Ink jet printing of aqueous inks for single layer deposition of Al doped ZnO thin films

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Abstract:

In this paper, Al doped ZnO thin films deposited by a one single layer approach are studied. An aqueous precursor solution was prepared for the deposition of Al doped ZnO thin film via ink jet printing. The physical properties of the ink were studied in detail by rheology measurement and drop visualisation. The wetting of the ink with the substrate was studied by the use of wetting envelopes. A single layer of the ink was deposited on the substrate and fully processed. The thin films were studied by X-ray diffraction, scanning electron microscopy, resistivity measurements and optical transmission measurements. The optimal dopant concentration was set at 3 at% which resulted in thin films with a resistivity of 2.54 c cm and an optical transmission larger than 90% over the visible range of the electromagnetic spectrum.

1. Introduction

Recently, research towards the development of transparent conductive oxides (TCO) with a low resistivity and high transmittance in the visible region has been gaining more and more interest. Tin doped Indium oxide (ITO) is the most widely applied TCO material for optoelectrical devices[1](#_ENREF_1). However, the high cost and the resource availability problem of indium promote the search to alternative materials[2](#_ENREF_2), [3](#_ENREF_3). By doping ZnO with group-III elements such as B, Al, Ga and In a good transmittance in the visible region of the electromagnetic spectrum and a high electrical conductivity is obtained, which renders those materials attractive as transparent conductive materials and as possible alternatives for ITO[4](#_ENREF_4), [5](#_ENREF_5), [6](#_ENREF_6), [7](#_ENREF_7). Especially, aluminium doped zinc oxide (AZO) turns out to be a very promising candidate due to its good transparency, high conductivity, low cost of Al and Zn and non-toxicity[2](#_ENREF_2), [8](#_ENREF_8). AZO thin films can be deposited by various techniques such as chemical vapour deposition (CVD)[9](#_ENREF_9), sputtering[10](#_ENREF_10), [11](#_ENREF_11), pulsed laser deposition (PLD)[12](#_ENREF_12) and chemical solution deposition (CSD)[13](#_ENREF_13), [14](#_ENREF_14) . Chemical solution deposition is non-vacuum technique that is simple, cost effective and allows a high controllability of the dopant concentration[14](#_ENREF_14). By selecting the CSD method several deposition methods can be applied such as dip-coating[15](#_ENREF_15), [16](#_ENREF_16), spin-coating[17](#_ENREF_17), spray-coating[18](#_ENREF_18) and ink jet printing[19](#_ENREF_19), [20](#_ENREF_20).

In this paper, the CSD approach is favoured. Contrary to the frequently used toxic organic solvents[21](#_ENREF_21), [22](#_ENREF_22), [23](#_ENREF_23), [24](#_ENREF_24), a water based CSD process is explored which makes the process more environmental friendly and easier to handle. The physical parameters of the precursor solution were optimised towards ink jet printing. This deposition technique is favoured for its multiple benefits: (1) Via ink jet printing there is no direct contact between the solution and the substrates, as a closed ink container prevents ink losses and solvent evaporation can be avoided resulting in an increase of the ink’s lifetime. (2) High precision of the deposited ink droplets allows printing of thin films but also high-resolution patterns. (3) By using a multi-nozzle print head an easy scalable industrial process can be obtained. (4) Only one side of the substrate will get coated[25](#_ENREF_25). A lot of different ink jet printing setups are on the market. Here, a piezoelectric drop-on-demand nozzle is used that jets small ink droplets. These droplets were deposited on a glass substrate with high precision. By controlling the spacing between the droplets and the number of printed lines on substrate, homogenous AZO thin films are achieved.

The AZO thin films presented here, are deposited in one single coating step. Many authors[26](#_ENREF_26), [27](#_ENREF_27), [28](#_ENREF_28), [29](#_ENREF_29) make use of multiple coating steps with thermal treatments in between. Such a multiple coating process reduces the simplicity and cost effectiveness of the CSD approach. Therefore, we strive towards a simple and effective single coating process that can be easily extended to printing of tracks and patterns. This will allow skipping or reducing the etching process which is otherwise still needed to produce patterns.

