Preparation of transparent, electrically conducting ZnO film from zinc acetate and alkoxide

Y. OHYA, H. SAIKI, Y. TAKAHASHI
Faculty of Engineering, Gifu University, Yanagido 1-1, Gifu 501-11, Japan

Very uniform and transparent zinc oxide thin films doped with aluminium and indium were fabricated by the dip-coating technique using solutions prepared by the ethanolamine method. As starting materials, zinc acetate and zinc n-propoxide were used. Zinc acetate and propoxide are soluble in Pr^iOH in the presence of diethanolamine, although they are hardly soluble without the amine. The prepared solutions were very stable and suitable for dip-coating. Zinc oxide was crystallized by heating above 500 °C, and doping of aluminium and indium retarded the crystallization. The electrical resistivity of the film was decreased by doping with aluminium and indium. The lowest resistivity of $2 \times 10^{-2} \, \Omega \, cm$ was obtained by post-coating treatment in a nitrogen atmosphere.

1. Introduction
Zinc oxide (ZnO) film exhibits a wide range of techno-logical applications, such as SAW devices, transparent conducting films, gas sensors, etc. [1–3]. A wide variety of coating techniques for the transparent thin film are known, including vacuum sublimation, chemical vapour deposition (CVD), spray pyrolysis, molecular-beam deposition and sputtering. A sol–gel method is another attractive technique for obtaining thin films and has the advantages of easy control of the film composition and easy fabrication of a large-area thin film with low cost. The usual starting materials of the sol–gel process are metal alkoxides and they are hydrolysed to form a sol. Some kinds of acid are often added to accelerate or control the hydrolysis. A problem in the sol–gel process is the stability of the sol. Sometimes precipitation or gelation occurs during its storage and application, depending on the type of solvent used, the amount of water, the kind and amount of acid, and the temperature. This unavoid-able nature brings lower reproducibility to the method.

Recently, we proposed an effective stabilizer, ethan-olamines, for sols derived from alkoxide [4–9]. By adding some kinds of these amines, the sol remains stable and clear for a long period, in some cases more than 2 years. The effective type of alkanolamine de-pends on the starting metal alkoxide. For example, diethanolamine is effective to make TiO_2 thin films from the $Ti(OPr^i)_4$–H_2O–Pr^iOH system, and trieth-anolamine is effective for $Al(OPr^i)_3$, $Sn(OPr^i)_4$, $Y(OBu^n)_3$, and $In(OPr^i)_3$. The ethanolamine method is also very successful for fabricating multi-component oxide thin films from alkoxides, i.e. Al_2MgO_4, PZT, YAG, YIG, etc. [4–9].

Another problem in the sol–gel process is starting reagents. Metal alkoxides are commonly used. How-ever, the metal alkoxides easily hydrolyse in ambient atmosphere and are thus expensive. Therefore, we have attempted to obtain a suitable sol from simple salts such as acetates [10], which are more convenient to use and less costly. In the present work, we applied the ethanolamine method to fabrication of trans-parent conducting ZnO thin films. As starting mater-ials, $Zn(OPr^n)_2$ and $Zn(OCOCH_3)_2$ were examined. The zinc oxide thin films were formed by the dip-coating method. The effects of Al^{3+} and In^{3+} addi-tion, and annealing in a nitrogen atmosphere, on the electrical conductivity were also investigated.

2. Experimental procedure
Commercially available zinc n-propoxide ($Zn(OPr^n)_2$, 99.99% pure, ZnPr), zinc acetate 2-hydrate (extra-pure grade, ZnAc), aluminium isopropoxide (extra-pure grade) and indium isopropoxide (extra-pure grade) were used without further purification. The solvent was dehydrated Pr^iOH. Examined sol stabiliz-ers were commercial extra-pure grade monoethanola-mine ($H_2NCH_2CH_2OH$, MEA), diethanolamine ($HN(CH_2CH_2OH)_2$, DEA) and triethanolamine ($N(CH_2CH_2OH)_3$, TEA). The ZnPr and ZnAc were dispersed into Pr^iOH and then the amine as a stabil-izer was added. The amounts of added amines were equimolar ($R = 1$) or double molar ($R = 2$) to the metal cation. The final concentrations of the solution were 0.5 and 0.6 mol l^{-1}. To make the solution more stable, second additives, i.e. acetic acid, diethylamine and distilled water, were also examined. Aluminium i-propoxide (AlPr) and indium i-propoxide (InPr) were added into the solution up to 10 at % to pre-pared aluminium- and indium-doped ZnO films. All the operations using alkoxide, before adding any am-ines, were done under an atmosphere of dry nitrogen.

