The Precursor Ratio Effects on the Electrical and Optical Properties of the ZnO:Al Transparent Conducting Oxide Grown by ALD Method

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Abstract

Aluminium-doped ZnO (ZnO:Al) films were grown by atomic layer-controlled deposition on glass substrates at temperature of 200℃ using diethylzinc($Zn(C_2H_2)_2$; DEtZn), water(H_2O) and trimethylaluminium ($Al(CH_3)_3$; TMA) as precursors. As the cycle ratio of TMA to DEZn(TMA/DEZn) increased, the resistivity of the films decreased and the roughness increased. In the case of TMA/DEZn pulse ratio of 1 to 10, the film had a resistivity of $9.7\times10^{-4}\,\Omega\cdot cm$ and a roughness of 2.25nm(rms), while in the case of only DEZ injection the film had a resistivity of $3.5\times10^{-3}\,\Omega\cdot cm$ and a roughness of 1.07nm(rms)

1. Introduction

Transparent conducting oxide(TCO) has attracted much attentions for use in a variety of applications. Most important applications include flat panel displays, solar cells, transmittance-variable windows and gas sensors. At present, the most widely used TCO is Tin-doped indium oxide(ITO) and ITO offers the best available performance in terms of conductivity, transmissivity, and stability. But, it has expensive cost. Impurity-doped ZnO, an inexpensive and abundant binary compound material, has been developed. Recently, Al-doped ZnO(ZnO:Al) and Ga-doped ZnO(ZnO:Ga) have attracted much attention as the transparent electrode for thin-solid solar cells. ZnO is a direct band gap semiconductor with an energy gap of 3.3eV. ZnO is also transparent and electrically conductive with appropriate dopants such as Ga and Al.

As an alternative candidate preparation method besides of d. c. and r. f magnetron sputtering, the atomic layer deposition (ALD) method offers many advantages. The ALD method depends on alternate pulsing of the precursor gases and vapors onto the substrate. Between the precursor pulses, the reaction chamber is purged with an inert gas such as argon or nitrogen. Under the proper experimental conditions such as precursor pulse duration, pulse ratio between precursors, and purge time, the growth can be stable and the thickness is accurately controlled due to the intrinsically self-limiting growth mechanism.

In this study, we report about the precursor pulse ratio dependence of the electrical, structural, and optical properties of the ZnO:Al films prepared by ALD method.

