Comparative investigation on cation-cation (Al-Sn) and cation-anion (Al-F) co-doping in RF sputtered ZnO thin films: Mechanistic insight

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Abstract:

Herein, we report a comparative mechanistic study on cation-cation (Al-Sn) and cation-anion (Al-F) co-doped nanocrystalline ZnO thin films grown on glass substrate by RF sputtering technique. Through detailed analyses of crystal structure, morphology, microstructure, UV-VIS-NIR absorption, and electrical transport property, the inherent characteristics of the co-doped films were revealed and compared. All the nanocrystalline films retain the hexagonal wurtzite structure of ZnO and show transparency above 90% in the visible and NIR region. As opposed to expectation, Al-Sn (ATZO) co-doped film show no enhanced carrier concentration consistent with the probable formation of SnO₂ clusters supported by the X-ray photoelectron spectroscopy study. Most interestingly, it has been found that Al-F (AFZO) co-doped film shows three times enhanced carrier concentration as compared to Al doped and Al-Sn co-doped films attaining a value of $\sim 9 \times 10^{20} \text{ cm}^{-3}$ due to the respective cation and anion substitution. The carrier relaxation time increases in AFZO while it decreases significantly for ATZO film consistent with the concurrence of the impurity scattering in the latter.

Keywords: AZO film; Al-Sn; Al-F; Co-doping; Carrier relaxation time; Resistivity

I. Introduction

An immense importance of transparent conducting oxide (TCO) has been realized due to its wide utilization in transparent electronic devices e.g light emitting diode [1], flat panel display [2], thin film transistor [3-4], low emittance window [5], and most importantly transparent front contact in Si solar cell [6-8]. Sn-doped In_2O_3 (ITO) has been one of the most commonly used TCO materials. However, In is relatively scarce and very expensive element, use of which as TCO material for a rapidly growing optoelectronic industry is not desirable. On the other hand, impurity doped ZnO has acquired a major interest, due to their significant band-gap energy of >3 eV and modest resistivity of the order of 10^{-4} $\Omega\text{-cm}$, which is being used in various transparent optoelectronic devices relevant in the near-ultraviolet to near infrared spectral range (400-1000 nm). Besides low cost, ZnO has other advantages over ITO like non-toxicity, higher chemical and thermal durability against hydrogen plasma process etc [9]. A good discussion and research history on Al, Ga, In doped ZnO as an alternative to ITO has been summed up by Minami [10] including several individual reports on Ga and In doping [11-14]. Though a reasonably low resistivity of $\sim 10^{-4}$ - 10^{-5} $\Omega\text{-cm}$ [9,12] has been reached in case of ZnO doped with impurity like Al, Ga, still there are lots of efforts going on to enhance the conductivity of Al doped ZnO (AZO) by several tricks which indicate the potential relevance of AZO-based TCO films as Al is most preferable being cheaper, abundant and most importantly Zn^{2+} and Al^{3+} have comparable ionic radius (0.53 Å for Al^{3+} and 0.75 for Zn^{2+}) [15-16]. Trivalent cation doped ZnO prepared by various chemical and physical methods show minimum resistivity depending on the dopant content as well as deposition technique. Particularly in RF magnetron sputtering, a wide variation of Al dopant concentration has been attempted wherein the variation of resistivity from 2.2×10^{-3} - 1.4×10^{-4} $\Omega\text{-cm}$ has been reported [17-20]. Some post-deposition treatment has been adopted to enhance the conductivity of the films [20-22] further. There are several process parameters like gas pressure, deposition temperature, RF power which are found to affect the resistivity significantly [23-27].

Much of the studies on co-doped ZnO films have been carried out by using cationic dopants like Al, Ga, and In (i.e two different cations substituting Zn ion at the same time) [28-33]. Among these Al is the most widely studied one. The lowest resistivity of 4×10^{-3} $\Omega\text{-cm}$ has been obtained by Pan et al. [34] for 1 at% Al with 2 at% Sn doped sol-gel processed thin films. A lowest resistivity of 2.5×10^{-4} $\Omega\text{-cm}$ has been obtained by Pham et al. in sample containing 0.1 at% In and 4.9 at% Ga [35]. A sputter deposited thin film by Lee et al. with film composition $\text{Zn}_{0.959}\text{Al}_{0.020}\text{Ga}_{0.021}\text{O}$ has the lowest resistivity of 1.1×10^{-3} $\Omega\text{-cm}$ after annealing at 450 °C [28]. As both the cations try to substitute Zn ions, there arises a competition in between those two cations resulting strain and defects in the thin film.