ZnO film was coated on a glass substrate (7059, Corning Glass Works) by a dip-coating method. After the substrate had been dipped in a solution for 30 s, it was pulled up at various rates (2–30 cm min^{-1}), mainly 18 cm min^{-1}. Following drying at 110 °C for 15 min in air, the substrate was quickly put into a furnace at 400–700 °C and heated for 30 min or 1 h. This cycle was repeated several times to obtain the desired thickness for measurements.

The crystalline phases, crystal orientation, and crystallite size of ZnO films were determined by X-ray diffractometry (Model 2024, Rigaku Co.). The crystallite size was calculated according to Scherrer's equation using X-ray diffraction profiles. The thickness and refractive index were measured by interference bands in the visible light spectrum (Model 330, Hitachi Co.). Grain sizes and microstructure of the films were also observed using a transmission electron microscope (TEM, H-800, Hitachi Co.). The electrical resistivity of the films was measured by a four-probe method in the dark and a nitrogen atmosphere at room temperature. The resistivity of the films annealed in nitrogen at 500–700 °C for 30 min was also measured.

3. Results and discussion
3.1. Preparation of the dip solution
Zinc n-propoxide (ZnPr) is almost insoluble in Pr^{i}OH. Among the examined amines, only DEA could make ZnPr dissolve in Pr^{i}OH. The DEA-added solution became clear within 1 day, leaving a small amount of insoluble particles, which would be ZnPr hydrated during storage. This solution was so stable for hydrolysis that precipitation or gelation did not occur even after the addition of much water (H$_2$O/Zn > 3). The addition of MEA and TEA caused gelation of the solutions after several tens of minutes and after several days, respectively.

In the case of ZnAc, which is also insoluble in Pr^{i}OH, MEA and DEA were effective in making clean solutions, but double the amounts of amines are required to keep the solutions stable and clear for a long period. By adding a second stabilizer, the solutions prepared with equimolar DEA were further stabilized. Of the second stabilizers examined, water was the best. Although acetic acid was effective against precipitation and gelation, it rendered the films opaque. Diethylamine reduced the wettability of the solution on the substrate used. The solution prepared by adding equimolar DEA ($R = 1$) and double molar water ($W = 2$) was used as the dip solution.

Addition of aluminium isopropoxide and indium isopropoxide into both alkoxide- and acetate-derived clear solutions did not cause any change in the appearance of the solutions.

3.2. Dip-coating and coated films
Fig. 1 shows examples of visible spectra of coated and heat-treated films. These films are fabricated using ZnPr solution with and without AlPr addition, coated ten times at 600 °C for 1 h. The films were transparent with a transmittance of more than 90%. Every film
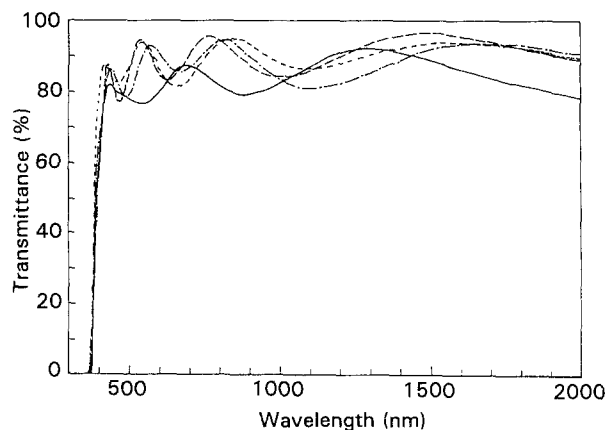

Figure 1 Visible spectra of ZnO films doped with (——) 0, (— — —) 2, (— · —) 4 and (- - -) 8 mol % aluminium.

exhibited regular interference bands in the visible light spectra. The presence of the bands confirms the uniformity of thickness of the film. From the absorbance edge, the band gap was estimated to be about 3.3 eV. The refractive index and film thickness were calculated using the interference bands. The calculated refractive index was about 1.8–1.9 at 560 nm. This value is close to or higher than 90% of the value reported for ZnO single crystal, 2.013 and 2.029 at 590 nm [11]. The high index suggests the low porosity of the films.