1. Experimental

**Precursor chemistry**

Al doped ZnO thin films have been deposited on glass substrates using the CSD method. A Zn precursor solution and an Al precursor solution were prepared separately. The Al precursor was prepared as follows: a 0.01 mol of Al(NO3)3.9H2O (Sigma Aldrich, 98%) and 0.03 mol of malonic acid (C3H4O4, Sigma Aldrich, 99%) were dissolved in 10 mL water and stirred for 30 minutes. The pH was raised with ethanolamine (C2H7NO, Sigma Aldrich, 99%) till a clear, colourless solution was obtained at pH 9.5. Finally, the pH was adapted with formic acid (CHOOH, Acros Organics, 98%) till 7 and the precursor solution was diluted till a clear 0.5 mol L-1 Al precursor was obtained.

The Zn precursor was prepared by dissolving 0.01 mol of Zn(CH3COO)2.2H2O (Sigma Aldrich, 99%) in 10 mL water and ethanolamine was added till a clear, colourless solution was obtained. The pH was adapted with formic acid till 7. At the end a clear 0.5 mol L-1 Zn precursor was achieved by diluting the precursor solution. The final AZO precursor was obtained by adding a small amount of the Al precursor to the Zn precursor. The exact amount is determined by the final intended dopant concentration (eq. 1).

Eq. 1

The printability of the ink was improved by the addition of 10 v% ethanol (Panreac, absolute). The amount of ethanol is added to the Zn precursor solution before diluted till 0.5 mol L-1.

**Preparation of Al doped ZnO thin films**

The ink has been deposited using a piezoelectric drop-on-demand printing system and a computer controlled XY plotter. The used orifice (Microfab, MJ-ABP-01) has a diameter of 30 µm. By applying a bipolar waveform to the piezoelectric filament droplets are jetted. The waveform reached a voltage of 14 V in 4 µs and holds its voltage for 4 µs. The droplets are jetted at a frequency of 2 kHz during the coating process. The synchronic movement of the nozzle and jetting of the ink resulted in homogeneous coatings on 0.7 mm thick cleaned EAGLE2000 glass substrates (Präzisions Glass&Optics). Before printing, the inks were filtered with a 0.20 µm PET filter. **All coatings were built up from printing lines with droplets spacing of 50 m. The longitudinal spacing between each printed line was also fixed at 50 µm.** The printed layers were dried at 120°C on a hotplate for 10 minutes before they were thermally treated in a tube furnace till 500°C in a wet 200 ppm O2/N2 atmosphere. The heating rate was kept at 10°C/min with a dwell at 250°C and 500°C for 1h. The wet atmosphere was established by bubbling the dry atmosphere through 2 glass bottles containing water at 20°C. Finally, samples were post-heated at 450°C during 30 min in a dry Ar/5% H2 atmosphere.

The substrates were cleaned to improve wetting. First, the glass substrates were immersed in isopropanol and ultrasonicated for 1hour. Secondly, they were rinsed with demineralised water and soaked during 1h at 25°C in the acid piranha solution (3:1 ratio H2SO4 and 30wt% H2O2). Afterwards, the substrates were rinsed with demineralised water and soaked during 1h in a 3 mol L-1 NaOH solution. Finally, they were rinsed with a 3 v% HCl solution, demineralised water and isopropanol before the substrates are dried in a dry and filtered N2 flow.

**Characterisation**

The density of the inks was determined using a 10 mL glass pychometer (Duran). The surface tension of the aqueous inks and contact angles on the glass substrates were characterised using a drop shape analyser (DSA 30 Krüss GmbH). Diiodomethane (Fischer Scientific) and glycerol (Sigma Aldrich, >99.5%) were used to determine the polar and dispersive component of the surface free energy of the cleaned substrates. The polar and dispersive components of the inks surface tension were determined by subtracting the dispersive component from the total surface tension. The dispersive surface tension component was determined by the contact angle on a PFTE substrate. The ink viscosity was measured at 25°C with a RheoStress600 (Haake Technik) rheometer. **Drop formation and fluid behaviour were also imaged in situ during printing, using a camera (Allied Vision Technologies, Stingray F-125B) with a telecentric zoom lens (Moritex, MLZ07545) and strobed collimated LED illumination (bespoke, University of Cambridge). The LED, mounted behind the nozzle, was illuminated for 500 ns at an adjustable delay time after each droplet was ejected, allowing the evolution of the drop shape with time to be imaged with 500 ns time resolution. For a jetting frequency of 1 kHz, images were acquired with a shutter time of 40–50 ms, such that each frame represented an average over approximately 40 successive droplets. Custom-written software (University of Cambridge, Applied Superconductivity and Cryoscience Group- dr. Simon Hopkins) was used to control image acquisition and to quantitatively analyse the drop volume and velocity20.** Shape and size of single droplets printed on substrates were determined through optical profilometry (Veeco, NT9080). The morphology and cross section of the processed AZO coatings were analysed with a FEI Nova 600 Nanolab Dual Beam FIB-SEM. The crystalline phases of the obtained AZO coatings were characterised via a powder X-ray diffractometer equipped with a line detector and irradiated with Cu Kα (λ = 0.154 nm) (Bruker D8 Discover). The rocking curves were measured making use of a diffractometer equipped with a point detector and irradiated with Cu Kα (λ = 0.154 nm) (Siemens D5000). The sheet resistance was measured by a four point wafer prober (Veeco, FPP-5000) while the carrier concentration and mobility were measured by a Van der Pauw setup.

