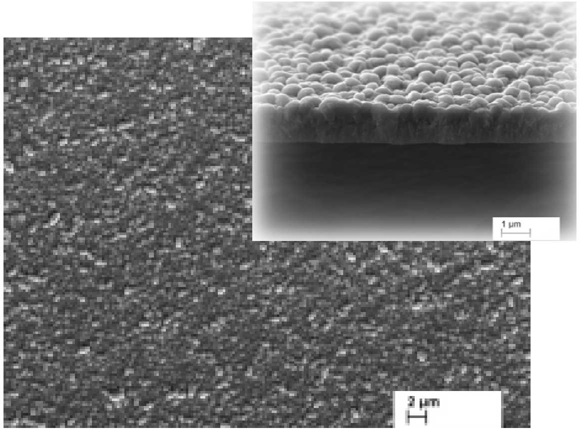

Figure 26 SEM image of a bilayer consisting of 30 ml of ZnO grown at 350°C with v=2 ml/min and 50 ml of ZnO:In grown at 400°C with v=3 ml/min.

It is visible from Figure 26 that the surface of the bilayer is continuous and homogeneous compared to other obtained bilayers presented in paragraphs 4.3.1 and 4.3.2.

Figure 27 represents the most homogeneous ZnO/ZnO:In bilayer grown in our laboratory by spray pyrolysis.

Figure 27 The most homogeneous ZnO/ZnO:In bilayer on polyimide substrate grown in laboratory of thin film chemical technologies by spray pyrolysis.

4.3.4. The electrical resistivity of bilayer

The electrical resistivities were measured for films with continuous surface. The resistivities of bilayers presented in Figure 24 a) and b) were $7 \cdot 10^{-1}$ Ω·cm and $5 \cdot 10^{-2}$ Ω·cm, respectively, and the resistivity of bilayer presented in Figure 26 was $2 \cdot 10^{-2}$ Ω·cm.

Bilayer presented on	Figure 24 a)	Figure 24 b)	Figure 26
Resistivity, Ω·cm	$7 \cdot 10^{-1}$	$5 \cdot 10^{-2}$	$2 \cdot 10^{-2}$

According to SEM images presented in paragraph 4.3, the formation of aggregated structures characterizes bilayers grown at T_{Sub}=400°C independent of spraying rate. The use of faster spraying rates leads to higher number of aggregated structures per area than for slower spraying rates for bilayers. The use of thinner seed layer (30 ml of ZnO instead of 50 ml) results in smoother ZnO/ZnO:In bilayers independent of growth temperature. In addition, the use of slower spraying rates leads to smoother bilayers. The use of lower growth temperature results in continuous and homogeneous bilayers.

5. Conclusions

ZnO and ZnO:In thin films were grown on glass and polymeric substrate by chemical spray pyrolysis. Also the growth temperature during deposition was determined. It was concluded that the growth temperature is strongly dependent on carrier gas supply. The growth temperature of film is approximately 50°C lower than the heater tin bath temperature the under spraying process when carrier gas and spray solution were used. In addition, specific spraying rate was determined. The dependence between specific spraying rate and spraying rate is linear.

The structural properties of ZnO and ZnO:In thin films depend on growth temperature and spraying rate. While the preferred orientation remains the same ((002) plane parallel to the substrate for ZnO and peak (101) plane parallel to the substrate for ZnO:In thin films). In addition, the crystallite size decreases with an increase in temperature at constant spraying rate. At constant temperature, the crystallite size increased with increasing the spraying rate.

The optical properties of ZnO thin films are slightly dependent of growth temperature and spraying rate. Whilst, the optical properties of ZnO:In thin films, especially in the near IR region, are affected by spraying rate and slightly by growth temperature. The increase in spraying rate decreases the transmittance of ZnO:In thin films in near IR region. The decrease in optical transmittance is proportional to an increase in free carrier concentration.