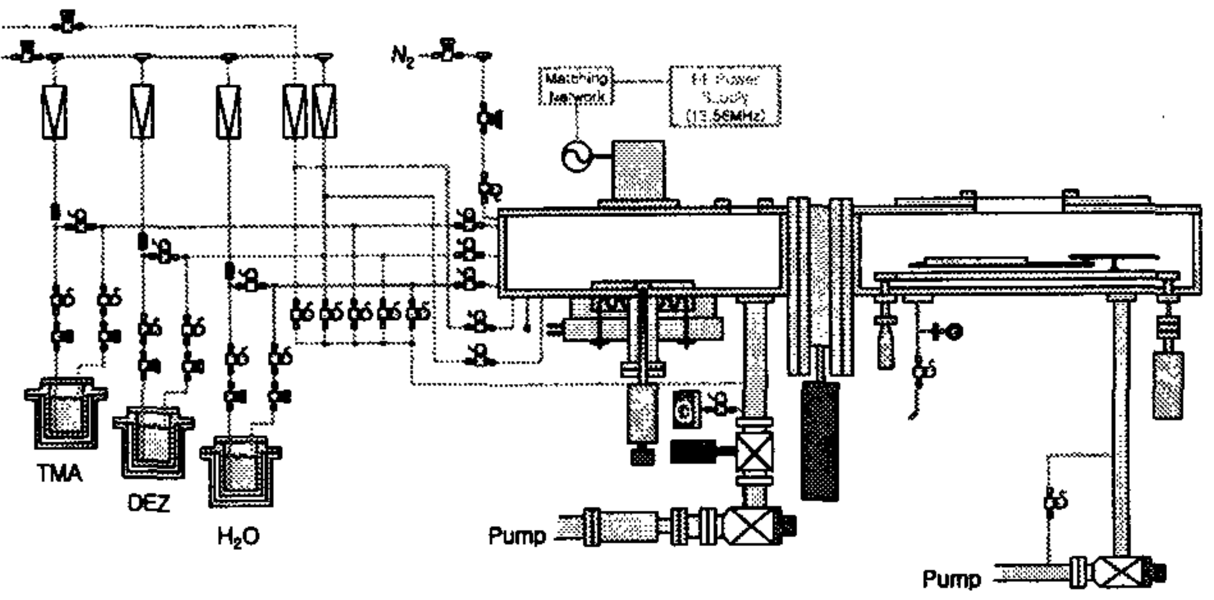


Fig. 1. Schematic representation of the experimental setup for the atomic layer controlled reaction.

2. Experimental

The configuration for the atomic layer reaction system is shown in Fig.1. The reactor consists of a reaction chamber with load-lock chamber, a computer-controlled source manifold, precursor reservoirs, and mechanical pump. Precursor sources consist of DEtZn for Zn source, TMA for Al source, and H_2O for oxygen source. Temperatures of all precursors were maintained at 10°C controlled by each chiller. The base pressure obtained ultimately from the pump was 3mtorr. Substrate temperature controlled by an external control system was maintained at 200°C during reaction. Substrates used for this experiment were soda-lime glasses. For the undoped ZnO films, DEZ and H_2O

precursors were alternately fed into the reaction chamber. For the Al-doped ZnO films, TMA precursor was introduced once in every 10, 30 pulses DEZ or H_2O injection. In our experiments, typical pulse lengths of the precursors for reaction were 2sec and the Ar purge times for evacuation between the precursor injections were 7sec. The injection sequences for the undoped and doped ZnO reactions are shown in Fig. 2. Chamber pressure during reaction was typically 1torr. The flow rates of the precursors were controlled by the temperature of reservoirs which were adjusted at 10°C.