Fig. 2 shows typical X-ray diffraction patterns of the 3 mol % Al-doped ZnO films from ZnPr. They were heated at 400–700 °C for 30 min in air. At 400 °C, the film was amorphous and crystallized at 500 °C. The crystallization temperature of the films varies with the content of aluminium and indium. With increasing additive content, the crystallization temperature was raised and the X-ray diffraction peak width became broader, as shown in Fig. 3. In particular, the addition of indium oxide strongly retarded the crystallization, even at the high temperature of 700 °C. This drastic retardation would be due to the difference in ionic radius between Zn^{2+} and In^{3+}, 0.060 and 0.080 nm (after Shannon), respectively. The crystallite sizes of ZnO were also decreased on doping with aluminium and indium. The size was 55 nm for undoped films derived from ZnAc and heated at 500 °C for 30 min, and the sizes reduced to 40 and 20 nm for films doped with 2 mol % Al and 2 mol % In, respectively.

The relative intensities in the X-ray diffraction peaks depend on the starting materials. Zinc oxide film from zinc acetate (ZnAc) exhibited a strong orientation of the c-axis perpendicular to the surface of a glass plate. Fig. 4 shows this tendency of preferred orientation. The degree of orientation also depends on the amount of added water and the temperature of heat treatment. The mechanism of the orientation is now under consideration, but many films from the sol–gel method, for example TiO$_2$ [4], show the orientation even on a glass substrate.

A change in thickness with the increasing heating temperature is shown in Fig. 5. The film was fabricated using ZnPr, containing 3 mol % Al and dipcoated six times. At 400 °C the film was amorphous
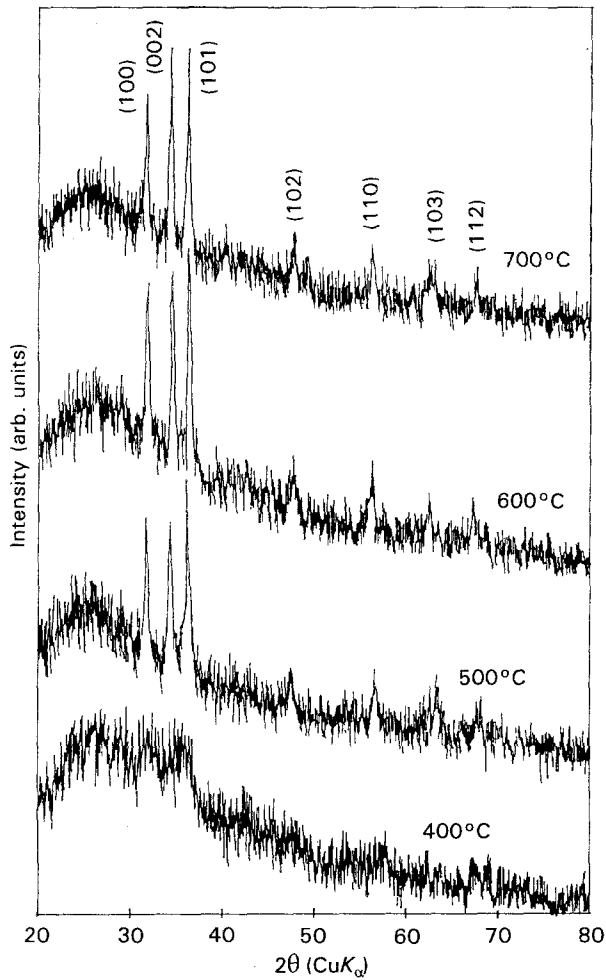
Figure 2 X-ray diffraction patterns of ZnO films doped with 3 mol % Al and heated at 400–700 °C for 30 min.

