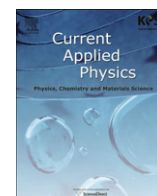


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Enhancement of electrical properties in Al-doped ZnO films by tuning dc bias voltage during radio frequency magnetron sputtering

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ABSTRACT

Al-doped ZnO (AZO) thin films were deposited at room temperature on glass substrates by rf magnetron sputtering with simultaneous dc bias through an external inductor coil. The deposition rates of AZO films deposited using simultaneous rf and dc power along with an inductor coil were 20% higher than those deposited using only rf power. The effects of simultaneous rf and dc bias voltage during the deposition of AZO films were investigated in terms of their resistivity and compressive stress. It was observed that the AZO films deposited at 120 W rf power with 600 μ H inductor coil exhibit the lowest resistivity of $6.71 \times 10^{-4} \Omega \cdot \text{cm}$.

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1. Introduction

Transparent conductive oxide (TCO) films, as front electrodes, find applications in a wide range of devices, such as liquid crystal displays (LCDs) [1], light emitting diodes [2], and thin film solar cells [3–5], because of their excellent electrical conductivity and high optical transparency in the visible wavelengths (400–800 nm). Indium Tin Oxide (ITO) has been, so far, the dominant TCO material studied and used extensively in the devices due to its good electrical and optical properties [6]. However, these ITO films face some severe problems such as high cost, toxicity and limited resources. In contrast, the ZnO-based films are relatively inexpensive, nontoxic and abundant compared to ITO films and are considered to be emerging alternative TCO materials [7].

Recently, the devices on flexible substrates received considerable attention due to the very advantage of flexibility. However, due to the poor thermal endurance of these flexible substrates, the devices on these substrates need to be deposited at low substrate

temperature. This leads to a compromise on the crystalline quality of the deposited films. Hence, it has been a major challenge for the researchers to deposit high quality crystalline films on flexible substrates. In this regard the advantages of rf magnetron sputtering, over other techniques, are exploited in depositing the films of high crystalline quality with required resistance and the transparency at temperatures less than 100 °C, often without additional heat treatment [8]. If, in addition, a negative dc bias is applied to the substrate during rf-sputtering, cations in the plasma are attracted towards the substrate and bombard the growing film on the substrate. Such a bombardment gives additional energy to the molecules and clusters condensed on substrate and re-sputter those which are weakly bonded. Danson et al. reported that this bombardment was beneficial to the films crystallinity and was equivalent to the energy provided by a higher substrate temperature to achieve better crystallinity [9]. In this work, we report on the growth of high quality crystalline AZO films with low specific resistivity by tuning the applied dc bias voltage during the rf magnetron sputtering. We present the data on the influence of plasma parameters, in pure Argon plasma with different target-bias voltages, on the resistivity and deposition rate of AZO films.

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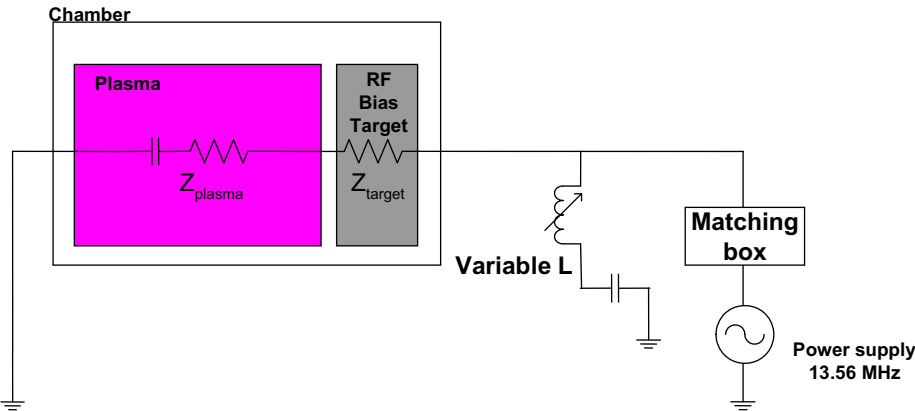


Fig. 1. Schematic of the experimental setup: The external inductor coil installed between the chamber and matching box.