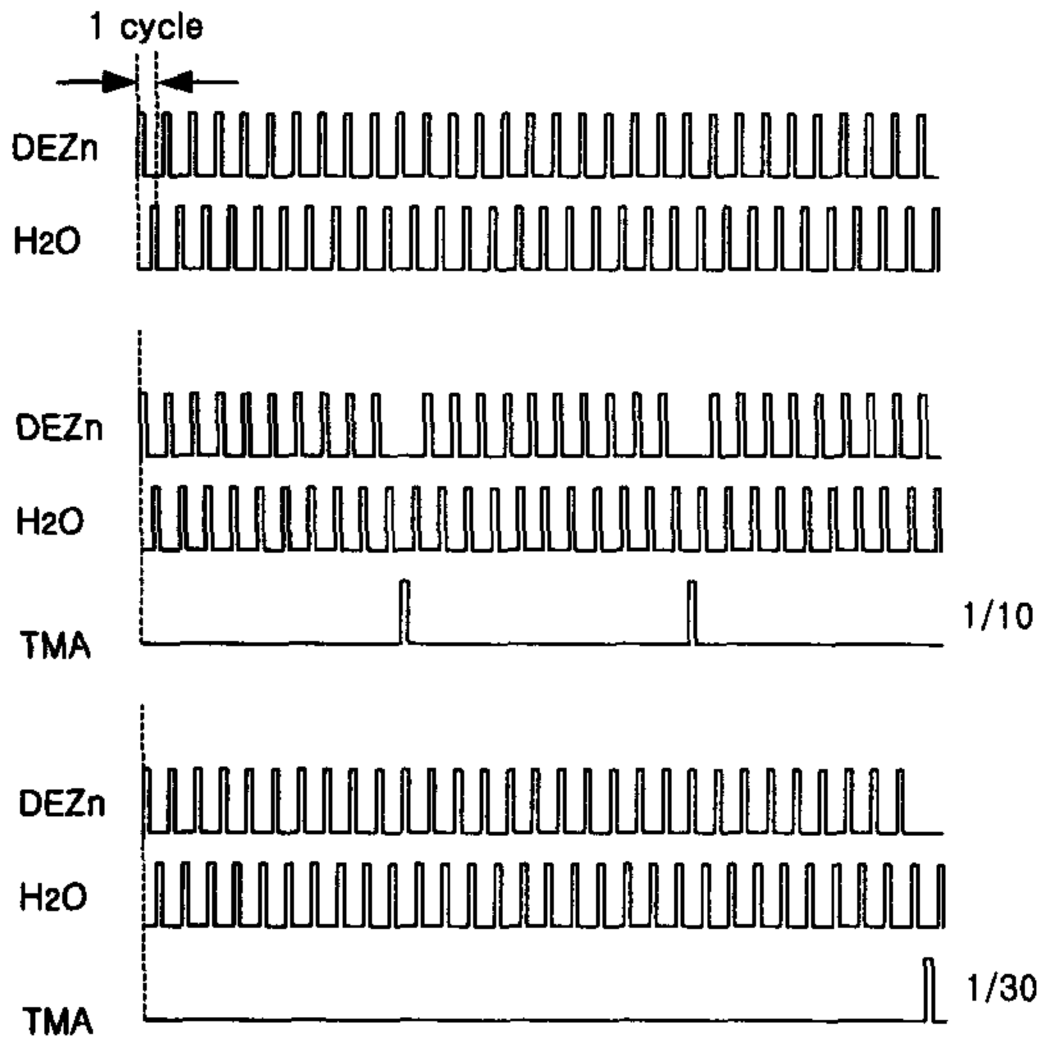


Fig. 2. Pulse sequences for various TMA injection.

3. Results and discussion

We examined the impurity doping effects on the electrical and optical properties by introducing the TMA precursor. Trimetylaluminium(TMA) was introduced into the reaction chamber by substituting for DEZn pulses once in every 10 or 30 pulses of DEZn, and none for comparison. The amount of the injected TMA can be represented by the pulse ratio of TMA to DEZn(TMA/DEZn). Pulse duration of TMA was 2 sec same as DEZn, which was introduced after the last pulse of DEZn in each period as shown in Fig. 2. Ar purge time was 7 sec at 300sccm, in order to put the reaction mechanism at the self-limiting atomic layer-controlled growth regime. The resistivity decreases gradually as TMA/DEZn pulse ratio increases as shown in Fig. 3. As results, a low resistivity of $9.7\times10^{-4}\Omega\cdot$cm was obtained at TMA/DEZn=1/10 ratio while higher values of 1.45×10^{-3} and $3.47\times10^{-3}\Omega\cdot$cm were measured at 1/30 ratio and undoped ZnO, respectively. It indicates that in the undoped ZnO film, the free electrons are provided by the native oxygen vacancies, while in the Al-doped films those are mainly attributed by the interstitial Al atoms as external donors. Whereas, the growth rate per cycle(one DEZn pulse + one H_2O pulse) increases as the percentage of TMA injections increases. The increase of the growth rate can be attributed to the extension of the interplanar distances between crystallographic planes of ZnO due to the interstitial Al atoms. The interplanar distances for the simple planes of as-grown ZnO films were reported by 2.816, 2.602 Å for (100), (002) orientation, respectively[9]. In our results as shown in Fig. 3, the thickness per cycle was about 3.0 Å for the undoped ZnO film which is according to about an atomic monolayer of ZnO. However, in the Al-doped film with the 1/30 ratio of TMA/DEZn which is according to substituting the 3.2% of DEZn pulses with TMA pulses, the growth rate in average over the entire film thickness increases to 3.5 Å per cycle. In the case of 1/10 TMA/DEZn ratio(according to 9.1% of DEZn pulses), the growth rate increased up to 5.2 Å per cycle.