1. Results and discussion

**Physical properties of the ink**

The ink properties such as viscosity, surface tension and density are of great importance during the printing process. The ejection of discrete droplets via a drop-on-demand printhead is a rather complicated process where physics and fluid mechanics play an important role. According to Fromm[30](#_ENREF_30), the printability of inks can be estimated by the inverse of the Ohnesorge number (*Oh-1*). The Ohnesorge number is the appropriate grouping of physical constants to describe the droplet formation. This dimensionless number is independent of the drop velocity that relates the viscous force to inertial and surface tension forces. In fact, the *Oh* is the ratio of the square of the Weber number (*We*) and the Reynolds number (*Re*), where the *We* is the ratio between the internal forces and the surface tension. The *Re* is the ratio between the internal forces and the viscous forces:

Eq. 2

Where *γ* (J m-2), *ρ* (kg m-3), *ν* (m s-1), *η* (Pa s) are respectively the surface tension, the density, velocity and the viscosity of the ink, while *α* (m) is the diameter of the nozzle opening. Simulations to print single droplets by Reis and Derby[31](#_ENREF_31) defined a value for the inverse of the Ohnesorge number between 1 and 10. However, Jang *et al*.[32](#_ENREF_32) studied the DOD printability of various mixtures and redefined the limit of *Oh-1* by taking specific characteristics of printing into account, leading to an interval between 4 and 14. Beneath 4 the positional accuracy is degraded due to long lifetime of the droplet’s tail. Above 14 it’s impossible to form a single droplet. Between 10 and 14 the formation of a single droplet is possible when the formed satellite droplets have a velocity higher than the primary droplet (figure 2). Due to the difference in speed between satellite and primary droplet, they can recombine to a single droplet before the substrate’s surface is reached[32](#_ENREF_32). For each ink, fluid characteristics are shown in table 1.

The addition of ethanol reduces the surface tension and increases the viscosity, resulting in improved inverse Ohnesorge numbers. Nevertheless, all inks were printable, the inverse Ohnesorge numbers of the inks don’t always meet the criteria Jang *et al*.[32](#_ENREF_32). A possible explanation for this phenomenon is that shear thickening of the inks at high shear rates occurs, as represented in figure 1. During printing processes shear rates of 105 – 106 s-1 will be applied to the ink[30](#_ENREF_30), [33](#_ENREF_33), [34](#_ENREF_34). These high shear rates can induce shear thickening or thinning. In this special situation shear thickening will lower the actual *Oh-1*. The shear rate reached with the rheometer was limited to approximately 45300 s-1. This is still lower than the shear rate encountered during jetting conditions, but it gives a good indication of the ink’s behaviour at higher shear rate. For example, ink *AZO4* has a viscosity of 3.66 mPa s at shear rate of 13000 s-1, implementing an *Oh-1* of 11, while an *Oh-1* of 8.84 is obtained for a viscosity of 4.55 mPa s measured at shear rate of 45300 s-1. This results in an *Oh-1* that drops below 10 when the ink is exposed to high shear rates and single droplets can be printed (figure 3). The jetting analysis of the ink *AZO4* is represented in figure 3 and figure 4. Starting at 30 µs after jetting, a liquid filament is formed. At 50 µs, the droplet breaks off resulting in a droplet with tail. Finally, the tail merges with the droplet and satellite droplets were prevented, leading to a single droplet with a volume of 23.8 pL, a droplet diameter of 37 µm and a velocity of 2.29 m/s. The other inks still have an *Oh-1* above 10 resulting in the formation in satellite droplets which finally merges with the main droplet (figure 2). The formed liquid filament breaks off between 50 and 60 µs after initiating the printing process. The main droplet has a tail that breaks off and recombines after 80 µs.