2. Experimental

The schematic diagram of the deposition system is shown in Fig. 1. The cathode was excited simultaneously by a RF generator and dc bias voltage with an inductor coil. The inductor coil also helps avoiding the short circuiting of the rf voltage. The RF power was coupled capacitively via a matching network, which was tuned for minimum reflected power. The target-bias voltage was controlled by varying inductance in an inductor coil. AZO films were deposited on corning glass by a 13.56 MHz RF magnetron sputtering system using a 2 inch Al-doped ZnO (AZO) target of purity 99.99%. The sputtering chamber was evacuated to a base pressure of about 1×10^{-6} Torr using a turbo molecular pump. Working pressure was maintained at 5 mTorr under high-purity Ar (99.999%) gas. The glass substrates were ultrasonically cleaned in acetone, methanol, ethanol, and distilled water, sequentially, and finally dried with nitrogen gas. The AZO films were deposited on clean glass substrates for 10 min at room temperature (RT) with varied RF power from 50 to 130 W under pure Ar plasma.

The structural and surface morphological characterization were carried out using X-ray diffraction (XRD, Bruker D8) and atomic force microscope (AFM, Veeco DM 3100), respectively. The growth rate and the thickness of the films were determined by a reflectometer (ST2000-DLXn, K-MAC). The electrical properties such as the resistivity, carrier concentration and hall mobility were measured through hall-effect-measurement in van der Pauw geometry (HMS-3000, ECOPIA).

3. Result and discussion

Table 1 summarize the thicknesses of the deposited AZO films under various combinations of the simultaneous rf and dc bias voltages with varied inductance from 0 to 600 μH . Target-bias voltage was measured through monitoring system attached to rf

Table 1
The dc bias voltage and thickness of the AZO films deposited with simultaneous rf and dc power with inductance of 0, 300, and 600 μH .

Rf power (W)	Dc bias voltage (V)			Thickness (nm)		
	0 μH	300 μH	600 μH	0 μH	300 μH	600 μH
50	-160	-180	-190	150	160	200
60	-180	-190	-200	170	180	250
80	-230	-240	-250	280	330	350
100	-260	-270	-280	350	423	446
120	-290	-300	-310	450	509	550
130	-300	-310	-320	450	520	600

generator. The rf power with an external inductor coil helps in achieving higher target-bias voltage by a factor of 20–30 V, compared to the case of only rf power with no inductance. The film thickness increases with the increase in the simultaneous dc and rf powers, as expected. The maximum thickness of the film achieved, for the 130 W rf power and fixed 10 min deposition, increases from 450 nm to 520 nm and then to 600 nm for increase in inductance value from 0 to 300 μH and then to 600 μH , respectively.

Fig. 2 shows the deposition beam flux as a function of the rf power for films deposited with simultaneous rf and dc power through external inductor coil (0, 300 and 600 μH). The observed deposition rate of the AZO films increases linearly from 17 nm/min for 50 W of rf power to 51 nm/min for 130 W of rf power. For the films deposited with rf power and an inductor coil (600 μH), the deposition rate increases by about 20% higher compared to those with no inductor coil. The increase of target-bias voltage, at constant rf power, just by adding an inductor coil increases the deposition rate of AZO films. The increase could be attributed to the