Figure 4 Preferred orientation of ZnO films from ZnPr and ZnAc, and powder from ZnAc.
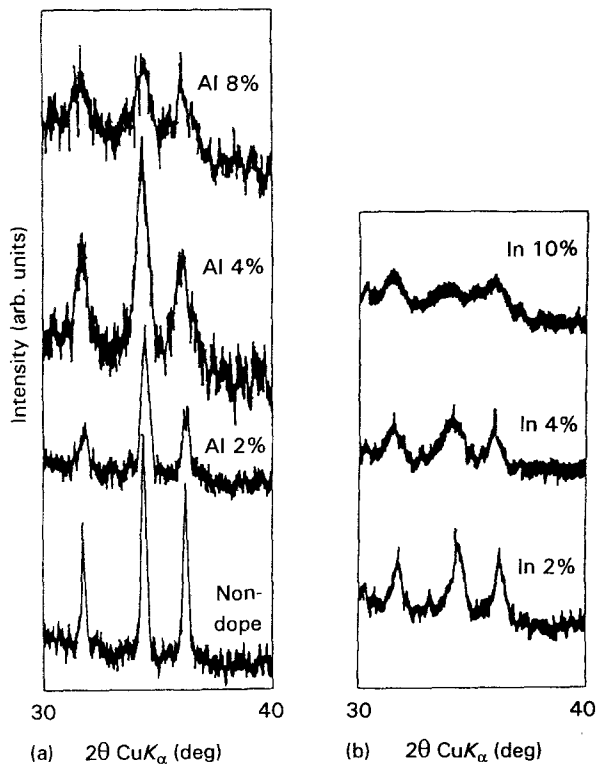

Figure 3 Zinc oxide films (a) doped with aluminium and heated at 600 °C for 30 min, and (b) doped with indium and heated at 700 °C for 30 min.
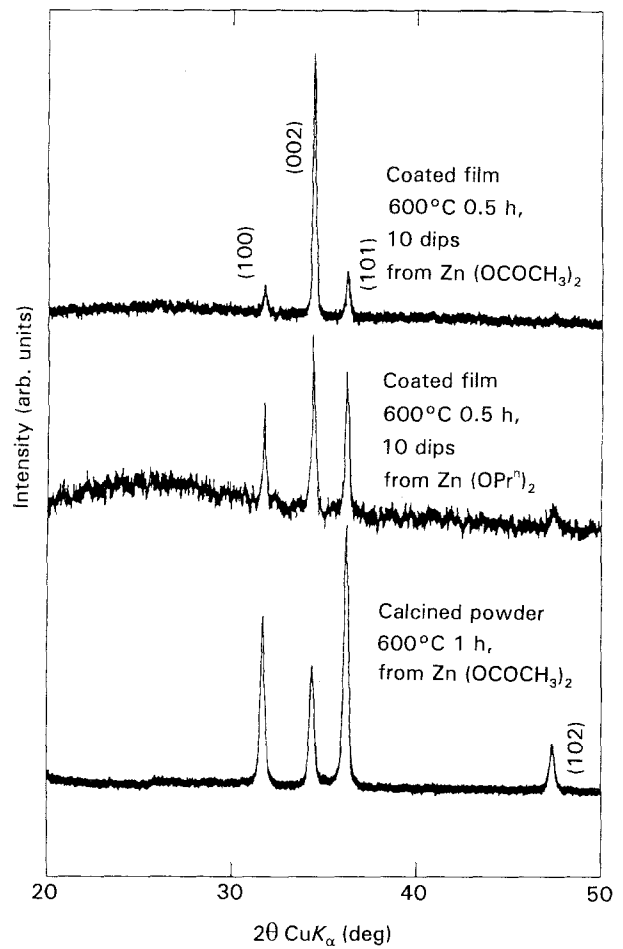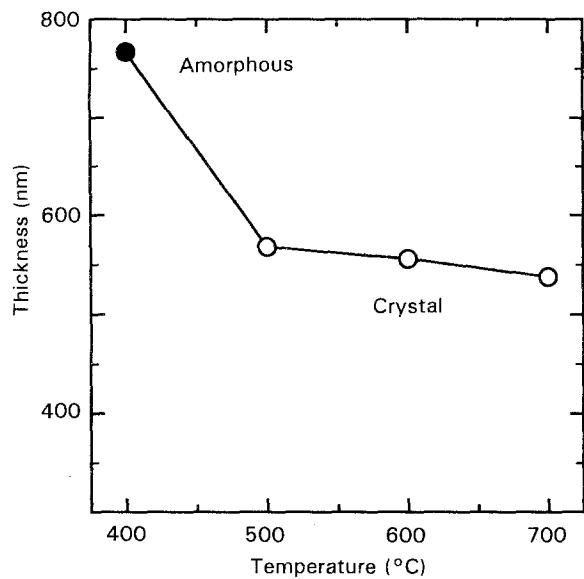

Figure 5 Change in thickness with increasing heating temperature.

with a thickness of 770 nm. At 500 °C the film crystallized and decreased in thickness to 570 nm. Above 500 °C, the thickness continually decreased but the rate reduced. The large decrease in thickness was caused by crystallization.