The morphology of ZnO and ZnO:In thin films is affected by growth temperature and spraying rate. ZnO films grown at T_{Sub}=400°C consist of needle-like structures while ZnO:In film grown at T_{Sub}=400°C is smoother and homogeneous thin film. Independent of spraying rate, the growth of ZnO thin films leads to rough film surface with needle- and cauliflower-like structures that were not present for ZnO:In thin films. ZnO:In thin film grown with higher spraying rate is smoother without any insistent structure.

The resistivity of ZnO thin film was in the order of 10 Ω·cm or more independent of growth temperature and spraying rate. The electrical properties of ZnO:In thin films depend on the growth temperature and spraying rate. Thin films with the lowest resistivity ($\rho=3\cdot10^{-3}$ Ω·cm) were obtained at T_{Sub}=400°C. With an increase in spraying temperature (from 0.5 ml/min up to 4.7 ml/min), the resistivity decreases rapidly (from $6 \cdot 10^{-2}$ Ω·cm to $3 \cdot 10^{-3}$ Ω·cm), charge carrier mobility and concentration increased up to 15.5 $cm^2/(Vs)$ and $1.4 \cdot 10^{20}$ cm^{-3}, respectively. The further increase in spraying rate up to 6.7 ml/min slightly increases the resistivity and decreases the mobility and concentration of charge carriers.

ZnO thin films could be deposited onto polyimide substrate named Kapton®. ZnO:In thin films peeled off from Kapton® polymer while ZnO thin films stayed on polyimide substrate. The cause for ZnO:In peeling off could be the film orientation. To grow ZnO:In thin films on polyimide substrate, ZnO seed layer was used. To obtain smooth bilayers (ZnO/ZnO:In on Kapton®), the seed layer had to be as smooth as possible. The morphology of the seed layer is dependent on the thickness of the layer, growth temperature and spraying rate.

6. Résumé

ZnO can be used in many applications, e.g. in solar cells as a window layer and instead of ITO and FTO as front contact. To use ZnO as front contact, ZnO has to be as transparent (in the visible light region) and as conductive as possible. The electrical resistivity and optical transmittance of ZnO thin films can be increased by doping with suitable elements. Fluorine, chlorine and III group elements are considered as suitable elements for doping ZnO due to producing a free electron in the ZnO crystal structure.

The aim of this thesis was to give an overview of literature on ZnO thin films made by spray pyrolysis, to grow ZnO and ZnO:In thin films by spray pyrolysis on glass and polymeric substrates and study the effect of growth temperature and spraying rate on the properties of deposited thin films. Spray pyrolysis was used due to its advantages compared to other methods, e.g. simplicity, low cost. The growth temperature and specific spraying rate was determined before the study. The growth temperature and spraying rate were varied for films deposited on glass and on polymeric substrates. Structural, optical, morphological and electrical properties of ZnO and ZnO:In thin films were studied.

It was concluded that the optical, morphological and electrical properties of thin films depend on growth temperature and spraying rate beside other deposition parameters.

It was concluded that an optimal growth temperature exists where films with low resistivity are obtained. In addition, the use of spraying rates lower than 3 ml/min are not suitable to grow ZnO:In thin films when grown at optimal growth temperature.

90% of transmittance in visible light region, resistivity as low as $3\cdot10^{-3}$ $\Omega\cdot$cm, high mobility (15.5 $cm^2/(Vs)$) and charge carrier concentration ($1.4\cdot10^{20}$ cm^{-3}) were obtained for ZnO:In thin films if following deposition parameters $T_{Sub}\approx400°C$ and $v\geq3$ ml/min.

ZnO and ZnO:In bilayers were grown on polyimide substrates at $T_{Sub}=350°C$ and $T_{Sub}=400°C$ with spraying rates of 2 ml/min and 3 ml/min. The smooth and continuous surface of bilayer depends on the seed layers roughness. The morphology of ZnO seed layer is dependent on the growth temperature, spraying rate and layer thickness.