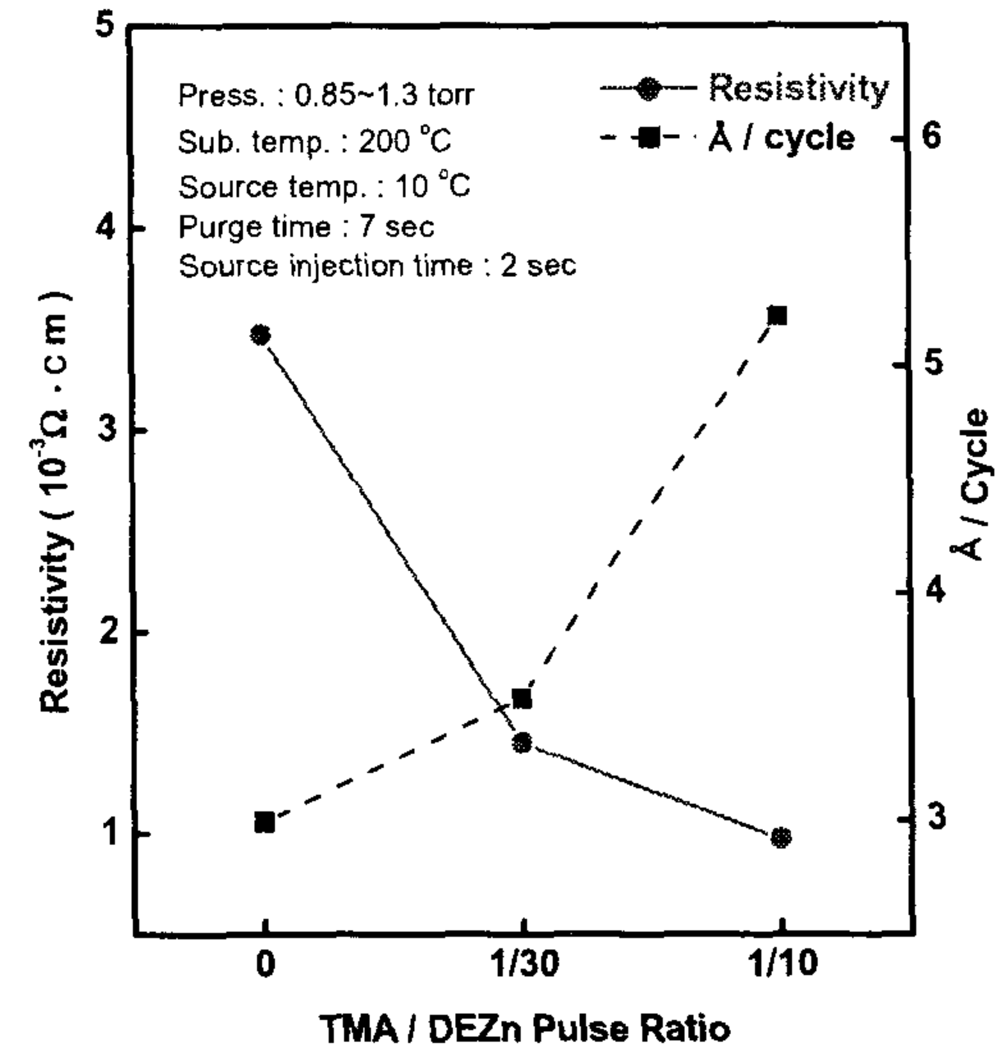


Fig. 3. Resistivity and growth rate of Al-doped ZnO films vs. TMA/DEZn pulse ratio.

These may indicate that the average interplanar distance increases by introducing Al interstitial atoms into the ZnO films. The average increase of the growth rate varied from 1.16 to 1.73 times than as-grown ZnO film depending on the substitution of TMA pulses ranging from 3.2% to 9.1% of DEZn pulses

Figure 4 shows XRD spectra for films deposited on glass at different injection of TMA precursors. The films are crystalline ZnO of which orientation are influenced by the Al doping. In the undoped ZnO, the (002) preferential orientation is favored, whereas in the Al-doped ZnO films (100) orientation is observed predominantly. This property coincides with the behaviors that the interplanar distance for (100) orientation is larger than that for (002) orientation and as shown in our result the growing thickness per cycle(approximately the interplanar distance) of the doped ZnO film is higher than that of the undoped ZnO film.