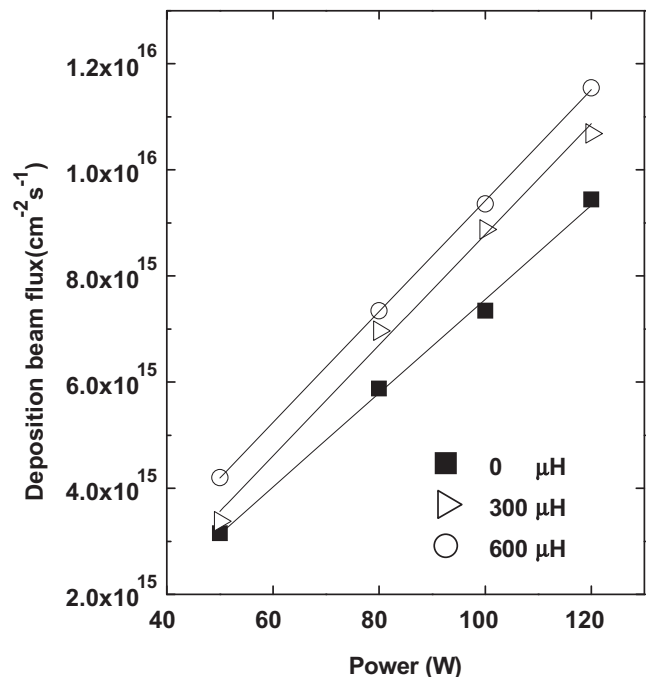


Fig. 2. Deposition beam flux as a function of discharge power with inductor coil (0, 300 and 600 μH) for AZO films.

Ar^+ bombardment due to the accelerating voltage between plasma potential and floating potential, which enhances the surface migration on the growing film.

Fig. 3 shows the XRD patterns of the AZO films deposited at various rf powers with inductance of 0, 300 and 600 μH . It is clear from the figures that all deposited films are polycrystalline with a hexagonal structure. The (002) peak, observed at around $2\theta = 34.40^\circ$, is very close to that of JCPDS value for bulk ZnO crystal (34.47°). The smaller peak located at $2\theta = 72.5^\circ$ correspond to the (004) diffraction. The intensities of XRD peaks are normalized with the measured film thickness. For films deposited with zero inductance, as shown in Fig. 3(a), the intensity of (002) peak slightly decreases with increase of rf power until 100 W and there after it increases. However, for the films deposited with inductance of 300 μH (Fig. 3(b)) and 600 μH (Fig. 3(c)), there is no such variation observed in the intensity of the (002) peak. From the above figures, it is also evident that the position of (002) peak shifts slightly towards the higher 2θ side with the increase in rf power. This

suggests that the c- lattice parameter decreases with rf power and can be correlated to the induced residual stress in the film.

The residual stress in the deposited film was calculated based on biaxial strain model using the peak position of the (002) peak [10]. The strain $\epsilon = (C_{\text{film}} - C_{\text{bulk}}/C_{\text{bulk}})$ along the c-axis, i.e., perpendicular to the film surface, was estimated using the lattice parameters calculated from the XRD patterns. To derive the film stress σ_{film} parallel to the film surface, the following formula was used, which is valid for a hexagonal lattice:

$$\sigma_{\text{film}}^{\text{XRD}} = \frac{2c_{13}^2 - c_{33}(c_{11} + c_{12})}{2c_{12}} \cdot \frac{c_{\text{film}} - c_{\text{bulk}}}{c_{\text{bulk}}} \quad (1)$$

For elastic constants, C_{ij} , data of single crystalline ZnO were used; $C_{11} = 208.8$, $C_{33} = 213.8$, $C_{12} = 119.7$, $C_{13} = 104.2$ GPa [11]. This yields the following numerical relation for the stress derived from XRD : $\sigma_{\text{film}} = -233\epsilon$ [GPa]. Fig. 4 shows the induced residual stress in the deposited AZO films as a function of the bias voltage. As the bias voltage