7. Resümee

ZnO on võimalik kasutada mitmetes rakendustes, näiteks päikesepatareides aknakihina ning ITO ja FTO asemel juhtiva elektroodi. Selleks, et kasutada ZnO juhtiva elektroodina, peab ZnO olema suhteliselt kõrge elektrijuhtivusega ja hea optilise läbilaskvusega nähtavas spektri osas. ZnO õhukeste kilede optilist läbilaskvust ning elektrijuhtivust saab suurendada, legeerides ZnO elementidega, mis annavad ZnO kristallis vabu elektrone (III rühma elemendid, fluor, kloor).

Antud töö eesmärgiks oli anda kirjanduse ülevaade keemilise pihustamise meetodil valmistatud ZnO kiledest, kasvatada ZnO ja ZnO:In õhukesed kiled keemilise pihustamise meetodil klaas- ja polümeersetel alustel ning uurida kasvutemperatuuri ja pihustuskiiruse mõju saadud kilede omadustele. Pihustuspürolüüsi kasutati tänu tema eelistele teiste meetodite ees nagu näiteks lihtsus, odavus jm. Kilede kasvutemperatuur ning eripihustuskiirus määrati enne uurimust. Kilede kasvatamisel klaas- ja polümeeralustele muudeti kasvutemperatuuri ning pihustuskiirust. Uuriti valmistatud ZnO kilede struktuurseid, optilisi, morfoloogilisi ning elektrilisi omadusi.

Järeldati, et lisaks teistele pihustusparameetritele, sõltuvad kilede optilised, morfoloogilised ja elektrilised omadused ka kasvutemperatuurist ning pihustuskiirusest.

Töö käigus selgus, et kilede kasvatamisel eksisteerib optimaalne kasvutemperatuur, mille puhul eritakistus on väikseim. Lisaks ei ole soovitatav kasutada pihustuskiirusi alla 3 ml/min, et kasvatada ZnO:In õhuke kile optimaalsel kasvutemperatuuril.

Töö käigus kasvatati ZnO:In kile optlilise läbilaskvusega 90%, eritakistusega $3\cdot10^{-3}$ Ω·cm, kõrge liikuvuse (15.5 $cm^2/(Vs)$) ning laengukandjate kontsentratsiooniga ($1.4\cdot10^{20}$ cm^{-3}) kui $T_{Sub}\approx400$°C ja $v\geq3$ ml/min.

ZnO ja ZnO:In koosnevad kaksikkihid kasvatati polüimiid alustele temperatuuridel $T_{Sub}=350$°C ja $T_{Sub}=400$°C, kasutades pihustuskiiruseid 2 ml/min ja 3 ml/min. Kaksikkihtide tisane pind sõltub aluskihi pinnakaredusest. Aluskihi morfoloogia sõltub kasvutemperatuurist, pihustuskiirusest ning kihi paksusest.

8. References

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APPENDIX 1

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The effect of growth temperature and spraying rate on the properties of ZnO:In films

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ZnO:In thin films were deposited by chemical spray pyrolysis from zinc acetate solutions containing 3 at.% of $InCl_3$. The films were grown in the temperature region of 400-500 °C using solution spraying rates 0.6-7.1 ml/min. ZnO:In films were characterized by XRD, Hall and van der Pauw methods. The dependence of the film resistivity vs growth temperature is parabolic. ZnO:In films with resistivity minimum of $3x10^{-3}$ Ωcm can be deposited at 450 °C. The solution spraying rate has strong effect on the film resistivity, deposition rates below 3 ml/min result in high resistivities.