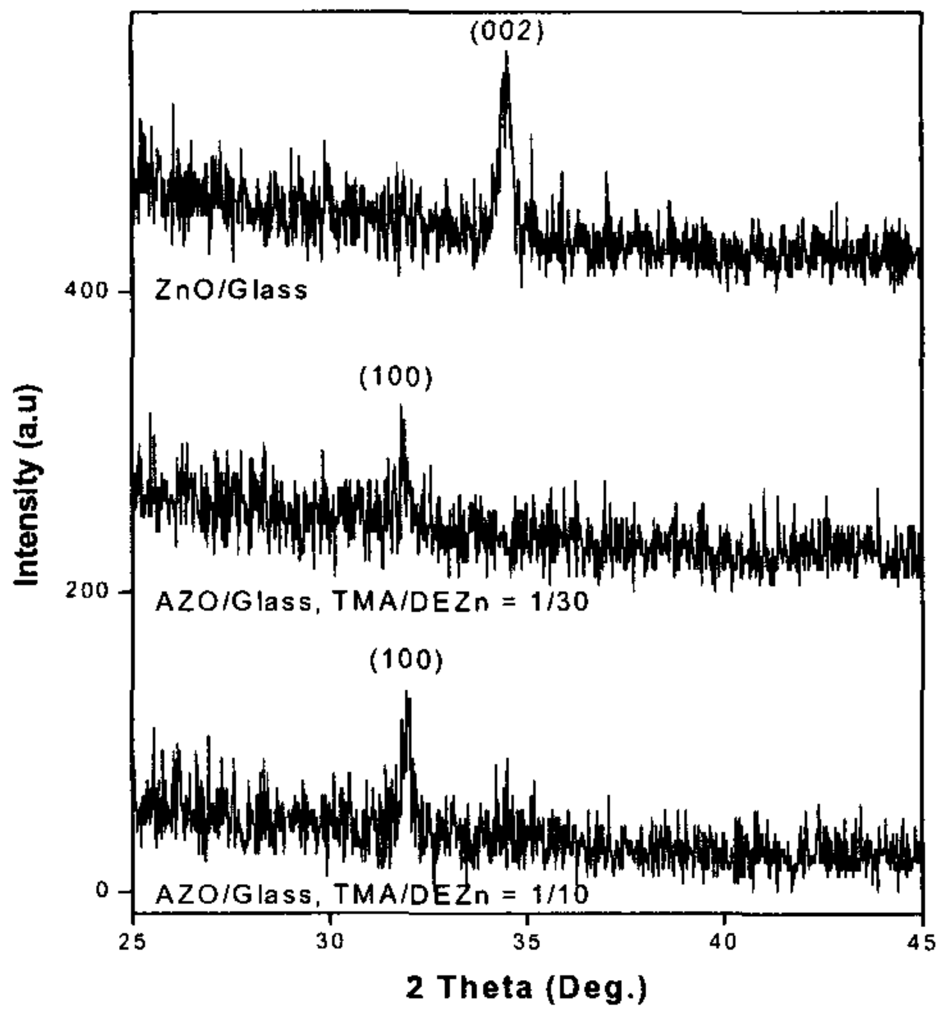


Fig. 4. Effect of the Al doping on the X-ray diffraction diagram of ZnO films.

Figure 8 shows the transmission spectra of the undoped and Al-doped ZnO/glass samples. For comparison, the corresponding optical transmission curve of the only glass is presented. UV-Vis spectroscopy showed that the overall transmittances were in excess of 80% for ZnO/glass and Al-doped ZnO(AZO)/glass films, with a better performance for undoped ZnO at short wavelengths less than 45nm, for 1/30-doped AZO at middle wavelengths between 45 and 62nm, and for 1/10-doped AZO at wavelengths longer than 62nm.