Unlike trivalent cation, doping with anion has always received less attention and thus it is much less discussed. Some anions like F, Cl have been reported to improve the conductivity of ZnO film [36-40]. The reports on anionic dopant F are very few as compared to that of metallic

cationic dopants although it is also attractive because substitution of O by F is known to perturb the valence band mostly, leaving the conduction band relatively free of scattering. Further, due to compatibility of the ionic radius of F^- (131 pm) with that of O^{2-} (138 pm) [41-42], F can easily be introduced into ZnO lattice by substituting O atom. Depending on the deposition process as well as concentration of dopant, a wide range of resistivity has been reported. Zhang et al. [43] have reported a lowest resistivity of $7.66 \times 10^{-2} \Omega\text{-cm}$ for 3% F doped ZnO thin film prepared by magnetron sputtering. Pulsed laser deposited (PLD) ZnO film containing 1 at% ZnF_2 with resistivity of $4.83 \times 10^{-4} \Omega\text{-cm}$ has been obtained by Cao et al [41]. In contrast, 2 at% F doped sol-gel ZnO thin film exhibits the lowest resistivity of only $1 \Omega\text{-cm}$ in light [44]. A lowest resistivity of $6.53 \times 10^{-2} \Omega\text{-cm}$ has been obtained while using 0.48 at% F for chemical vapor deposited ZnO film [45]. As compared to F, studies on Cl doping are quite a few [38-39,46]. Due to a large ionic radius of Cl as compared to O^{2-} and its corrosive nature a substantial amount of Cl doping into ZnO is not feasible. The few reports on cation-anion co-doped ZnO films are [47-52] but none of them discussed the effect of each co-dopant and the co-relation between structural and electrical results in detail.

Therefore, from the above literature, it is evident that though a lot of efforts have been given in this area for optimizing the electrical properties of impurity doped ZnO film as TCO, a mechanistic investigation on the effect of cation-anion co-doping using Al and F and its comparison with cation-cation using Al and Sn doped ZnO film is not available till date to our knowledge. Therefore, in order to have a clear understanding on the dissimilar co-doping effect, we have grown cation-cation i.e Al-Sn (ATZO) and cation-anion Al-F (AFZO) co-doped ZnO films by RF sputtering technique as per the scheme in Fig. 1. In this paper, we have presented a comprehensive and comparative study on the structural, optical and electrical properties of AZO, ATZO and AFZO films. An increase in the band gap and about four time enhanced carrier concentration in AFZO film as compared to AZO have been observed although no improvement in the carrier concentration has been found for ATZO film. A suitable scattering mechanism in the cation-cation and cation-anion co-doped film is provided. Our cation-anion co-doped AFZO film shows promising optical and electrical property suitable for a highly VIS-NIR transparent and conducting substrate.

II. Experimental

AZO, ATZO and AFZO thin films were deposited on cleaned glass substrates using a 1at% Al, 1at% Al + 1 at% Sn and 1at% Al + 1at% F doped ZnO commercial target (99.99% purity, MTI Corp., USA) using RF magnetron sputtering system (Rocky mountain vacuum tech. model: RMS T-4065). Prior deposition, the sputtering chamber was evacuated to a base pressure of 4×10^{-6} Torr. Pressure during growth was fixed at 25 mTorr and a constant flow of 20 sccm pure Ar gas and the substrate temperature of 500 °C during deposition were maintained. To get uniform deposition the substrate holder was rotated at 20 RPM. Films with thickness 200 nm were grown at a RF power of 120 watt. After deposition, all the films were annealed at 550 °C

for 2 hours in vacuum. All the experimental conditions are optimized for best transmission as well as conductivity.

Fig. 1: Schematic representation of doping type.

The crystalline phase of the thin films was confirmed by X-ray diffractometry (XRD; BRUKER model: D8) with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation. The surface morphology of the films has been analyzed by a field-emission scanning electron microscopy (FESEM; JEOL model: JSM-6700F) and Atomic Force Microscope (AFM; VEECO model: diCP-II). The optical transmission spectra were recorded using a UV-VIS-NIR spectrophotometer (model: Cary-5000) within range of 3300-300 nm. The values of resistivity, carrier concentration, sheet resistance and mobility at room temperature were estimated using Hall Effect measurement system (HEMS, Nano Magnetic Instruments) using four probe technique in Van der Pauw geometry. X-ray Photoelectron Spectroscopy (XPS; Omicron, serial no: 0571) was carried out to identify the elemental states of the dopants and the constituent elements in the thin films.