**Wetting of the ink on the substrate**

Each of the above mentioned inks produce discrete droplets on the substrate when the droplet and line spacing are larger than the droplet’s dimensions after impact. In order to obtain homogeneous thin films, the line and droplet spacing were decreased till separate droplets could merge together. Because of this, good wetting of the ink with the substrate is important. Low contact angles allow droplets to spread out easily upon impact with the substrate’s surface and they can merge with the already deposited neighbouring droplets to form a continuous wet coating.

In order to predict the wetting properties of an ink on cleaned substrates, a wetting envelope is simulated where the polar part of the solution is plotted as a function of the dispersive part by using a reverse Owens-Wendt model (figure 5). A wetting envelope can only be plotted when the substrate’s polar and dispersive part of the surface free energy ( & ) are known. Therefore, the Owens-Wendt equation[35](#_ENREF_35) (Eq. 3) is solved making use of 2 contact angles of liquids with known polar and dispersive surface tension on a cleaned substrate. Experimentally, the surface free energy and its polar and dispersive components were determined of diiodemethane (mJ m-2P = 0 mJ m-2 and D = 50.8 mJ m-2) and glycerol ( = 62.4 mJ m-2P = 25.72 mJ m-2 and D = 36.68 mJ m-2). The contact angles of diiodomethane and glycerol on the cleaned substrate were 40 and 20° respectively.

Eq. 3

The wetting envelope indicates that only inks *AZO3* and *AZO4* have a contact angle of 5° or smaller, as they **lay** within the wetting envelope. This agrees with the measured contact angles represented in Table 1. The exact contact angle of ink *AZO4* couldn’t be measured as the equipment is not suited for accurate determination of very low contact angles. However, making use of the footprint of the droplets upon impact the contact angle can be estimated. According to Derby19, the final spreading of the droplet will have a contact diameter, *dcon*, which is determined by its volume and contact angle at equilibrium, *eqm*:

Eq. 4

Where *d0* is the diameter of the droplet in flight[19](#_ENREF_19), [33](#_ENREF_33). The contact diameter was measured by optical profilometry (figure 6). The measurement was immediately performed after printing to avoid drying effects and droplet shrinkage. The estimated contact diameter is between 158 and 162 µm. The jetting analysis of the droplet in flight is estimated a droplet diameter of 37 µm (figure 4), resulting in an equilibrium contact angle between 3.5 and 4° which is in accordance with the wetting envelope given in figure 5.

Printing droplets with substantial longitudinal and lateral overlap didn’t always result in smooth and continuous wet coatings. The printing of a homogenous coating was only successful with ink *AZO4* while printing of the other inks resulted in a thick liquid front at the end of the substrate. In conclusion, continuous coatings were obtained when the ink obeys to the following properties: (1) the balance between surface tension, viscosity and density should be ideal to allow jetting of the ink from a 30 µm orifice. (2) A good wetting of the ink on substrate’s surface should been obtained. It has been experimentally determined that the contact angle should be smaller than 5° to obtain continuous, homogenous layers. Ink *AZO4* is the only one who fulfils those requirements and is thus retained in the further experiments. By adjusting the added amount of the aluminium precursor to the zinc precursor, the dopant concentration of AZO was controlled following Eq. 1. Finally, the layers were printed with a line and point spacing of 50 µm resulting in a thermally treated AZO thin film of around 80 nm thick.