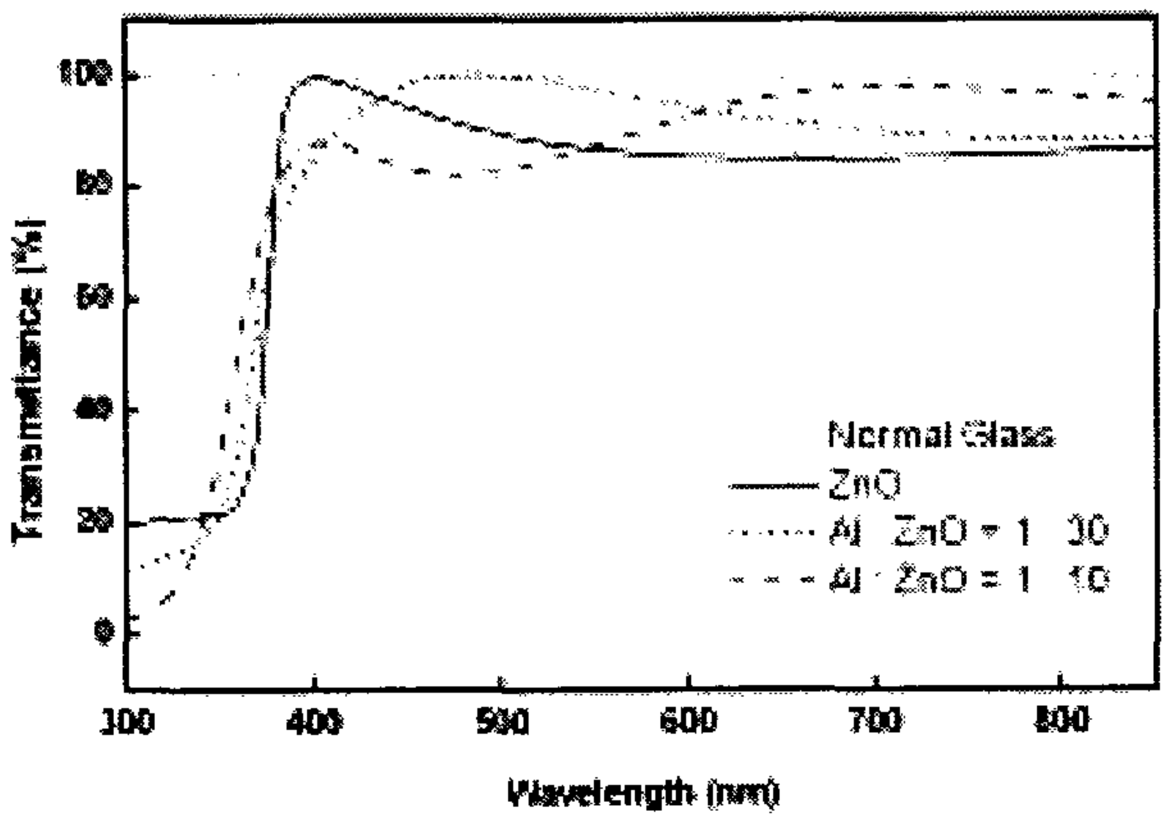
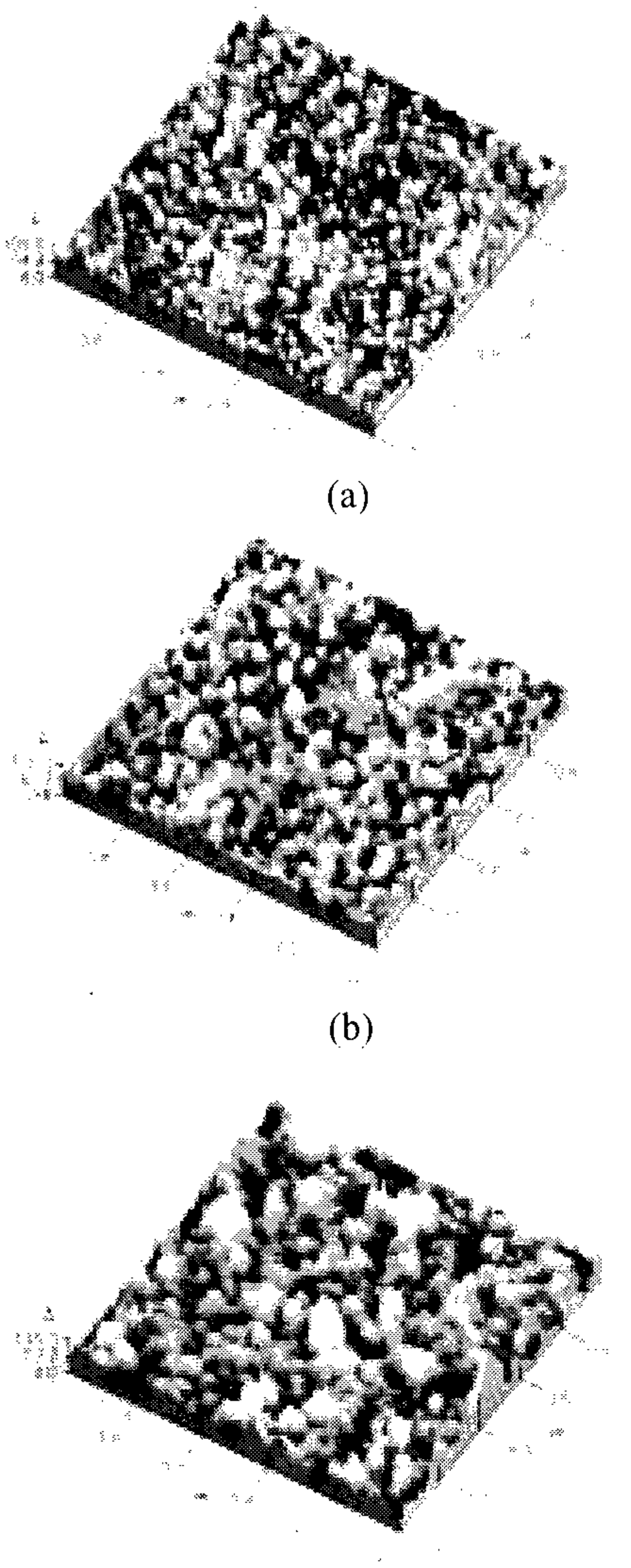