Results and Discussions

1. Structural and micro-structural properties

In the XRD patterns a sharp peak around 34.4° has been appeared for all the films which correspond to the (002) peak of the hexagonal wurtzite structure of ZnO as shown in Fig. 2. The presence of the highly intense (002) peak implies that the growth of all the films have been favored only along c-axis. No significant shift in the (002) peak positions for ATZO and AFZO film w.r.t that of AZO has been observed implying no change in the lattice parameter (Table 1). Due to comparable ionic radii of the cations and anions ($\text{Sn}^{4+} = 69 \text{ pm}$, $\text{Al}^{3+} = 53 \text{ pm}$, $\text{Zn}^{2+} = 75 \text{ pm}$ and $\text{F}^- = 131 \text{ pm}$, $\text{O}^{2-} = 138 \text{ pm}$) [16,41-42], no significant change in the lattice parameter should be expected. In case of ATZO, there may be several possibilities of substitution. For simplicity, few possibilities can be considered as follows: i) All the Al^{3+} and Sn^{4+} dopants

replace Zn^{2+} in the lattice site. ii) Most of the Al^{3+} replaces Zn^{2+} while most of the Sn^{4+} may sit in the interstitial position. iii) Most of the Sn^{4+} may replace Zn^{2+} while most of the Al^{3+} sits in the interstitial position. None of the above possibilities would change lattice parameter ‘c’ significantly. However, it should be noted that in order to maintain the solid solubility limit, there will be high competition between the two cation dopants to occupy the Zn sites. Thus, though the doping concentration for each dopant is 1 at%, possibility of case (i) is less likely to occur. However, the electrical results as discussed later would confirm the most plausible case.

Fig. 2: X-ray diffraction patterns of ATZO, AZO, AFZO films. The inset shows the enlarged view of the (002) peak.

In case of AFZO, the possibility that all Al^{3+} and F^- dopants replace Zn^{2+} and O^{2-} is favored due to comparable ionic radius as well as separate cation and anion substitution. The FWHM values

Fig. 3: FESEM and AFM images of ATZO, AZO, AFZO films.

have been shown in Table 1. A significant increase in the FWHM (Table 1) has been found for both ATZO and AFZO film, indicates presence of more crystal defects in the co-doped films. The SEM images shown in Fig. 2 (top panel) indicate a granular structure of the films. The film

texture is compact and the grains are well connected with each other. The crystallite size calculated from Scherrer formula (Table 1) has found to decrease in both the co-doped films as compared to AZO indicating strain in the co-doped films. This may arise due to the defects for additional Sn and F inclusion in AZO film. The grain size as estimated from the SEM images have been noted in Table 1. Minimum size of grains has been found in ATZO films with average dimension of 75 nm. Moderate grains of average size of 140 nm were found for AZO film.

Table 1: (002) XRD Peak position, FWHM, lattice parameter (c), crystallite size, average grain size and band-gap of the films.

Sample Name	Peak Position (degree)	FWHM (degree)	Lattice (c) (Å)	Crystallite Size (nm)	Average Grain Size (nm)	Band gap (eV)
ATZO	34.47	0.94	5.204	10	75	3.28
AZO	34.49	0.33	5.201	26	139	3.32
AFZO	34.51	0.89	5.198	10	214	3.42

AFZO films have grain with maximum average size of around 215 nm. The grain size is found to be larger than the crystalline size because of agglomeration. The AFM images of the films in Fig. 2 (bottom panel) show that ATZO, AZO and AFZO films have average roughness of 13.4, 12.9 and 18.3 nm respectively. This result is at par with the FESEM results showing maximum grain size for the AFZO film.

2. Transmission Property

The transmission characteristics of all the films as a function of wavelength in Fig. 4A show sharp band-edge absorption below 380 nm and transparency above 90% in the visible range of the solar spectrum. The transparency of AFZO falls rapidly beyond 1300 nm while other two films show the fall at much higher wavelength due to free carrier absorption [53]. The values of

Fig. 4A: UV-VIS-NIR transmission spectra of ATZO, AZO, AFZO films. The inset shows the Tauc plot and shift in band-gap.