**Study of the AZO thin film opto-electrical properties**

In order to study the effect of the aluminium concentration on the microstructural and opto-electrical properties, samples were prepared with varying concentrations of aluminium (1-4 at%). The printed wet thin films were thermally treated as discussed in the experimental section. The XRD spectra of these samples are shown in figure 7. The films are crystalline with a preferential growth along the *c*-axis without any secondary phase being noticeable. All reflections can be assigned to ZnO. The diffraction peaks at 31.77° (100) and 36.26° (101) are almost negligible compared to those at 34.42° (002) and 72.57° (004) (JCPDS 89-7102). The preferred orientation is due to a self-ordering mechanism. According to Fujihara *et al.* [36](#_ENREF_36), the self-ordering mechanism is a result of the pursuit to a minimal surface energy. The crystallisation starts at the substrate/layer interface due to the high interfacial energy of the amorphous layer with the substrate. The pursuit for a minimal surface energy leads to the growth of a crystalline film along the *c*-axis.

The XRD measurements illustrate the strong preferential orientation of the synthesised thin films. The crystallinity has an optimum around a doping level of 2 at% and has a minimum at 4 at%. This can be explained by taking two phenomena in to account: (1) Cebulla *et al.*[37](#_ENREF_37) noticed an increase of texturing by doping ZnO with Al where it acts as a mineraliser or surfactant. (2) An excess of dopant can induce stresses due to the large difference in ionic size of both. The ionic size of Zn2+ is 0.074 nm, while Al3+ has an ionic size of 0.054 nm[38](#_ENREF_38). This indicates that a certain amount of dopant helps the texture while an excess of the dopant concentration deteriorates the crystallinity of these thin films.

An optimum in electrical properties of the AZO thin films is noticed at a dopant level of 3 at%, where a resistivity of 2.54 c cm is obtained (figure 8).This is not in line with the XRD measurements. The higher preferential growth along the *c*-axis would suggest a possible candidate for good electrical conductivity at 2 at% AZO. A higher dopant concentration (3 at% AZO) can induce more charge carriers if the solubility limit isn’t exceeded. But an increasing amount of charge carriers doesn’t always directly lead to an increased electrical conductivity. The mobility of these charge carriers also plays a vital role in the final electrical properties. Diverse scattering events such as grain boundary scattering, lattice scattering, ionised-impurity scattering etc. limit the charge carrier’s mobility[39](#_ENREF_39). The synthesised thin films have a maximum carrier concentration of 2.23 x 1019 cm-3, meaning the grain boundary scattering will play a dominant role in the occurring scattering events because this in the dominating scattering mechanism when a carrier concentration beneath 1020 cm-3 is obtained[40](#_ENREF_40), [41](#_ENREF_41), [42](#_ENREF_42). In the case of high dopant concentration one should be aware of segregation of the dopant at the grain boundaries which hampers the charge carrier’s mobility [38](#_ENREF_38).

To understand the relationship between the electrical properties and crystallinity of these thin films, the full width half maxima (FWHM) of the rocking curves of the (002) reflection are compared. The FWHM of these rocking curves are 7.04°, 7.38°, 7.00° and 9.07° for dopant levels of 1 to 4 at% respectively. The FWHM values up till dopant levels of 3 at% are comparable while for 4 at% there is a significant increase. The larger misfit of the uniaxial grown grain can introduce more defects and dangling bounds at the grain boundaries which reduces the charge carrier’s mobility, especially with the more porous morphology (figure 9). The thin film of 3 at% AZO has the most densified morphology. The morphology of the coatings made of 1 at% and 2 at% AZO shows grains that are less connected. The grains of these coatings look loosely stacked while those of 3 at% AZO thin films are more connected and densified. The coating with the lowest FWHM value and a more densified morphology results in the highest mobility (11 cm2 v-1 s-1). Coupled with the large number of charge carriers (2.23 x 1019 cm-3) obtained due to a higher dopant concentration, the lowest resistivity is obtained (2.54 c cm).

The optical transmittance of the fully processed thin film is represented in figure 10. The inset shows the transmittance in the wavelength range just before the absorption of the substrate becomes dominant. All of the films exhibit a transmission higher than 90% in the visible range of the spectrum with a sharp absorption edge around 385nm. The absorption edges shift towards lower wavelengths by increasing the dopant concentration. This shift was confirmed by plotting the absorbance squared versus the photon energy, h (figure 10). The optical band-gap, Eg, is determined by making use of the absorption coefficient, , and the following relation[43](#_ENREF_43):

eq.5

where the absorption coefficient is obtained from the transmittance data ( = (1/d)ln(1/T)), and d and T are the thickness and transmittance of the films. The optical band-gap can be obtained by extrapolating the Tauc plot towards the x-axis[44](#_ENREF_44), resulting in an optical band-gap of the thin films varying with the dopant concentration. Bulk ZnO has a band gap of 3.37 eV [45](#_ENREF_45). In case of 1 at% dopant concentration the band-gap reaches 3.27 eV while a thin film with a dopant concentration of 2 to 4 at% have a band-gap of 3.29, 3.32 and 3.34 eV. The blue shift in the absorption onset of Al doped ZnO thin films is commonly associated with the increase of carrier concentration blocking the lowest states of the conduction band, as described by Burstein[46](#_ENREF_46) and Moss[47](#_ENREF_47).