Fig. 5. Transmission spectra of ZnO films depending on the Al doping conditions.

The other aspect interesting to observe concerns the surface roughness depending on the preparation conditions. Smoothness of the transparent conducting oxide is an important consideration for flat panel display and piezoelectric device applications. However, individual spikes or contaminating particles ruin a display, especially in passive matrix OLED(Organic Light Emitting Display) panels. A simple specification is to require that the root-mean-square (rms) roughness be less than a certain value, typically 2 nm. Peak-to-valley limits are thus more useful. The surface morphology in the Al doping conditions was observed by AFM imaging. Figure 6 shows AFM images of 1×1 μm^2 area of the undoped ZnO and Al-doped ZnO films. A slight changes in surface morphology were presented in the figure, with increasing roughness as increasing Al doping ratio.

The characteristic values of the surface morphology by means of the root mean square roughness(R_{ms}) and the peak-to-peak value(R_{p-v}) were measured and presented in Table 1. The highest R_{ms} roughness of 2.25nm was observed in the 1/10 TMA/DEZn ratio film, in comparison with a lower value of 1.45nm in the 1/30 ratio film and the lowest value of 1.07nm in the undoped ZnO film. It is noticeable that typical requirement for the passive matrix OLED is less than 2nm.


(a)

(b)

(c)

Fig. 6. AFM images of the ZnO films as a function of Al doping: (a)only DEZn, (b)TMA/DEZn=1/30, and (c)TMA/DEZn=1/10.

Table 1. Characteristic roughness values of differently doped ZnO films

Value Condition	R_{ms} (nm)	$R_{p\text{-}v}$ (nm)
Undoped ZnO	1.07	7.78
AZO; TMA/DEZn = 1/30	1.45	13.9
AZO; TMA/DEZn = 1/10	2.25	15.9

4. Conclusions

Al doped ZnO(AZO) films were deposited on glass substrates heated to 200°C by using the atomic layer controlled deposition method(ALD). The effect of Al doping on the properties of ALD deposited ZnO was examined using $Zn(C_2H_2)_2$, H_2O and $Al(CH_3)_3$ as precursors. The growth rate was affected by the substitution of ZnO pulses with TMA pulses. The preferential crystalline orientation was changed from (002) to (100) with Al doping from the undoped ZnO. From the optical transmission measurement, it was indicated that the overall transmittances were in excess of 80 for all samples, with specially a better performance for undoped ZnO at short wavelengths less than 45nm, for 1/30-doped AZO at middle wavelengths between 45 and 62nm, and for 1/10-doped AZO at wavelengths longer than 62nm. Besides of these characteristics, the smooth morphology observed from AFM imaging shows that ALD deposited AZO films can be applied for the transparent conducting oxide of the flat panel display with its R_{ms} value ranging from 1.07 to 2.25nm.

5. References

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