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# Effects of free carriers on the optical properties of high mobility transition metal doped $\text{In}_2\text{O}_3$ transparent conductors

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Transition metal doped  $\text{In}_2\text{O}_3$  with high mobility can be used as a transparent conductor with enhanced transparency spectral window. In this work, we carried out a comprehensive study on the electrical and optical properties of  $\text{In}_2\text{O}_3$  doped with several transition metal (TM) species ( $\text{In}_2\text{O}_3$  : TM) including W, Zr, Mo, and Ti. Detailed optical properties obtained by spectroscopic ellipsometry (SE) are correlated with electrical properties obtained by Hall effect measurements. We find that the mobility of  $\text{In}_2\text{O}_3$  : TM thin films lies in the range of  $50\text{--}75\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ , much higher than the typical mobility of  $30\text{--}40\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  for conventional ITO. The complex dielectric functions of the thin films reveal remarkable carrier density dependent changes in the optical properties. SE analyses show that the electron effective mass of  $\text{In}_2\text{O}_3$  : TM at the bottom of the conduction band  $m_o^*$  ( $0.11\text{--}0.14m_o$ ) is much smaller than the reported  $m_o^* \sim 0.18\text{--}0.30m_o$  for ITO, which directly results in their higher mobility. This low  $m_o^*$  is consistent with recent theoretical studies which proposed that  $4d$  donor states of the TMs are resonance in the CB. For films with comparably low resistivity of  $1\text{--}2 \times 10^{-4}\ \Omega\text{ cm}$ , we find that  $\text{In}_2\text{O}_3$  : TM films have  $\sim 4\text{--}10$  times lower absorption coefficient at  $\lambda = 1300\text{ nm}$  due to free carrier absorption and have their plasma reflection edge extended to  $\sim 1.7\ \mu\text{m}$  compared to  $\sim 1.2\text{--}1.4\ \mu\text{m}$  for ITO. Hence, using TM doping we have achieved transparent conductors with conductivity comparable to ITO but with transmission extended to  $>1600\text{ nm}$ . These materials will be potentially important as transparent conductors for optoelectronic devices utilizing NIR photons.

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## I. INTRODUCTION

Transparent conductive oxides (TCOs) which show high conductivity and visible light transparency have been applied as essential components and electrodes in many optoelectronic devices such as touch screen displays, low-emissivity windows and solar cells [1,2].  $\text{In}_2\text{O}_3$ -based transparent conductors show great potentials for applications and  $\text{In}_2\text{O}_3$  : Sn (ITO) with its high transparency, high carrier concentration and low resistivity is the dominant transparent conducting oxide in the market. ITO can be deposited on large area amorphous and polymer substrates and it can achieve a low resistivity of  $\sim 10^{-4}\ \Omega\text{ cm}$  with visible light transmittance greater than  $\sim 80\%$ , these desirable properties make ITO an excellent transparent conductor material [3–5]. Moreover, ITO also has a high work function which supports its application as transparent electrodes in many energy device systems [6]. However, polycrystalline ITO thin films with high conductivity ( $\sim 1 \times 10^4\text{ S/cm}$ ) have moderate to low mobility ( $< 40\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ ) and poor transmittance in the NIR spectrum ( $\lambda > 1100\text{ nm}$ ) [7]. It has been suggested that the low mobility in ITO arises from the strong hybridization of the Sn-5s and In-5s orbitals which leads to a larger effective mass

due to a broadening of the conduction band dispersion [8]. Since the conductivity depends on the product of carrier concentration and mobility, in order to achieve high conductivity for a material with low mobility, a high electron concentration is needed. The high density of Sn dopants ( $\sim 10\%$ ) required to achieve very high carrier concentration ( $> 10^{21}\text{ cm}^{-3}$ ) results in strong ionized impurity scattering, which further reduces the carrier mobility. As a consequence of the high carrier concentration, plasma reflection and free carrier absorption effects in this material limit its long wavelength applications. Hence, to maximize optical transparency across a large spectral range, materials with high mobility is desirable as this would lead to high conductivity with lower carrier concentration than ITO.

Transition metal (TM) (e.g., Ti, W, Mo) doping in  $\text{In}_2\text{O}_3$  ( $\text{In}_2\text{O}_3$  : TM) has been shown to lead to improved mobility compared to ITO. A number of studies on the electrical and optoelectronic properties of transition metal (TM) doped  $\text{In}_2\text{O}_3$  thin films have been reported [9–20]. In general, these transition metal doped  $\text{In}_2\text{O}_3$  thin films have lower carrier concentration of typically  $\lesssim 5 \times 10^{20}\text{ cm}^{-3}$  but improved mobility (as high as  $\sim 80\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ ), resulting in comparable conductivity with high quality ITO [8]. As a consequence, the optical transparency of  $\text{In}_2\text{O}_3$  : TM covers a wider spectral window, extending to the IR region ( $\sim 1500\text{ nm}$ ). However, detailed studies of the effects of different TM dopant on the optoelectronic properties of  $\text{In}_2\text{O}_3$

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are still lacking. Furthermore, free carriers in TCOs with high carrier concentration ( $\sim 10^{20}$ – $10^{21}$  cm $^{-3}$ ) are also known to play remarkable roles in their optical properties [21,22]. For instance, such effects as free carrier absorption at low energies and a blue shift of the band edge influence the determinations of their optical properties. But a comprehensive look at the effect of free carriers on the optical properties of these high mobility TM doped In $_2$ O $_3$  is yet to be reported.

In this study, we explore the effects of different TM dopants including W, Mo, Zr, and Ti on the transport and optoelectronic properties of sputter deposited polycrystalline In $_2$ O $_3$  thin films. The electrical characterization was carried out by Hall effect measurements and the detailed optical analysis was carried out by standard Spectroscopic ellipsometry (SE) measurements. SE offers a reliable technique for the accurate determination of optical properties of thin films and bulk samples. It has been used to extensively study the optical properties of metal oxide materials as well as the effects of free carriers on highly doped transparent conducting metal oxides [21–24]. In SE, by fitting the measured amplitude and phase difference of the ratio of the polarization state of the reflected and incident light over a wide spectral range using appropriate models, the real and imaginary parts of the complex dielectric function of the film can be obtained. From the dielectric function, various material properties such as the high-frequency dielectric constant, absorption coefficient, the optical gap, the optical mobility, the electron effective mass, and plasma reflection edge can be extracted.