The transmission electron micrograph in Fig. 6 shows a cross-section of a film with 3 mol % Al, heated at 600 °C, and dipped six times. Six layers can
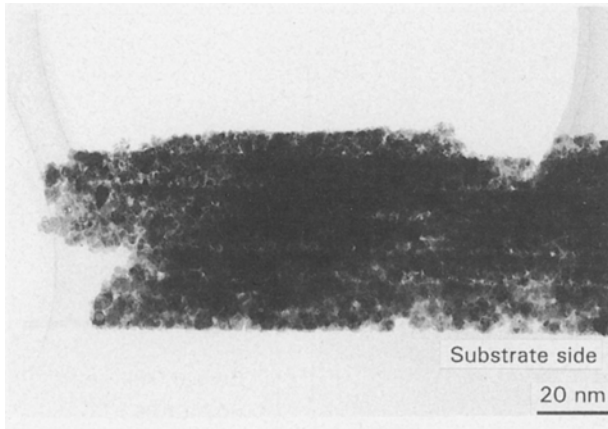
Figure 6 A transmission electron micrograph of a film with 3 mol % Al, heated at 600 °C and dipped six times.

Figure 7 Resistivity changes with heated temperature.

be seen in the film, in accordance with the number of dips. Dark contrasts existed between each layer. These contrasts would be caused by the flatness of each layer surface after each heat treatment, i.e. ZnO grains arranged in a surface top so that the density of the grain through which the electron beam passed became large. The grain size ranged from 10–50 nm and the bottom layer has a rather large grain size. Although the grains seem to be closely packed, the shape of the grains was round, indicating that the film was not tightly sintered. The grain size and shape are quite different from those of sputtered ZnO films [1].

3.3. Electrical resistivity

The undoped ZnO films prepared in the present work had a resistivity of about 10 Ω cm. The zinc oxide is an n-type semiconductor and trivalent ions, such as Al^{3+}, Cr^{3+}, Ga^{3+} and In^{3+}, are commonly doped to decrease the resistivity of ZnO [12–15]. Fig. 7 shows the change in resistivity of Al^{3+} doped films with firing temperature. The films were doped with 2 and 3 mol % Al, and prepared from ZnPr solution. The resistivity of the films with 3 mol % Al and heated at 400 °C was too high to measure with the equipment used in this work. The resistivity shows a minimum at 500 °C. As the heating temperature increased from 500–700 °C, the resistivity increased. The same tendency was found for antimony-doped SnO_2 films by the sol–gel method [7]. The addition of 2 or 3 mol % Al would produce enough defects in the host ZnO lattice. Higher temperature treatment would cause high mobility, because it induces high crystallinity and grain growth [16]. The experimental results are in contrast to this expectation and therefore they could not be interpreted only by the simple concept of the conductivity, the product of carrier density and its mobility. The factors, such as defects association, adsorption of various gases on the surface, diffusion of substrate components into the film, and stress of ZnO films due to thermal expansion mismatch with the substrate, should be considered to realize the results.