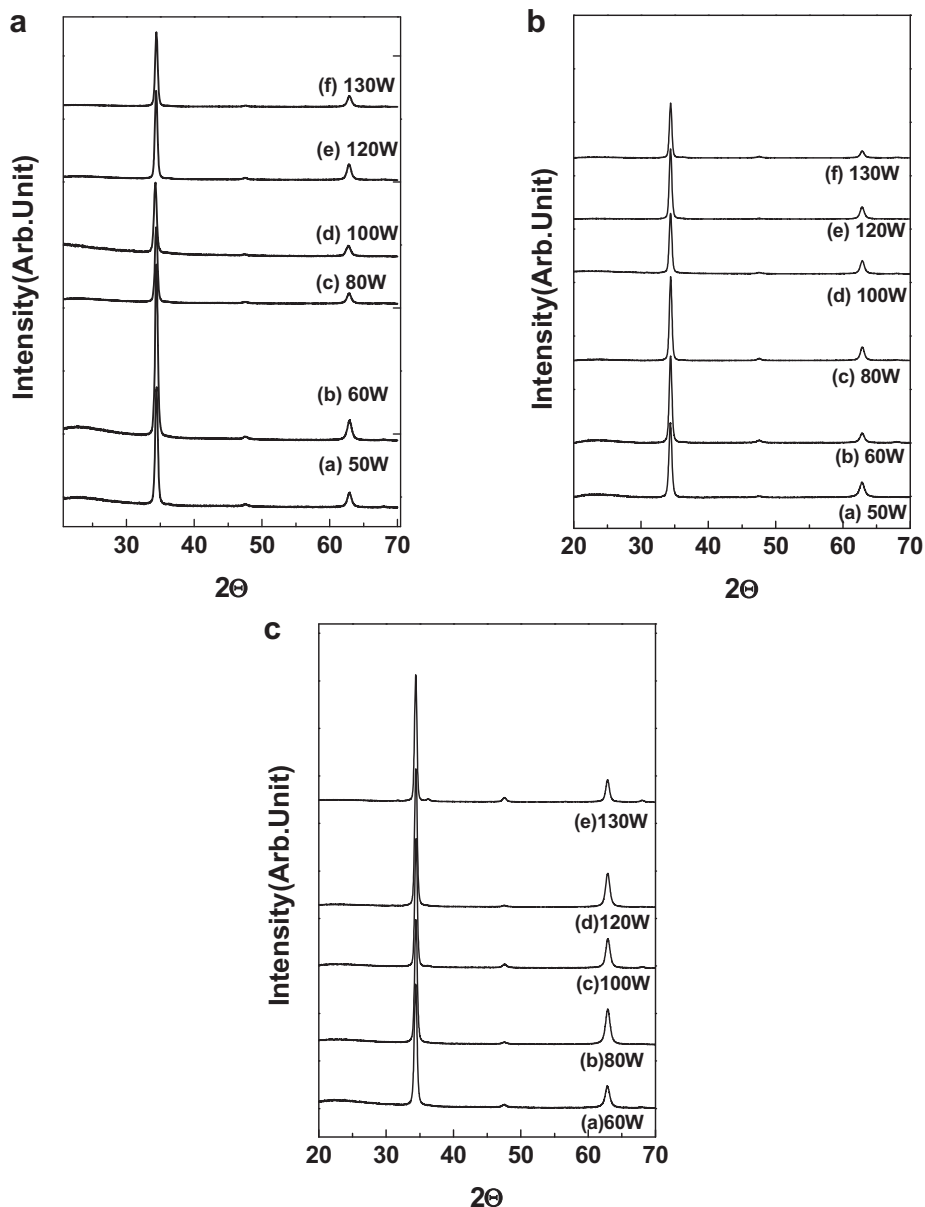


Fig. 3. XRD patterns for AZO films deposited at various simultaneous rf and dc powers with varied inductor coil: (a) 0 μH , (b) 300 μH and (c) 600 μH .