Our Hall measurements show that electron concentration in the range of  $1.2$ – $8.2 \times 10^{20}$  cm $^{-3}$  and mobility of up to  $75$  cm $^2$ /V-s were achieved in these In $_2$ O $_3$  : TM thin films. Compared to ITO thin films, these In $_2$ O $_3$  : TM have comparable conductivity but much lower carrier concentration and higher mobility, and hence their transmittance can be extended to  $>1500$  nm in the IR region with no observable free carrier absorption and plasma reflection. The higher mobility of In $_2$ O $_3$  : TM can be primarily attributed to their lower effective mass and the differences in the mobility for various In $_2$ O $_3$  : TM thin films are explained in terms of the nature of the interaction of the TM dopants with the host conduction band. Detailed effects of free carriers in these high mobility In $_2$ O $_3$  : TM were explored by SE, and these results offer further insights into the optical properties of these thin films.

## II. EXPERIMENT

Transition metal doped In $_2$ O $_3$  thin films were deposited by magnetron co-sputtering using a dual-gun radio-frequency magnetron sputtering system. All samples were grown at a substrate temperature of  $\sim 220$  °C on precleaned glass substrates. W, Mo, Zr, and Ti doping was achieved by using metal targets of these elements sputtered in the DC mode during the RF sputtering of an In $_2$ O $_3$  ceramic target. Since the electron density of doped In $_2$ O $_3$  is also affected by native defects, our sputtered thin film samples were annealed in N $_2$  gas using a rapid thermal annealing (RTA) system. Optimum electrical properties were obtained for thin films RTA at  $650$  °C for  $90$  s, and all further characterizations presented in this study were performed on these “optimized samples.” Also note that, the

maximum annealing temperature used in this study is limited by the glass substrates which would undergo glassy transition at  $\sim 750$  °C in RTA.

Dopant concentrations were determined by x-ray fluorescence (XRF) and x-ray photoelectron spectroscopy (XPS) measurements [25]. Film thicknesses in the range of  $70$ – $180$  nm were estimated from an optical profilometry and confirmed by SE modeling. Grazing Incidence x-ray diffraction (GIXRD) with an incident angle of  $1^\circ$  was used to obtain the x-ray diffraction spectra of the thin films as shown in Fig. S1 of Ref. [26]. The diffraction spectra showed that all the films are polycrystalline with the cubic bixbyite In $_2$ O $_3$  structure with typical grain size in the range of  $16$ – $20$  nm as calculated using the Scherrer equation. To characterize the electrical properties of our thin films, Hall effect measurements in the *van der Pauw* configuration were carried out using a Ecopia HMS5000 Hall system with a magnetic field,  $B = 0.54$  T. The optical properties were characterized by room temperature standard Spectroscopic ellipsometry in the spectra range of  $0.73$  to  $6.5$  eV using a J.A.Woollam RC2 system. The angle of incidence was varied from  $55^\circ$  to  $75^\circ$  with an increment of  $10^\circ$ . Translucent plastic tapes were used to eliminate backside reflection on the glass substrates.

## III. SE ANALYSIS

Due to the high carrier concentration  $\sim 10^{20}$ – $10^{21}$  cm $^{-3}$  in heavily doped TCOs, the Drude model which describes the optical response of free electrons in metal-like materials has been successfully used to describe TCO materials in combination with other models describing contributions from inter-band optical transitions [21,22]. Equation (1) is the expression of the complex dielectric function in the Drude free electron model used to describe the optical properties in TCOs with high carrier concentration which has the form of a Lorentz oscillator with zero center energy [27];

$$\varepsilon(E) = \varepsilon_1(E) - i\varepsilon_2(E) = \varepsilon_\infty - \frac{A_D}{E^2 - i\Gamma_D E} \quad (1)$$

In Eq. (1), the amplitude,  $A_D$  and the broadening,  $\Gamma_D$  are the two free parameters, while the term  $\varepsilon_\infty$  is the high-frequency dielectric constant. Based on the Drude theory,  $A_D$  can be expressed as  $A_D = \varepsilon_\infty E_p^2$ , where  $E_p$  is the plasma energy which corresponds to the energy at which the real part of the dielectric function drops from positive to negative values. This characteristic Drude metal-like optical property depends on the carrier concentration and occurs in the near infrared (NIR) to mid-IR frequencies in TCOs. The frequency at which this transition occurs is called the epsilon-near-zero (ENZ) frequency, which corresponds to the plasma frequency,  $\omega_p$ . The plasma energy  $E_p$  can be related to the optical carrier concentration  $N_{\text{opt}}$ , and the electron effective mass  $m^*$  as

$$E_p = \hbar\omega_p = \sqrt{\frac{\hbar^2 e^2 N_{\text{opt}}}{m^* \varepsilon_0 \varepsilon_\infty}}, \quad (2)$$

where  $\hbar$ ,  $e$ , and  $\varepsilon_0$  are the reduced Plank’s constant, electron charge and vacuum permittivity, respectively. The dielectric function according to the Drude model in Eq. (1) can also be

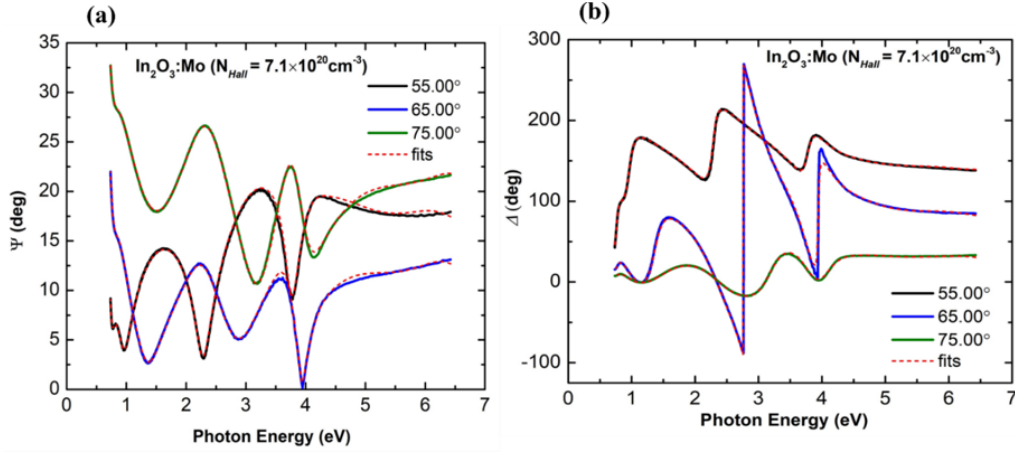


FIG. 1. The measured and fitted (red dashed lines) SE spectra [ $\Psi$  and  $\Delta$  in (a) and (b), respectively] of  $\text{In}_2\text{O}_3\text{:Mo}$  thin film with  $N_{\text{Hall}} = 7.1 \times 10^{20} \text{ cm}^{-3}$  for angle of incidence:  $55^\circ$ ,  $65^\circ$ , and  $75^\circ$ .