1 Introduction Zinc oxide (ZnO) is a widely used semiconductor material for applications such as gas sensors, reflecting coatings and transparent conductive layers in photovoltaic devices [1–7]. ZnO thin films could be deposited by several methods, such as magnetron sputtering, metal-organic chemical vapour deposition, and pulsed laser deposition. Chemical spray pyrolysis, used in this study, is a simple and fast method to obtain electrically conductive and highly transparent ZnO thin films at low cost. Electrically conductive ZnO thin films can be obtained by doping with suitable elements (e.g. Al, Ga, In) [1, 6, 7]. The effect of dopant concentration in spray solution has been vastly studied [2–6]. It is reported that 3 at.% of dopant in the spray solution is optimal to grow electrically conductive ZnO films [1, 5, 6]. The effect of the growth temperature to the electrical and optical properties of ZnO films has been studied [5, 6], the film growth temperatures close to 400 °C are reported to be optimal. The influence of spraying rate has been less studied, it is found that the spraying rate affects the film morphology [8]. The aim of this study is to investigate the effect of growth temperature and spraying rate to structural and electrical properties of ZnO:In thin films.

2 Experimental ZnO films were deposited by pneumatic spray of precursor solution onto preheated glass substrate (thickness 1 mm). $Zn(CH_3COO)_2{\cdot}2H_2O$ (Merck, 99.5%) was used as the precursor dissolved in a mixture of deionized water and isopropyl alcohol (2:3 by volume). The precursor concentration in solution was fixed to 0.2 mol/l, few drops of acetic acid were added to avoid precipitation of zinc hydroxide. Indium(III)chloride ($InCl_3$) was used as doping agent added to the spray solution. Indium to zinc concentration was kept constant at 3 at.%. Glass substrates were placed onto a hot plate with a temperature (T_S) ranging from 400 °C to 550 °C. The growth temperature of thin films is about 50 °C lower than the T_s depending slightly on the spraying rate. Spray solution volumes of 50 ml and 100 ml were used for deposition and the spraying rate (v) varied from 0.5 to 7.1 ml/min. The structure of the films was characterized by X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer with monochromatic Cu Kα radiation. Crystallite size was calculated using the Debye-Scherrer method. Electrical properties (resistivity, Hall mobility and carrier concentration) of the thin films were measured by Van der Pauw and Hall method at room temperature.

3 Results and discussions

3.1 Effect of solution volume and growth temperature on the film electrical properties The resistivity of the sprayed ZnO:In films has a parabolic dependency on the growth temperature (Fig. 1). As the temperature (T_S) increases from 400 °C to 450 °C, the resistivity (ρ) of thin films decreases from $1.5x10^{-2}$ to $4x10^{-3}$ Ωcm as both mobility (μ) and carrier concentration (n) are increasing. Mobility increased from 10 to 15 $cm^2V^{-1}s^{-1}$ due to larger crystallite sizes of films deposited at 450 °C (32 nm) compared to that at 400 °C (25 nm), and n increased from $3x10^{19}$ to $2x10^{20}$ cm^{-3}. Further increase in T_S from 450 to 550 °C increases the ρ from $4x10^{-3}$ to 1.8 $x10^{-2}$ Ωcm as μ and n decrease. The decrease in μ could be explained by decreased film thickness (from 700 to 500 nm) and crystallite size (from 33 to 25 nm). Dependence of μ on the film thickness and crystallite size is well-known [10, 11].

Followingly, to eliminate the limitations caused by the film thickness, 100 ml of solution was sprayed instead of 50 ml. The films with thicknesses of 1100-1500 nm were obtained. The film resistivity had a parabolic dependency vs T_S with an optimum temperature of 450°C which corresponds to a minimum of the resistivity ($3x10^{-3}$ Ωcm) (not shown). Similarly to the films from 50 ml of solution, n decreases (from $2x10^{20}$ to $5x10^{19}$ cm^{-3}) while increasing the T_S. Decrease in n while increasing film growth temperaure is similar to that reported for ZnO:Al [6]. Likely, the lowered carrier concentration could be explained by the oxidation of the dopant at elevated temperatures. As higher solution amount results in thicker films with μ>10 $cm^2V^{-1}s^{-1}$ then our next experiments on the effect of the solution v at different T_S were performed using solution volume of 100 ml.