The effects of the amount of additives on resistivity are shown in Fig. 8. These films were prepared by dip-coating eight times and firing at 500 °C for 30 min.
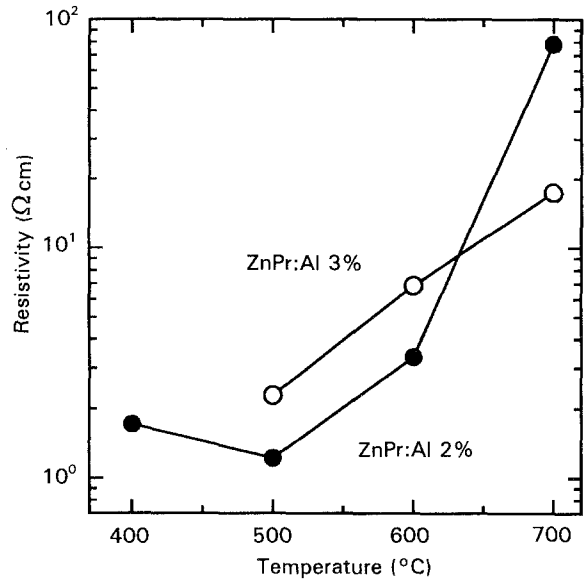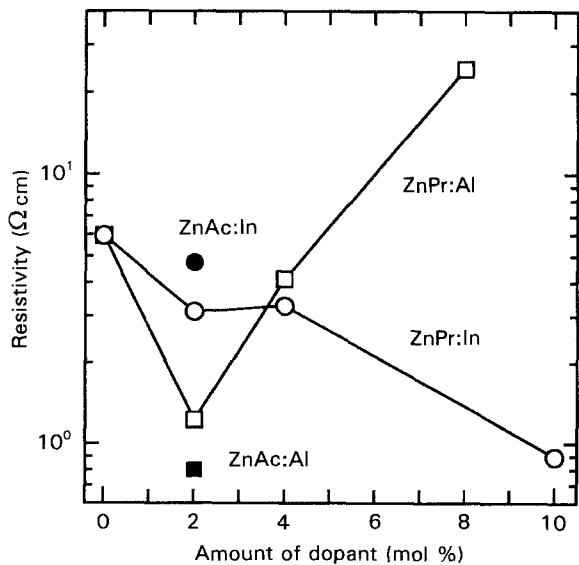

Figure 8 Effects of amount of additives on resistivity.

The addition of aluminium and indium had quite different effects on resistivity. The increasing addition of indium decreased the resistivity of the films, though aluminium increased it. At the heating temperature of 500 °C, indium oxide-doped ZnO has lower crystallinity, and X-ray diffractometry revealed that the film doped with 10 wt % In was amorphous. This reduction in crystallinity should induce lower electron mobility, although the resistivity of indium-doped films decreased. On the other hand, the difference in the starting reagents, ZnPr and ZnAc, makes no significant difference to resistivity, and the films have almost the same ranges of resistivity.

It is well known that annealing in an inert atmosphere decreases the electrical resistivity. Fig. 9 shows the changes in resistivity after heat treatment in nitrogen gas at 500 °C for 30 min. By the treatment, the resistivity becomes smaller by two orders of magnitude than those of as-fired films. The lowest resistivity
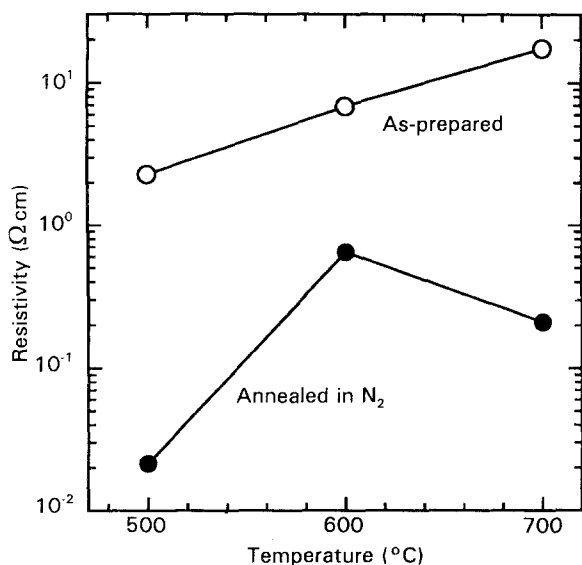
Figure 9 Changes in resistivity after heat treatment in nitrogen.

of 2×10^{-2} Ω cm was obtained. Although the resistivity was very low among sol–gel ZnO films, it is much higher compared with the films prepared by vapour-phase techniques [3, 12, 17]. As discussed in the previous section, aluminium- and indium-doped ZnO films were composed of small grains, suggesting large scattering of carriers at the grain boundary. Therefore, the resistivity of sol–gel films would be lowered by reducing the number of conduction barriers, i.e. grain boundaries.

4. Conclusion

A solution suitable for dip-coating could be prepared using both zinc alkoxide and zinc acetate by the ethanolamine method. The solution from zinc acetate was stabilized by water for a long time. The films prepared by dip coating were transparent and uniform. The grain size of the films was very small, less than 50 nm. Both additives, aluminium and indium,

reduced the crystallinity of ZnO. The minimum electrical resistivity, 2×10^{-2} Ω cm, was found for the 2 mol % Al-doped films prepared at 500 °C and subsequently heat treated in nitrogen at 500 °C for 30 min.

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