described in terms of the optical resistivity  $\rho_{\text{opt}}$  and the mean scattering time,  $\tau$  as [28]

$$\varepsilon(E) = \varepsilon_1(E) - i\varepsilon_2(E) = \varepsilon_\infty - \frac{\hbar^2}{\varepsilon_0 \rho_{\text{opt}} (\tau E^2 - i\hbar E)}, \quad (3)$$

where the optical carrier concentration, optical carrier mobility and electron effective mass are related to the optical resistivity as follows:

$$\rho_{\text{opt}} = \frac{m^*}{N_{\text{opt}} e^2 \tau} = \frac{1}{e N_{\text{opt}} \mu_{\text{opt}}}. \quad (4)$$

The complex dielectric functions of the  $\text{In}_2\text{O}_3$  : TM thin films were obtained by fitting the SE spectra (i.e., the amplitude ratio  $\Psi$  and the phase difference  $\Delta$ ). A three-layer structure comprising a thin surface roughness layer, the bulk  $\text{In}_2\text{O}_3$  film layer and the glass substrate was used for the data analysis using the *CompleteEASE* software. The line shape of the layer dielectric functions, and the thickness of the thin film layer were first estimated using a numerical B-spline approximation. The layer thickness was kept fixed and the dielectric function parameters were used as adjustable parameters for

the fittings. SE data obtained from different incident angles were fitted simultaneously. An oscillator model composed of a combination of a Drude model and two Tauc-Lorentz models were then used to parameterize the dielectric function. Figure 1 shows typical experimental SE spectra (solid lines) taken at different incident angles and dielectric function oscillators fitting (dashed red lines) of a  $\text{In}_2\text{O}_3\text{:Mo}$  thin film with carrier density  $\sim 7 \times 10^{20} \text{ cm}^{-3}$ . From Fig. 1, it is evident that the adopted dielectric function oscillator parameters shown in Table S1 of Ref. [26] can fit the experimental SE data well across the measured spectral range.

## IV. RESULTS AND DISCUSSION

### A. Electrical properties of TM doped $\text{In}_2\text{O}_3$

The electrical properties of magnetron sputtered polycrystalline W, Mo, Zr, and Ti doped  $\text{In}_2\text{O}_3$  thin films after RTA in  $\text{N}_2$  at  $650^\circ\text{C}$  for 90 s are shown in Fig. 2. The electrical properties of these  $\text{In}_2\text{O}_3$  : TM thin films improve with annealing compared to the as-grown samples likely because of improved crystallinity and substitution of the dopants in the

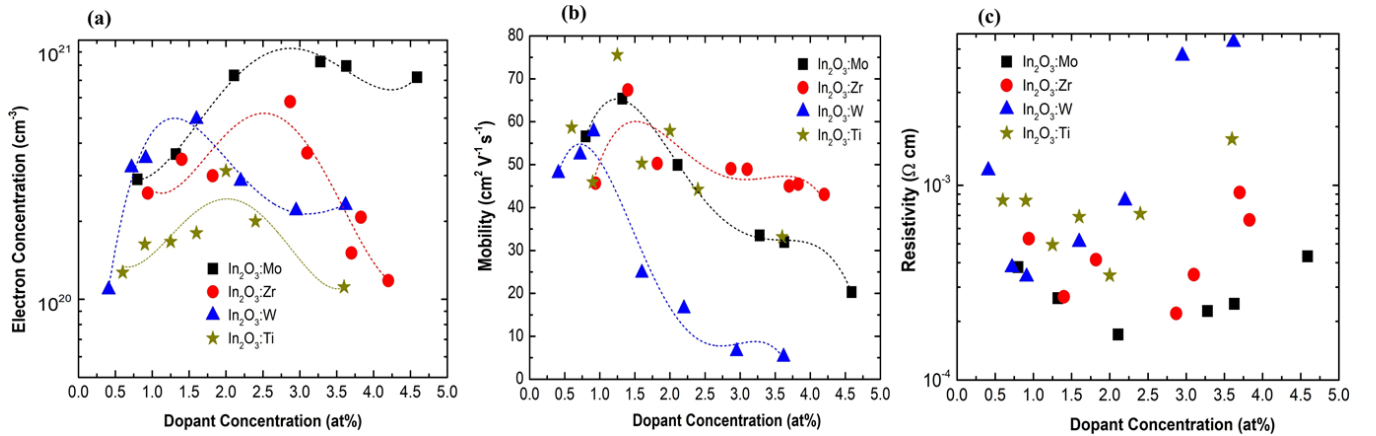


FIG. 2. Electron concentration  $N_H$  (a) mobility  $\mu_H$  (b) and resistivity  $\rho$  (c) for  $\text{In}_2\text{O}_3$  thin films doped with TM dopants (Ti, W, Mo, and Zr) with increasing dopant concentration  $N_d$ . Dashed lines are guide to the eyes.



TABLE I. A comparison of values of several experimentally obtained electrical properties, plasma energy,  $E_p$  and electron effective mass,  $m^*$  of TM doped  $\text{In}_2\text{O}_3$  reported in the literature using different deposition techniques.

Dopant	Conc.	Dep. <sup>a</sup> Technique	$T_g$ (°C)	$N$ (cm <sup>-3</sup> )	$\mu$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\rho$ (Ω-cm)	$E_p$ (eV)	$m^*$	Ref.
Mo	1 mol%	AACVD	450	$3.1 \times 10^{20}$	107	$1.9 \times 10^{-4}$	—	—	[17]
Mo	5wt%	Thermal Evaporation	350	$4 \times 10^{20}$	>100	$2.1 \times 10^{-4}$	0.56	—	[34]
Mo	0.7 at%	<sup>b</sup> Mist-CVD	400	$2.2 \times 10^{20}$	89	$3.2 \times 10^{-4}$	—	—	[35]
Mo	1.3 at%	RF Sputtering	500	$1.5 \times 10^{20}$	93	$4.4 \times 10^{-4}$	0.33	—	[35]
Mo	0.5 at%	<sup>b</sup> Spray Pyrolysis	400	$9.5 \times 10^{19}$	122.4	$5.3 \times 10^{-4}$	—	—	[9]
Mo	2 wt%	RF Sputtering	450	$3.0 \times 10^{20}$	83	—	—	0.32	[36]
Mo	0.5 at%	<sup>b</sup> Spray Pyrolysis	400	$1.0 \times 10^{20}$	149	$4.0 \times 10^{-4}$	—	—	[37]
Mo	2 wt%	RF Sputtering	RT	$5.2 \times 10^{20}$	20	—	—	—	[38]
Mo	1.3mol%	<sup>b</sup> RF Sputtering	220	$3.6 \times 10^{20}$	65	$2.6 \times 10^{-4}$	0.65	0.3	Thiswork
Zr	0.2at %	PLD	650	$\sim 3.0 \times 10^{20}$	$\sim 70$	$\sim 3.0 \times 10^{-4}$	—	—	[15]
Zr	1-2 wt%	RF sputtering	$\sim 600$	$\sim 5.0 \times 10^{20}$	$\sim 75$	$\sim 1.6 \times 10^{-4}$	—	—	[39]
Zr	1.4 mol at%	<sup>b</sup> RF Sputtering	220	$3.4 \times 10^{20}$	67	$2.7 \times 10^{-4}$	0.52	0.25	This work
Ti	1.7 at%	RF Sputtering	550	$1.5 \times 10^{20}$	83.3	$2.6 \times 10^{-4}$	$\sim 0.56$	—	[40]
Ti	1wt%	<sup>b</sup> RF Sputtering	500	$3.06 \times 10^{20}$	105	$1.95 \times 10^{-4}$	—	—	[13]
Ti	1.2mol%	<sup>b</sup> RF Sputtering	220	$1.7 \times 10^{20}$	75	$4.9 \times 10^{-4}$	0.5	0.2	This work
W	$\sim 3.5\text{wt}\%$	DC Sputtering	320	$2.8 \times 10^{20}$	67	$3.1 \times 10^{-4}$	—	—	[41]
W	0.5 at%	<sup>b</sup> Spin Coating	RT	$5.0 \times 10^{20}$	23	$5.3 \times 10^{-4}$	—	—	[42]
W	0.03	PLD	400	$2.9 \times 10^{20}$	66	$3.2 \times 10^{-4}$	—	0.3	[43]
W	1.15wt%	RPD	200	$\sim 1.4 \times 10^{20}$	80	—	$\sim 0.41$	—	[14]
W	0.91mol %	<sup>b</sup> RF Sputtering	220	$3.5 \times 10^{20}$	58	$3.3 \times 10^{-4}$	0.64	0.28	This work