Fig. 4B: Digital image shows the comparable transparency of the films w.r.t bare glass substrate.

optical band-gap of the films have been noted in Table 1 as calculated from the Tauc plot shown in the inset of Fig. 4A. The average transmission of ATZO, AZO and AFZO films are calculated for 500-900 nm range and indicated in the bottom-right of Fig. 4A. A decrease and an increase in the band gap values in ATZO and AFZO respectively to 3.28 eV and 3.42 eV from a value of 3.32 eV in AZO have been noted. Burstein–Moss effect is primarily responsible for an enhancement in the band-gap in AFZO. A decrease in band gap in ATZO indicates formation of defect states. Fig. 4B shows the high transparency of ATZO, AZO and AFZO as the logo is quite visible through the films.

3. Electrical Properties

To get a comparative idea, resistivity, sheet resistance, carrier concentration, mobility has been shown in Table 2. A significant change in the sheet resistance from a value of 155 Ω/sq in AZO to 1200 Ω/sq in ATZO has been observed. Unexpectedly there is no significant change in

Table 2: Resistivity, sheet resistance, carrier concentration, Hall mobility and Seebeck coefficient of the films.

Sample Name	Resistivity ($\Omega\text{-cm}$)	Sheet Resistance (Ω/sq)	Carrier concentration (cm^{-3})	Mobility (cm^2/Vs)	Seebeck Coefficient ($\mu\text{V/K}$)
ATZO	2.42×10^{-2}	1200	2.04×10^{20}	1.27	-54
AZO	3.11×10^{-3}	155	2.89×10^{20}	6.95	-78
AFZO	1.18×10^{-3}	59	8.58×10^{20}	6.14	-70

the carrier concentration in ATZO as compared to AZO film and, 5 times lower mobility value of 1.27 cm^2/Vs has been observed. It indicates that Al-Sn co-doping rather causes defect formation in the lattice structure. An insignificant change in the carrier concentration of ATZO as compared to that of AZO implies that Sn^{4+} is not contributing any extra free carriers. This may happen when Sn^{4+} is not substituting Zn^{2+} which is confirmed later by the XPS results. In contrast to ATZO, the sheet resistance in AFZO is lowered to 59 Ω/sq as compared to 155 Ω/sq in AZO and almost 3 times enhancement in the carrier concentration is occurred. Interestingly, no significant change in the mobility value has been obtained. This result indicates F^- ion is probably replacing the O^{2-} ion in the wurtzite lattice.

For a TCO, metallic reflection and absorption phenomena in the near infrared is expected. At the reflection edge, the screened plasma energy can be calculated following the equation as given below [54],

$$\hbar\omega_p = \hbar \sqrt{\left[\left(\frac{n}{m^*}\right)\left(\frac{e^2}{\epsilon_0\epsilon_r}\right)\right]} \dots\dots\dots (1)$$

where, ϵ_0 , ϵ_r are the vacuum and relative permittivity and e is the electronic charge, $\hbar$ is reduced Plank's constant, n is the carrier concentration and ω_p is the Plasmon frequency. In metals, the effects due to free carriers are almost always studied by reflectivity techniques because of the high optical absorption of metals at higher wavelengths. Here, ω_p has been approximately estimated from wavelength vs reflectance plot and noted in Table 3 for all the films.

Also the electrical conductivity of the film is given as,

$$\sigma = ne\mu = e^2\tau\left(\frac{n}{m^*}\right).....(2)$$

where, μ , m^* , τ be the electron mobility, carrier effective mass and carrier relaxation time. Combining the equations (1) and (2), the carrier relaxation time has been calculated using following equation:

$$\tau = \frac{\sigma}{\epsilon_0\epsilon_r\omega_p^2}.....(3)$$

Table 3: Approximate values of plasmon energy, carrier relaxation time, carrier effective mass and impurity scattering mobility of the films.

Sample	$\hbar\omega_p$ (eV)	τ (fs)	m^* (m_e)	μ_i	E_{00} (eV)
ATZO	0.44	0.10	0.14	1.23	240
AZO	0.44	0.81	0.20	7.12	239
AFZO	0.61	1.10	0.32	5.91	329

Fig. 5: Reflection vs Wavelength plot of the thin films.