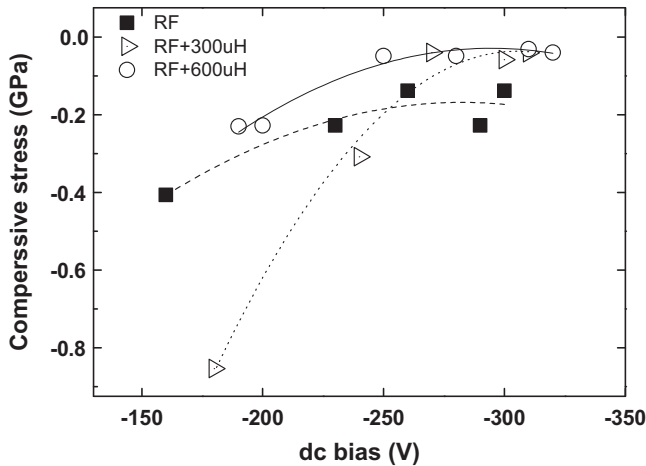


Fig. 4. Compressive stress of AZO films as a function of Ar⁺ ion energy estimated by thermalization model.

increases, in the films deposited with rf power and inductance of 300 and 600 μH, the stress decreases from a negative value and then saturates to a minimum value nearing zero. Effects of the bombardment near the substrate were neglected, because of the flux of reflected gas atoms much lower than that of sputtered atoms.

Fig. 5 shows the estimated average final energy of the sputtered Zn and O atoms as a function of dc bias voltage. The average final energies were estimated through the calculations of transport of the sputtered atoms from source to substrate. First the energy of atoms emitted from the source was simulated using the transport of ion in matter (SRIM) [12] code. Table 2 summarizes the initial energy of sputtered Zn and O atoms and the number of sputtered atom per incident ion. The energy loss of sputtered atom as it passes through the Ar sputtering gas can be estimated from

$$E_F = (E_0 - k_B T_G) \exp \left[n \ln \left(E_i / E_f \right) \right] + k_B T_G, \quad (2)$$

where E_0 is the energy of the sputtered particle as it leaves the target (out-put file from trim code in Table 2, T_G is the sputtering gas temperature, E_i/E_f is the ratio of energies before and after a collision, and n is the number of collisions that take place in the

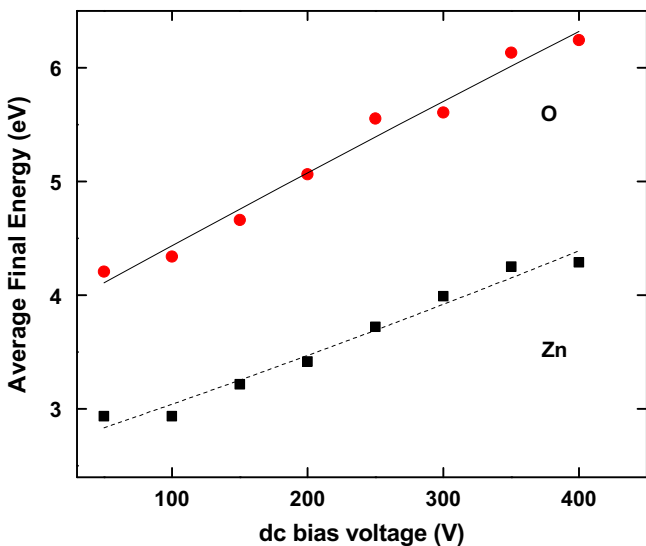


Fig. 5. The average final energy of the sputtered Zn and O atoms as a function of dc bias voltage.

Table 2
The initial energy of sputtered Zn and O atoms and the number of sputtered atom per incident ion.

(μH)	DC bias (V)	Atom/Ion		eV/Atom (eV)	
		Zn	O	Zn	O
0	160	0.78	0.40	9.31	7.21
	230	1.05	0.58	7.50	6.51
	290	1.29	0.66	9.95	8.20
300	180	0.86	0.45	8.18	7.11
	240	1.16	0.62	8.76	7.05
	300	1.33	0.67	10.60	8.19
600	190	0.93	0.48	8.78	6.59
	250	1.14	0.58	8.20	7.68
	310	1.32	0.66	9.58	7.74

Table 3
The input parameters used for the calculation of energy distribution.