<sup>a</sup>AACVD = Aerosol-assisted chemical vapor deposition,  $T_g$  = Growth temperature. PLD = Pulsed Laser deposition, RPD = Reactive plasma deposition.

<sup>b</sup>Post deposition annealed.

cation site. It is also likely that annealing in  $\text{N}_2$  led to the formation of O vacancies which are known to be donorlike defects in Indium oxide and other metal oxides and these native defects can play significant roles in controlling their electrical properties [29,30]. Similar electrical properties improvement by post-deposition annealing have been reported for other oxide transparent conductors [31]. However, we also note that in most cases native defects formed and H donors incorporated due to annealing are on the order of  $<10^{20} \text{ cm}^{-3}$  [32], which is lower than the electron concentration we observed in these  $\text{In}_2\text{O}_3$  : TM films. Figure S2 (see Ref. [26]) shows changes in the electrical properties of  $\text{In}_2\text{O}_3$  : TM thin films with annealing temperature up to 650 °C.

The electrical properties obtained by room temperature Hall measurements are plotted as a function of doping concentration  $N_d$  given in cation mole % ( $[\text{TM}]/[\text{In}+\text{TM}]$  %) for the various TM dopants in Fig. 2. As shown in Fig. 2(a), the magnitude of the Hall measured carrier concentration  $N_H$  varies with different TM dopants, but in general the change in the carrier concentration with doping concentration  $N_d$  shares a similar trend, showing an increase of  $N_H$  with  $N_d$  up to a peak  $N_H$  value and a subsequent drop as  $N_d$  further increases. W doped  $\text{In}_2\text{O}_3$  shows a maximum  $N_H$  of  $4.5 \times 10^{20} \text{ cm}^{-3}$  at a  $N_d \sim 1.5\%$  with a subsequent decrease at higher  $N_d$ , while a maximum  $N_H$  values of  $5.8 \times 10^{20}$  and  $8.2 \times 10^{20} \text{ cm}^{-3}$  are obtained for  $\sim 3\%$  Zr and Mo doping, respectively.

High Hall mobility values  $\mu_H = 75$  and  $68 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  are achieved for Ti and Zr doping, respectively at a  $N_d$  of  $\sim 1.5\%$  as shown in Fig. 2(b). Mo doped sample also shows a high mobility at a similar  $N_d$  range with a maximum value of  $\sim 65 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , while a maximum  $\mu_H$  of  $58 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  is obtained for W doping at a  $N_d$  of  $\sim 1\%$ . The differences in

the carrier mobility at similar  $N_d$  (1%–1.5%) for different TM dopants can be understood in terms of the nature and interaction of the TM  $d$  states with  $\text{In } 5s$  due to the location of the  $d$ -states of the different TM dopants above the conduction band minimum (CBM). From the theoretical work of Xu *et al.*, and Swallow *et al.*, they identified that  $d$ -state levels of Mo, are located at resonant positions high above the CBM. This leads to negligible interaction of these  $d$  states with the  $5s$  states so that the CB dispersion is not disturbed, and this gives rise to a smaller effective mass which in turn leads to higher mobility values [8,33]. Xu *et al.*, further showed that unlike in Zr and Mo,  $d$ -states of W-dopant lie closer to the CBM of the host material, and hence a non-negligible hybridization is expected which may broaden the CB dispersion and lowers the mobility in  $\text{In}_2\text{O}_3$ :W. We note that reported RT mobility for polycrystalline ITO lies between  $20$ – $40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [4,12,14], and the maximum RT  $\mu_H$  obtained for our  $\text{In}_2\text{O}_3$  : TM films have significantly higher  $\mu_H$  values. Table I compares highest mobility values for our TM doped  $\text{In}_2\text{O}_3$  with previously reported works in the literature. In general high mobility have been reported for these TM doped  $\text{In}_2\text{O}_3$  polycrystalline thin films and the reported mobilities increases with growth temperatures for similar dopant concentration

From Fig. 2(b), the  $\mu_H$  of all  $\text{In}_2\text{O}_3$  : TM films also shows a remarkable decrease with increasing  $N_d$ . This mobility drop has also been observed in other TM doped metal oxides [44–47]. Li *et al.*, compared In and V doping in CdO and found that while the mobility in In doped CdO increased slightly with doping from  $\sim 100$  to  $120 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and stabilized at  $\sim 80 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  as the dopant concentration increased, the mobility of V doped CdO dropped rapidly from 100 to  $\sim 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at  $\sim 10\%$  V doping [44]. This difference in