and summarized in Table 4. The table shows that there is a small increase in the plasmon frequencies value for AFZO films and no change for ATZO film. However, the values are comparable to that of ITO [54]. Interestingly, the relaxation time increases in AFZO while it decreases significantly for ATZO film implying that the carriers encounter frequent scattering and thus the relaxation time between two scatterings is very small in ATZO film. In degenerately doped semiconductor, carrier scattering has many components. Phonon scattering is only effective at high temperature and can be neglected at room temperature measurement. At high carrier concentration ($>2 \times 10^{20} \text{ cm}^{-3}$) the depletion layers between crystallites are very thin hence influence of the grain boundary scattering on the carriers mobility measurement is insignificant [55-56]. The tunneling current dominates over the thermionic emission current in our doped

samples, since the E_{00} (tunneling parameter) values calculated following the equation (noted in Table 3)

$$E_{00} = 18.5 \times 10^{-12} \left(\frac{n}{\epsilon m^*} \right)^{1/2} \dots\dots\dots(4)$$

(where n is the carrier concentration, m^* is effective carrier mass and ϵ is the relative dielectric constant) are much greater than the KT value at room temperature. Therefore, the scattering mechanism for the present doped and codoped films may logically be assigned to ionized impurity scattering. In a degenerate semiconductor, the electrons near Fermi level take part in conduction. According to Conwell-Weisskopf formula when degenerate charge carriers are scattered by impurity ions, the energy dependence of mobility is [56]

$$\mu_i = \frac{e}{m^*} \tau_i (E_F) \dots\dots\dots(5)$$

Where $\tau_i(E_F)$ is the carrier relaxation time near Fermi level. The mobility calculated from equation (5) are noted in Table 3 quite comparable to those found as Hall mobility which supports our supposition of scattering mechanism i.e ionized impurity scattering for all these co-doped films. Therefore, a significant change in carrier relaxation time as well as mobility in ATZO is due to considerable impurity scattering. Further, co-doping mechanism has been investigated from the XPS results. Figure 6 displays the results of simple elemental analysis by means of XPS survey (wide scan) spectra for the films under study. It is clearly seen that both

Fig. 6(A): XPS spectrum of ATZO film. The inset shows the enlarged view of Sn 3d signal.

Fig. 6(B): XPS spectrum of AFZO film. The inset shows the enlarged view of F 1s signal.

the co-doped films have no XPS signals from alien impurities, except for the Sn, F, dopants. This analysis confirmed the declared empirical formulas and demonstrates the films' high purity. To clarify the formal valence states of Sn dopants in ZnO matrix, Sn 3d signal were acquired from the film under study (the inset in Fig. 6(A)). The inset in Fig. 6(A) shows signals at around 486.83 eV and 495.2 eV corresponding to Sn 3d_{5/2} and Sn 3d_{3/2} peaks which confirms the presence of

only Sn^{4+} in ATZO similar to other reports [57-58]. However, if Sn^{4+} substitutes Zn^{2+} , an enhanced carrier concentration would have been obtained. Since this is not occurred, it can be proposed that some Sn^{4+} accumulated as interstitials and in this situation, it cannot be ruled out that nonstoichiometric SnO_2 clusters might form, manifesting themselves as imperfections in the final co-doped ZnO microstructure. This implies that in case of co-doping with Al and Sn, Sn^{4+} occupies the interstitial sites due to a strong competition for the site occupancy. Therefore, among the possibilities discussed earlier for ATZO, only case (ii) wherein most of the Al^{3+} replaces Zn^{2+} and most of the Sn^{4+} sit in the interstitial position is favorable. Therefore, very low mobility and small relaxation time in ATZO as compared to AZO film may be attributed to interstitial defects related to the Sn^{4+} impurities. The presence of F peak at around 685.1 eV shown in the inset in Fig. 6(B) confirms the presence of Zn-F bond which is at par with the previous reports [42,50]. Thus, in case of Al and F co-doping, the respective cation and anion sites are being substituted by Al and F ions generating free carriers. This XPS data also supports three times higher carrier concentration in AFZO film as compared to AZO.

Conclusion

In summary, a comparative investigation on the effect of cation-cation and cation-anion co-doping in ZnO have been carried out and the mechanistic insight has been revealed. Al-Sn co-doped film show no enhanced carrier concentration rather shows a drastic decrease in the carrier relaxation time due to ionized impurity scattering. While the co-doped AFZO film shows three time improved carrier concentration as well as carrier relaxation time as compared to only Al (1 at%) doped film, due to the respective cation and anion substitution. Our work goes beyond the commonly investigated concepts of only cation, or cation-cation or cation-anion ZnO doping cases and demonstrates a systematic comparative study with a doping mechanism. It is expected that the present findings concerning the factors influencing the electrical properties of ZnO can be extended to other oxides also. Further, the present methodology is expected to aid the development of efficient TCO films which are particularly suited for solar cells and NIR transparent electronics.

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