3.2 Effect of growth temperature and spraying rate on the film structure and thickness Figure 2 depicts the effect of the T_S and v on the structure of sprayed ZnO:In films. The crystallites in ZnO:In films deposited at T_S of 450 °C (Fig. 2a) are preferably orientated (101) plane parallel to the substrate, which is in good accordance with that reported for sprayed ZnO:In films [3, 12], the spraying rate has insignificant effect. XRD patterns of ZnO:In films grown at T_S 500 °C with v<3.0 ml/min are similar to the films grown at 450 °C. Using v>3 ml/min, the relative intensities of (100) and (110) reflections increase (Fig. 2a) and the crystallites in ZnO:In film are preferably orientated parallel to the (110) plane. XRD patterns of the films grown at T_S of 400 °C with v<1.5 ml/min (Fig. 2b) are similar to the films grown at 450 °C. Increasing the v up to 3.9 ml/min increases the intensities of (002), (102) and (103) reflections. Further rise in v increases the intensities of (100) and (110) reflections. XRD study shows that spraying rate has strong effect on the crystallite orientation when deposited at 400 or 500 °C. Table 1 presents the film thicknesses (measured from the SEM cross-sections) and crystallite sizes depending on the T_S and v. At slower spraying rates the films are thinner and crystallite sizes are smaller. Crystallites in the films grown at T_S=500 °C are smaller than in the films grown at lower T_S. Similar tendency was observed by El Hichou et al. [13].

3.3 Effect of spraying rate on the film electrical properties Spraying rate has critical effect on the resistivity of ZnO:In films (Fig. 3). Using the slowest solution spraying rate of 0.6 ml/min the film resistivities are the highest independent of T_S. Increasing the v decreases the resistivities drastically and the lowest values are obtained for the films deposited with the v≥3 ml/min. It is interesting to notice that at T_S=400 °C, the ρ starts to in-

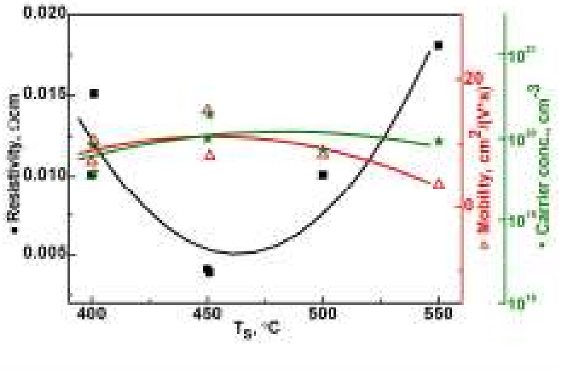

Figure 1 The resistivity (■), mobility (Δ) and carrier concentration (✱) of ZnO:In films grown at different temperatures from 50 ml of solution with spraying rate of 3.8 ml/min.

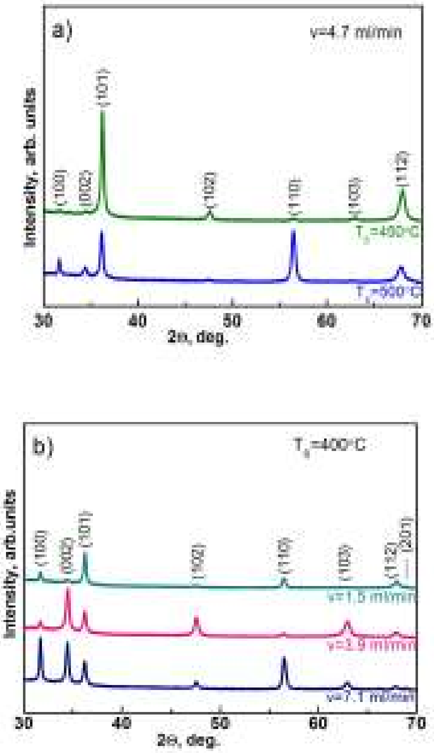

Figure 2 XRD patterns of sprayed ZnO:In films deposited at a) T_S of 450 °C and 500 °C, v= 4.7 ml/min; b) T_S of 400 °C with v=1.5, 3.9 and 7.1 ml/min.