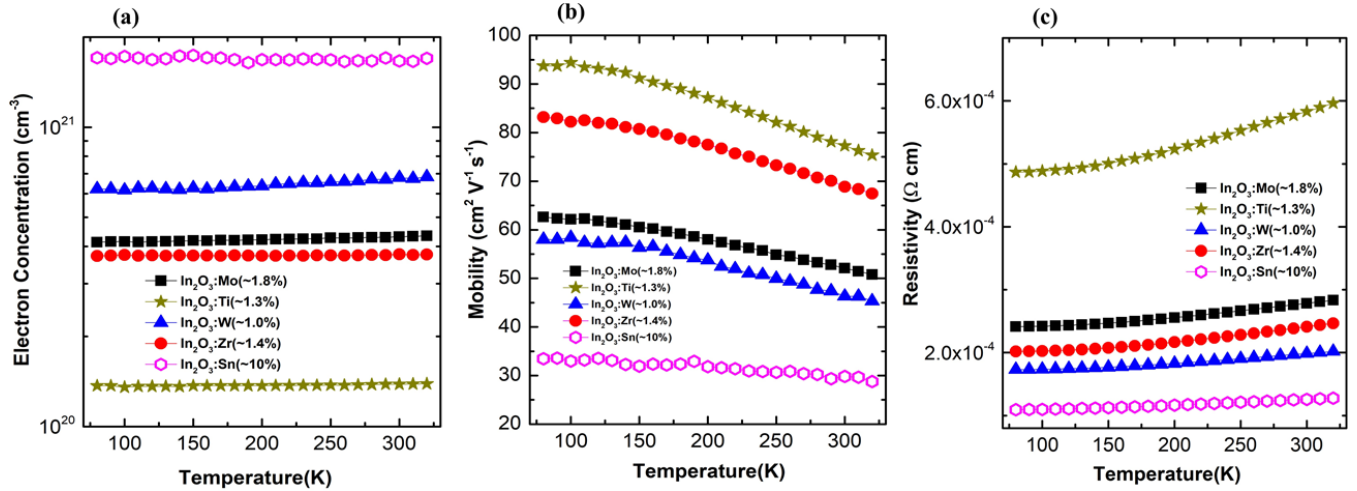


FIG. 3. Temperature dependence of (a) Electron concentration (b) Mobility and (c) resistivity of  $\sim 1\%$ – $2\%$  TM doped  $\text{In}_2\text{O}_3$  thin films with high mobilities. Data for ITO is shown in open symbol for comparison.

the behavior of the mobility with increasing dopant concentrations was attributed to the modification of the CdO conduction band (CB) due to the anticrossing interaction between the V localized  $d$  states and the CdO extended conduction band states. This anticrossing interaction results in the restructuring of CdO CB, leading to a drastic decrease in the mobility due to the large effective mass of the modified CdO. Similar anticrossing interaction between TM  $d$  states with oxide CB was also reported for V doped ZnO [45]. Such anticrossing interaction may also be responsible for the large drop in the mobility in our  $\text{In}_2\text{O}_3$  : TM at high doping concentration ( $>2.5\%$ ) as shown in Fig. 2(b).

Figure S3 [26] shows a plot of the mobility as a function of electron concentration obtained by Hall effect measurements for our  $\text{In}_2\text{O}_3$  : TM and ITO thin films. From the plot, a general trend of decreasing mobility with increasing electron concentration is observed and this is likely due to the increased ionized impurities scattering. However, at low carrier concentration, some  $\text{In}_2\text{O}_3$  : TM thin films such as  $\text{In}_2\text{O}_3$ :W and  $\text{In}_2\text{O}_3$ :Zr show a large spread in the data with some increase in mobility indicating that grain boundary scattering and other additional scattering is not negligible at these low dopant concentration [48,49].

Figure 3 shows the variable temperature Hall data obtained for  $\text{In}_2\text{O}_3$  : TM films with  $N_d \sim 1.0\%$ – $2.0\%$  at which the highest  $\mu_H$  was obtained. As expected, due to the degenerate nature of the  $\text{In}_2\text{O}_3$  : TM films, no observable temperature dependence on the  $N_H$  is evident as shown in Fig. 3(a). In contrast, Fig. 3(b) shows a decrease in  $\mu_H$  with increasing temperature for all  $\text{In}_2\text{O}_3$  thin films. This decrease in mobility is more evident in the  $\text{In}_2\text{O}_3$ :Ti thin film with higher  $\mu_H$  and is least observable in the lower  $\mu_H$  ITO. The large decrease in  $\mu_H$  for  $\text{In}_2\text{O}_3$ :Ti can be attributed largely to phonon scattering. At the temperature range studied,  $\geq 80$  K, ionized impurity scattering is negligible, however the plateau observed between 80–100 K indicates that at lower temperatures  $<80$  K,  $\mu_H$  may be limited by ionized impurity scatterings. Consequently, a slight increase in resistivity with temperature is seen in Fig. 3(c) due to  $\mu_H$  dominated by phonon scattering.

### B. Complex dielectric function, plasma energy, and high-frequency dielectric function

The real and imaginary parts of the complex dielectric function of  $\text{In}_2\text{O}_3$ :Mo thin films with different  $N_H$  are shown in Figs. 4(a) and 4(b), respectively. The peak of the  $\epsilon_1$  spectra at  $\sim 4$  eV shifts slightly to higher energy with increasing  $N_H$ , indicating an increase in the optical gap. The plasma energy,  $E_p$  can be extracted at the photon energy where  $\epsilon_1(E) = 0$  as shown in the inset of Fig. 4(a). Due to SE equipment limitation in the IR range, the plasma energy could not be extracted directly using the measured spectra for films with  $N_H < 4.8 \times 10^{20} \text{ cm}^{-3}$ . For these  $\text{In}_2\text{O}_3$  : TM films with low  $N_H$ , in order to extract their plasma energy,  $\epsilon_1(E)$  were extrapolated to zero by simulating the experimental  $\epsilon_1(E)$  data across the desired spectra range using the CompleteEASE software as shown by the dashed red lines in the inset of Fig. 4(a). Figure 4(b) shows the imaginary part of the dielectric function  $\epsilon_2(E)$ . An increase in  $\epsilon_2(E)$  at low IR energy with increasing  $N_H$  is observed signifying a non-negligible free carrier absorption which will be discussed later.

The inset of Fig. 4(a) shows that the plasma energy of the  $\text{In}_2\text{O}_3$ :Mo films increases with increasing  $N_H$  up to  $8.2 \times 10^{20} \text{ cm}^{-3}$  for increasing Mo dopant concentration in  $\text{In}_2\text{O}_3$ . At higher  $N_d$  the  $N_H$  drops slightly back to  $7.0 \times 10^{20} \text{ cm}^{-3}$ , leading to a slight decrease in the  $E_p$ . The plasma wavelength  $\lambda_p$  obtained for different  $\text{In}_2\text{O}_3$  : TM thin films with accuracies,  $\pm 0.25 \mu\text{m}$  are plotted as a function of film resistivity  $\rho$  in Fig. 5(a). Previously reported values of  $\lambda_p$  for other transparent conducting metal oxide materials ( $\text{In}_2\text{O}_3$  : Sn, and CdO:In) are also shown for comparison. A general trend of a monotonous decrease of the  $\lambda_p$  with decreasing  $\rho$  is observed for all the TCO samples. From Eq. (2),  $\lambda_p$  can also be related to  $\rho$  and the mobility  $\mu$  as follows:

$$\lambda_p = 2\pi c \sqrt{\frac{m^* \epsilon_\infty \epsilon_o}{e^2 N_{\text{opt}}}} = 2\pi c \sqrt{\frac{m^* \epsilon_\infty \epsilon_o \mu \rho}{e}}, \quad (5)$$

where  $c$  is the speed of light. Figure 5(a) shows that the plasma edge decreases to lower wavelength when the resistivity decreases as expected, due to the increase in carrier