Having a closer look to the 3 at% AZO thin films, one can state that this film has a high preferential growth along the *c*-axis, the most densified surface morphology and the best opto-electrical properties compared to the other samples. A cross-section view shows a 77 nm thick AZO layer (figure 11). A small number of pinholes are scattered throughout the cross-section of the films and a grainy structure can be observed. It looks like the thin film is built up from small grains stacked on each other. This kind of structure differs a lot from the thin films obtained through sputtering processes, where a more columnar growth is observed[48](#_ENREF_48).

1. Conclusion

This work describes the ink jet printing process of Al doped ZnO thin films. Preparation of an aqueous Al doped ZnO precursor solution which was adapted towards the deposition method by the addition of ethanol was the first step. Ethanol has a positive influence on the physical parameters of the ink, such as viscosity, surface tension and density what improved printability. Also, a positive effect on the wetting of the substrate was noticed. Finally, 10 v% of ethanol was added to obtain a perfect jettable ink which has a contact angle of 3.5-4° on the cleaned glass substrate. The fabricated AZO thin films showed highly preferential growth along the *c*-axis. A positive effect of the Al doping on the crystallinity was noticed up till 3%. Higher dopant concentrations resulted in a quenching of the crystallinity. The optimal dopant concentration for the electrical properties was 3 at% of Al. A thin film with a resistivity of 2.54 c cm, a carrier density of 2.23 x 1019 cm-3 and a carrier mobility of 11 cm2 v-1 s-1 was obtained. The optical transmittance is more than 90% in the visible range of the spectrum with an optical band-gap at 3.32 eV.

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*Table caption list:*

Table 1 Ink characteristics of the AZO inks where different amounts of ethanol are added. The viscosity is measured at a shear rate of 45300 s-1.

*Figure caption list:*

Figure 1 Viscosity of the inks as a function of the shear rate.

Figure 2 Droplet visualisation of ink AZO1 where the ejection trajectory is represented as a function of time. Droplet velocity is around 2.32 m/s. The droplets are fired at 14V.

Figure 3 Droplet visualisation of ink AZO4 where the ejection trajectory is represented as a function of time. Droplets are fired at 14V and have a velocity around 2.29 m/s.

Figure 4 Jetting analysis of ink AZO4 during jetting of single droplets. Drop volume ( ) , drop diameter ( ) and the vertically displacement of the centre of mass ( ) are shown as a function of time.

Figure 5 Wetting envelope with a contact angle of 5° for cleaned Eagle2000 glass substrates.

Figure 6 Profilometer analysis of printed droplets. a) Image of 4 single droplets with a drop spacing of 250µm and a line spacing of 200µm. b) Height profile of the second row of single droplets.

Figure 7 XRD measurements for a) 1% Al doped ZnO, b) 2% Al doped ZnO, c) 3% Al doped ZnO and d) 4% Al doped ZnO.

Figure 8 Electrical properties of the processed thin films. a) Resistivity of the thin films as a function of the dopant concentration. b) Carrier mobility and concentration as a function of the dopant concentration.

Figure 9 SEM analysis of the fully processed AZO thin film: a) 1% Al doped ZnO, b) 2% Al doped ZnO, c) 3% Al doped ZnO and d) 4% Al doped ZnO.

Figure 10 Optical properties of the synthesised thin films: a) Transmittance obtained from fully processed AZO coatings. The inset shows a more detailed view of the transmittance spectra between 365 and 380nm. b): Tauc plot, where (h)² is represented as a function of h with a) 1% Al doped ZnO, b) 2% Al doped ZnO, c) 3% Al doped ZnO, d) 4% Al doped ZnO and f) uncoated substrate.

**Figure 11 Cross-sectional view of a 3 at% AZO thin film.**