	Zn	O
Atomic mass M_2	65.39 g/mole	15.99 g/mole
Atomic radius	1.53 Å	0.65 Å
cross section σ	$1.82 \times 10^{-19} \text{ m}^2$	$7.35 \times 10^{-20} \text{ m}^2$
Gas parameter; Ar	Pressure = 5 mTorr	
$T_G = 300 \text{ K}$		
$M_1 = 39.9 \text{ g/mole}$		

gas. The number of collisions is given by $n = dp\sigma/k_B T_G$ where d is the distance travelled, p is the sputtering gas pressure, and σ is the collision cross section assuming hard core interactions. Table 3 lists the input parameters used in our calculation. As the bias voltage increases from 50 to 400 V, the final average energies of Zn observed increases from 2.01 to 2.94 eV, smoothly. In the curve of the final average energies of O, it increases from 3.71 eV to 5.50 eV.

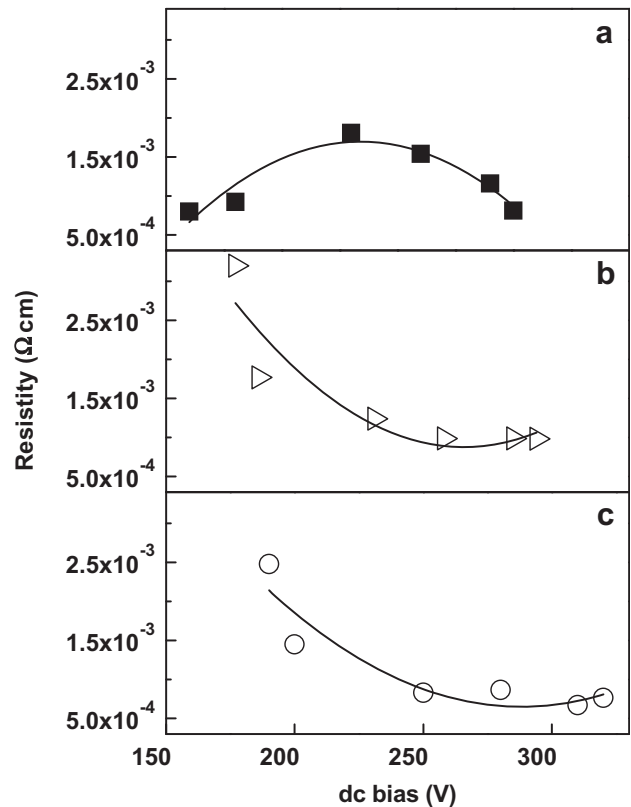


Fig. 6. The resistivity of AZO films deposited with simultaneous rf and dc power through an inductor coil of: (a) 0 μH (b) 300 μH (c) 600 μH.

It may be due to the collisions number of O were 50% smaller than that of Zn.

Fig. 6 shows the resistivity of the AZO films deposited with simultaneous rf and dc power through an inductor coil (0, 300 and 600 μH). It can be seen from the figure that, for films deposited with rf power only, the resistivity increases with bias voltage, reaches a maximum in the resistivity of $1.81 \times 10^{-3} \Omega\text{cm}$ at 230 V and then decreases in resistivity, $\sim 8.12 \times 10^{-4} \Omega\text{cm}$, continuously. For the films deposited with rf power and inductor coil (300 μH), a minimum in resistivity of $9.82 \times 10^{-4} \Omega\text{cm}$ occurred at 310 V, as shown in Fig. 6(b). For the films deposited with rf power and inductor coil (600 μH), a minimum in resistivity of $6.71 \times 10^{-4} \Omega\text{cm}$ occurred at 320 V, as shown in Fig. 6(c). Therefore, the resistivity decreases continuously with the increase of bias voltage and showing a tendency of increase at the far end of the voltages. This can be due to the stress relaxation induced by the effective increase in the sputtering power. Further, with the increase of the inductance from 300 to 600 μH , there is a constant decrease in the resistivity at all the voltages. These findings confirm reported results of interrelation between intrinsic stress and electrical parameters of reactively sputtered ZnO:Al films [8,13]. Since the average final energy at surface is same as surface diffusion energy that drives the grain growth processes in the AZO thin films, it seems reasonable that formation by sputtered Zn and O atoms (and ions) likely drives film crystallization and reduces the film stress. According to Ellmer et al., the formation energies of the oxide, related to on metal atom, are 3.6 eV (ZnO) explaining the thermodynamic stability of the zinc oxide [14]. Moreover, we know that the average final energy (3.6 eV, Zn) in the bias voltage range of 230 V is consistent with a lower compressive stress and resistivity.