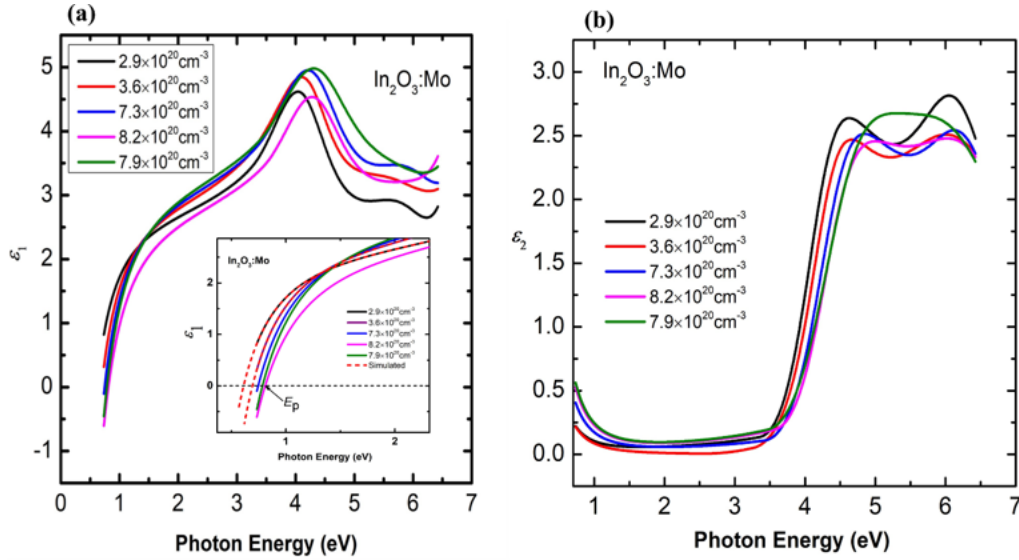


FIG. 4. Complex dielectric function of  $\text{In}_2\text{O}_3:\text{Mo}$  thin films showing (a) the real dielectric function and (b) imaginary part of the dielectric function with the variable  $N_{\text{Hall}}$ . The inset of Fig. 3(a) shows the extrapolation of the plasma energy of the thin films.

concentration. Since the  $\text{In}_2\text{O}_3$  : TM films have higher mobility than  $\text{In}_2\text{O}_3$  : Sn and  $\text{CdO}:\text{In}$ , they also show a higher  $\lambda_p$  for a given  $\rho$ . For example, for a low  $\rho \sim 1\text{--}4 \times 10^{-4} \Omega \text{cm}$ ,  $\lambda_p$  is in the range of  $1.2\text{--}1.6 \mu\text{m}$  for ITO but extends to  $\sim 1.7$  to  $2 \mu\text{m}$  for  $\text{In}_2\text{O}_3$  : TM films. Hence, because of their higher mobility,  $\text{In}_2\text{O}_3$  : TM films can achieve a much wider transparency window into the near infrared spectral range compared to ITO with comparable electrical conductivity.

At sufficiently low photon energies, according to the Drude model, the real part of the dielectric function can be expressed as  $\varepsilon_1(E) = \varepsilon_\infty - A_D/(E^2 + \Gamma_D^2)$ , where  $A_D$  is the Drude amplitude and  $\Gamma_D$  is the broadening. This allows us to obtain the high-frequency dielectric constant  $\varepsilon_\infty$  from the intercept of the  $\varepsilon_1$  versus  $1/E^2 + \Gamma_D^2$  plot [21]. The values of  $\varepsilon_\infty$  obtained from the intercepts of such plots for different  $\text{In}_2\text{O}_3$  : TM thin films are shown in Fig. 5(b). At low fre-

quencies, the dielectric function of a material has significant contributions from electrons, ions and dipoles, etc. However, at high frequencies, only electrons can respond, and hence the dielectric constant at high-frequency depends strongly on the electron concentration. Although the incorporation of small number of dopants does not significantly change the overall composition and structure of the material, it increases the electron concentration significantly [50]. Values of  $\varepsilon_\infty$  for  $\text{In}_2\text{O}_3$  doped with different species (TM and Sn) fall within the range of  $\sim 4.8\text{--}3.8$  and follow a general trend of lower  $\varepsilon_\infty$  as  $N_H$  increases. However, slight differences in  $\varepsilon_\infty$  are observed for different TM dopants with similar carrier density. Similar dependence of the high-frequency dielectric constant on carrier density have been reported earlier for transparent conducting metal oxides [21]. The obtained high-frequency dielectric constant of our ITO of  $\sim 3.85$  shown are in

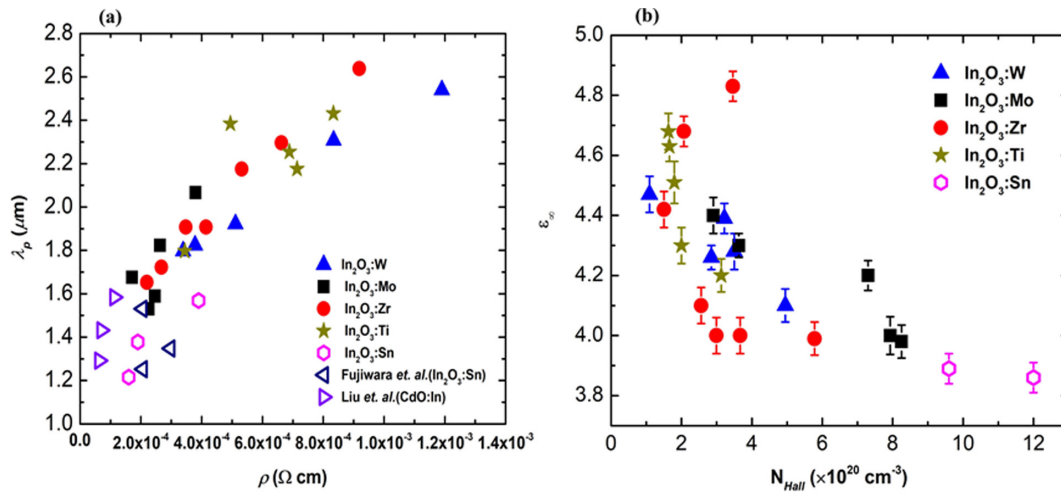


FIG. 5. (a): The plasma wavelength obtained from SE analysis as a function of the resistivity for different  $\text{In}_2\text{O}_3$  : TM samples, Previous experimental reported plasma energy of several TCOs are also shown [21,22] (b) The high-frequency dielectric constant of thin films vs  $N_{\text{Hall}}$  obtained from the intercept of the plot of  $\varepsilon_1$  vs  $1/(E^2 + \Gamma^2)$ .