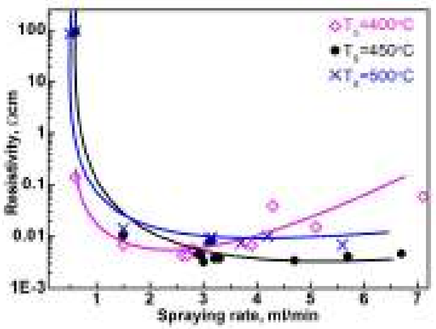

Figure 3 The resistivities of ZnO:In films deposited at different temperatures with various spraying rates.

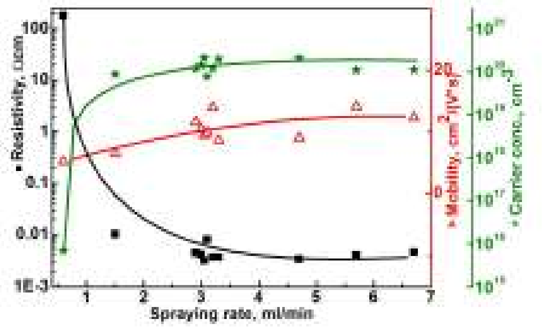

Figure 4 The resistivity (■), mobility (Δ) and carrier concentration (∗) of ZnO:In films grown from 100 ml of solution with various spraying rates at T_S=450 °C.

crease using v>4 ml/min. The films deposited at 450 °C and 500 °C show similar tendency with respect to spraying rate (Fig. 3), however, films grown at 500 °C remain less conductive. This could be explained by a smaller average crystallite size in films deposited at 500 °C (Table 1), leading to a decreased carrier mobility. In addition, a slightly lower carrier concentration is characteristic of the films deposited at T_S of 500 °C. The film resistivity of $1.8x10^2$ Ωcm obtained with the slowest spraying rate of 0.6 ml/min is mainly caused by low n in the order of 10^{16} cm^{-3}. In addition, a relatively low mobility of 5 $cm^2V^{-1}s^{-1}$ at lower spraying rates is observed, which can be explained by lower film thickness and smaller crystallite size (Table 1 and Fig. 4), compared to films deposited at higher spraying rates. Increasing spraying rate v up to 1.5 ml/min increases both, n and μ. Using spraying rates between 2.9 and 6.7 ml/min, n~10^{20} cm^{-3} and μ remains above 10 $cm^2V^{-1}s^{-1}$ for the whole set of samples deposited at T_S=450 °C. The highest obtained μ was 14 $cm^2V^{-1}s^{-1}$ and highest n was $2x10^{20}$ cm^{-3}. These results are close to that reported for ZnO:In films deposited by ultrasonic [9] or pneumatic spray [2, 3].

4 Conclusions

The effect of the temperature on the film resistivity was clearly parabolic, measurements indicated resistivity minimum of ca $3x10^{-3}$ Ωcm if grown at 450 °C. Low spraying rates result in high film resistivity as both carrier concentration and mobility are low. The results of this study show that chemical spray pyrolysis is a promising method for deposition of electrically conductive ZnO films.

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Table 1 Film thickness and crystallite size for ZnO:In films deposited from 100 ml of solution at different temperatures (T_S) and spraying rates (v).

Spraying rate (v), ml/min	Film thickness, nm			Crystallite size, nm		
	T_S=400 °C	T_S=450 °C	T_S=500 °C	T_S=400 °C	T_S=450 °C	T_S=500 °C
0.6	835	720	840	31	22	20
1.5	750	940	1180	38	21	22
3.0	1100	1300	1520	39	29	30
3.9	1310	1440	1220	32	35	29
5.6	-	1170	1520	-	35	24