4. Conclusion

In conclusion, ZnO:Al films were deposited on glass substrate by rf magnetron sputtering with simultaneous dc bias through an inductor coil. The obtained films were polycrystalline with the hexagonal structure and preferred orientation along the c-axis. The effective increase of the bias voltage leads to decrease in the compressive stress

of the films. Also the resistivity tendency is in good agreement with the variation of compressive stress. The film with lowest resistivity, $\rho \sim 6.71 \times 10^{-4} \Omega\text{cm}$, and simultaneously lower stress were obtained at the average final energy of 2.74 (Zn atom) and 4.95 (O atom) eV. We further conclude that formation by lower energy (3–5 eV) sputtered Zinc and oxygen species at the growing film surface was likely responsible for the dependence of AZO resistivity and stress.

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References

- [1] B.Y. Oh, M.C. Jeong, T.H. Moon, W. Lee, J.M. Myoung, J.Y. Hwang, D.S. Seo, *J. Appl. Phys.* 99 (2006) 124505.
- [2] X. Jiang, F.L. Wong, M.K. Fung, S.T. Lee, *Appl. Phys. Lett.* 83 (2003) 1875.
- [3] I. Repins, M.A. Contreras, B. Egaas, C. DeHart, J. Scharf, C.L. Perkins, B. To, R. Noufi, *Prog. Photovolt. Res. Appl.* 16 (2008) 235.
- [4] K. Schulze, B. Maennig, Y. Tomita, C. May, J. Hüpkens, E. Brier, E. Reinold, P. Bäuerle, K. Leo, *Appl. Phys. Lett.* 91 (2007) 073521.
- [5] M. Berginski, J. Hu Pakes, W. Reetz, B. Rech, M. Wuttig, *Thin Solid Films* 516 (2008) 5836.
- [6] B. Yaglioglu, Y.J. Huang, H.Y. Yeom, D.C. Paine, *Thin Solid Films* 496 (2006) 89.
- [7] T. Minami, *Thin Solid Films* 516 (2008) 1314.
- [8] R. Cebulla, R. Wendt, K. Ellmer, *J. Appl. Phys.* 83 (1998) 1087.
- [9] Danson I. Safi, G.W. Hall, R.P. Howson, *Surf. Coat. Technol.* 99 (1998) 147.
- [10] A. Segmüller and M. Murakami, in and K. Ellmer, *J. Appl. Phys.* 83, 1087 (1998) of *Ions in Solid* Rosenber (Academic Press, Inc., Boston, 1988) p. 143.
- [11] I. Broser, H. Nelkowsky, G. Nimitz, *Semiconductors, group III*, in: O. Madelung, M. Schultz, H. Weiss (Eds.), *Landolt-Börnstein*, vol. 17, Springer-verlag, Berlin, 1982.
- [12] J.F. Ziegler, J.P. Biersack, U. Littmark, *The Stopping and Range of Ions in Solids*, Pergamon, New York, 1985.
- [13] Y.S. No, D.H. Park, T.W. Kim, J.W. Choi, W.K. Choi, *J. Kor. Vac. Soc.* 18 (3) (2009) 79.
- [14] K. Ellmer, A. Klein, B. Rech, *Transparent Conductive Zinc Oxide*, Springer-Verlag, Berlin, 2007.