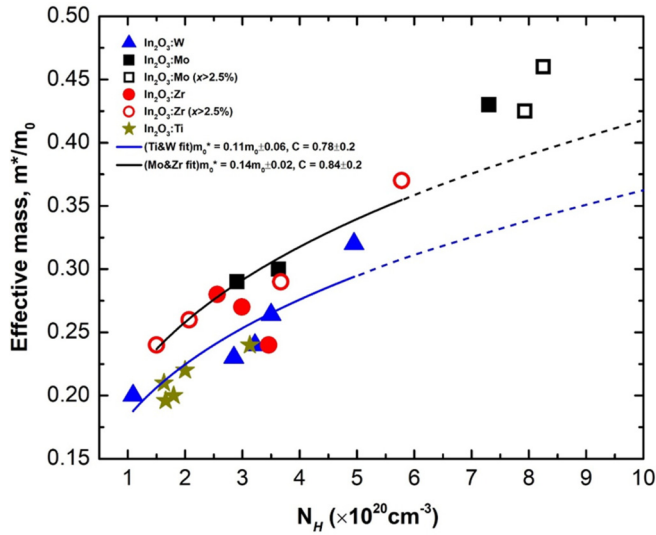


FIG. 6. Electron effective mass,  $m^*$  for  $\text{In}_2\text{O}_3$  thin films with different dopants as a function of  $N_H$ , accuracies are  $\sim \pm 5\%$ , where  $m_0$  is the free electron mass. The black solid line is the best fit for the data from Mo and Zr doped while the black dashed line is the best fit for Ti- and W doped  $\text{In}_2\text{O}_3$  samples of the conduction band nonparabolicity equation. The best fit curves were obtained for samples with  $N_H < 5 \times 10^{20} \text{ cm}^{-3}$ .

agreement but slightly lower than previously reported values (e.g., Fujiwara *et al.*, reported  $\varepsilon_\infty$  value of  $\sim 3.98$  for ITO film with  $N_{\text{Hall}} \sim 1.2 \times 10^{21} \text{ cm}^{-3}$  [22]).

### C. Electron effective mass and optical mobility

To understand the origin of the higher mobility in the  $\text{In}_2\text{O}_3$  : TM films, we extract their electron effective mass  $m^*$  using the expression for the plasma energy shown in Eq. (2), by assuming a time independent electric field. Hence, with the optical carrier density,  $N_{\text{opt}} \approx N_H$  and using the values of  $\varepsilon_\infty$  in Fig. 5(b), the electron effective mass is obtained and the results are plotted as a function of  $N_H$  in Fig. 6. In the figure, the  $m^*$  for highly doped samples with  $N_d > 2.5\%$  for Mo and Zr doped samples are plotted with open symbols. Figure 6 shows that the  $m^*$  increases with  $N_H$ , in particular, a more rapid increase is observed for  $\text{In}_2\text{O}_3$ :Mo at  $N_H > 7 \times 10^{20} \text{ cm}^{-3}$ . The increase in the  $m^*$  with  $N_H$  is consistent with the observed decrease in the Hall mobilities at high carrier concentration. We invoke the nonparabolicity of the conduction band to explain the dependence of the effective mass,  $m^*$  on  $N_H$  for  $\text{In}_2\text{O}_3$  : TM thin films. The nonparabolicity of the conduction band can be expressed in terms of the nonparabolicity factor,  $C$ , using the analytical expression by Pisarkiewicz *et al.* [51] given as

$$m^* = m_0^* \sqrt{1 + 2C \frac{\hbar^2}{m_0^*} (3\pi^2 N)^{2/3}}, \quad (6)$$

where  $m_0^*$  is the effective mass at the conduction band minimum and  $N$  is the electron concentration which is taken as  $N_H$ . We also notice that the  $m^*$  for the Mo and Zr doped samples follows a slightly different curve from that for W and Ti doped ones. With  $m_0^*$  and  $C$  as the fitting parameters, the

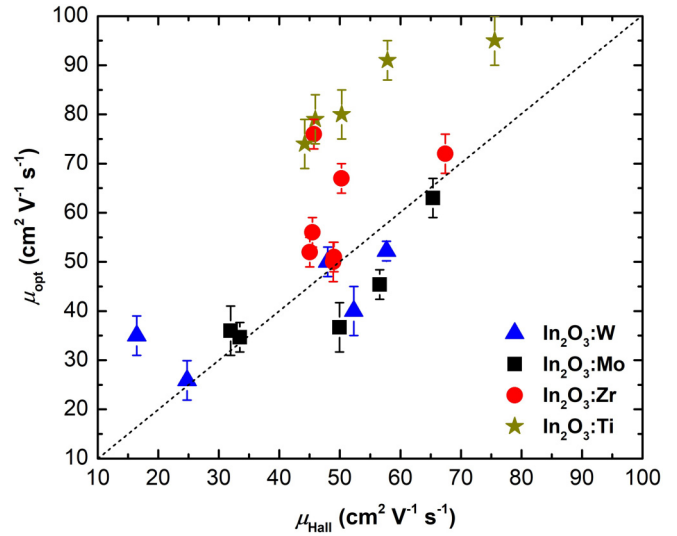


FIG. 7. Optical mobility of TM doped  $\text{In}_2\text{O}_3$  obtained from the SE analysis as a function of Hall mobility.

best fits for the effective mass data for Mo and Zr doped and W and Ti doped films with  $N_H < 5 \times 10^{20} \text{ cm}^{-3}$  are shown by the black and blue solid line respectively in Fig. 6. The best fit results for  $m_0^*$  and  $C$  are  $\sim 0.14 \pm 0.02 m_0$  and  $0.84 \pm 0.2 \text{ eV}^{-1}$ , respectively, where  $m_0$  is the free electron mass for the W and Ti doped samples. A slightly lower CB edge effective mass of  $\sim 0.11 \pm 0.02 m_0$  with a  $C$  value of  $\sim 0.78 \pm 0.1 \text{ eV}^{-1}$  is obtained for fitting using the data from the W and Ti doped samples. The obtained CB edge effective mass,  $m_0^*$  for  $\text{In}_2\text{O}_3$  : TM from the fittings lie in the range of  $0.11$ – $0.14 m_0$ , which is lower than previously reported values of  $m_0^*$  for  $\text{In}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  : Sn in the range of  $\sim 0.18$ – $0.3 m_0$  [22,52–54]. The smaller electron effective mass,  $m_0^*$  obtained here for samples with low carrier density  $\sim N_H < 5 \times 10^{20} \text{ cm}^{-3}$  supports the resonant doping picture described by Swallow *et al.* [8]. Table I also compares the electron effective mass of our  $\text{In}_2\text{O}_3$  : TM samples to previously reported values. Figure 6 also shows that for  $N_H > 5 \times 10^{20} \text{ cm}^{-3}$ , the  $m^*$  deviates from the fits and is much higher than the fits (extrapolated in the dashed blue and black line). This much higher  $m^*$  at higher  $N_H$  (and also higher  $N_d$ ) maybe related to the modification of the  $\text{In}_2\text{O}_3$  conduction band by the anticrossing interaction of increased number of localized  $d$  states of the TM dopants with host conduction band states as described in Refs. [44,55,56].

The Drude broadening parameter  $\Gamma_D$  from the SE analysis [Eq. (1)] is also related to the optical mobility  $\mu_{\text{opt}}$  and effective mass  $m^*$  from the expression  $\Gamma_D = \frac{\hbar e}{m^* \mu_{\text{opt}}}$ . The  $\mu_{\text{opt}}$  determined from  $\Gamma_D$  and  $m^*$  for the  $\text{In}_2\text{O}_3$  : TM thin films is plotted with respect to the Hall mobility,  $\mu_{\text{Hall}}$  in Fig. 7. The dotted line in Fig. 7 indicates the case where  $\mu_{\text{opt}} = \mu_{\text{Hall}}$ . A reasonable correspondence of  $\mu_{\text{opt}}$  with  $\mu_{\text{Hall}}$  is shown for films doped with most TM species (W, Mo, and Zr), especially for films with  $\mu_{\text{Hall}} < 50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . For the Ti doped sample with  $\mu_{\text{Hall}} > 50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , large deviations with  $\mu_{\text{opt}} > \mu_{\text{Hall}}$  are observed. Note that the optical mobility obtained from SE results describes the average mobility within the grain and is not affected by grain boundary scattering in polycrystalline



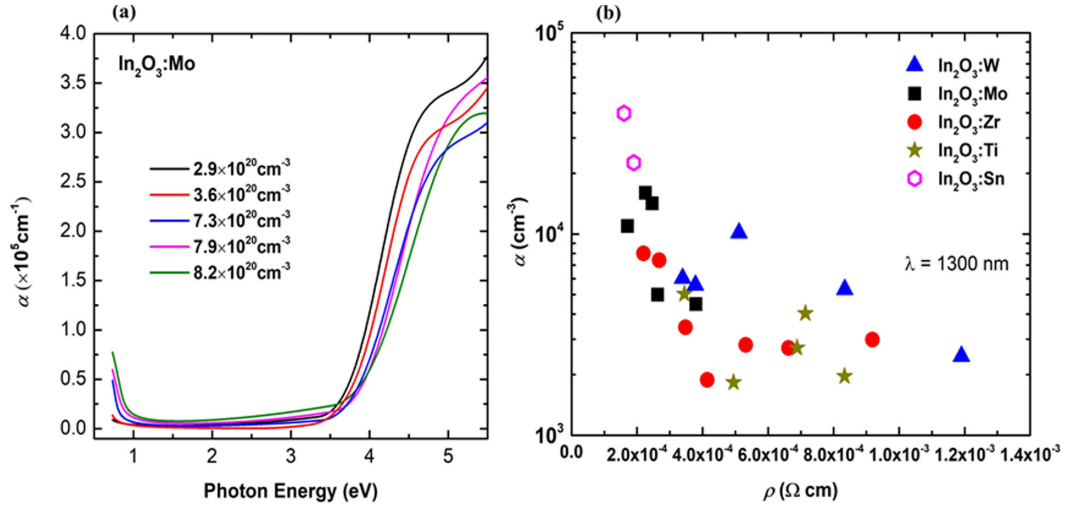


FIG. 8. (a) Absorption coefficient of Mo doped  $\text{In}_2\text{O}_3$  for samples different  $N_H$ . (b) Free carrier absorption for values of TM doped  $\text{In}_2\text{O}_3$  thin films at an IR wavelength of 1300 nm.

films, and hence is normally higher than the measured  $\mu_{\text{Hall}}$ . In the case of Ti doping, high  $\mu_{\text{Hall}}$  is obtained for samples with  $N_d < 2\%$ . At this low Ti doping,  $N_H < 3 \times 10^{20} \text{ cm}^{-3}$  and the effective mass  $m^* < 0.25$  the ionized impurity scatterings are low. Hence grain boundary scatterings become more significant in reducing the  $\mu_{\text{Hall}}$  as is observed in the plot of hall mobility vs hall electron concentration in Fig. S3 of Ref. [26]. Results shown in Fig. 7 also suggests that the mobility of Ti doped  $\text{In}_2\text{O}_3$  can be further enhanced for films with larger grains by optimizing the growth as well as post-growth annealing conditions.

#### D. Free carrier absorption, transmission intensity, and optical band gap

Because of the high electron concentration in the  $\text{In}_2\text{O}_3$  : TM, the free carrier absorption (FCA) becomes significant in the low photon energy region,  $E < 1 \text{ eV}$ , and FCA increases

with increasing  $N_H$  as shown in the absorption coefficient plots in Fig. 8(a) for  $\text{In}_2\text{O}_3:\text{Mo}$  thin films. The absorption coefficient spectra of the samples shown are obtained from SE spectra modelling. Due to the spectral range in the ellipsometry system used, we are limited to probing only up to 1700 nm and cannot show FCA data from samples with  $N_H < 10^{20} \text{ cm}^{-3}$ . The dependence of the absorption coefficient  $\alpha$  with resistivity at the wavelength of 1300 nm in the NIR region is shown in Fig. 8(b). For films with low  $\rho \sim 1\text{--}3 \times 10^{-4} \Omega \text{ cm}$ ,  $\alpha$  for ITO films is much higher ( $> 2 \times 10^4 \text{ cm}^{-1}$ ) due to FCA. In contrast,  $\alpha$  for  $\text{In}_2\text{O}_3$  : TM films are much lower ( $< 10^4 \text{ cm}^{-1}$ ), suggesting that  $\text{In}_2\text{O}_3$  : TM films are better suited as transparent conductors on devices where transmission of longer wavelength photons is needed.

Figure 9(a) shows the transmission intensity of 150-nm-thick  $\text{In}_2\text{O}_3$  thin films doped with different TM species for samples with resistivity in the range of  $\rho \sim 1.07 \times 10^{-4}\text{--}3.4 \times 10^{-4} \Omega \text{ cm}$ . Transmission spectra of ITO films are shown

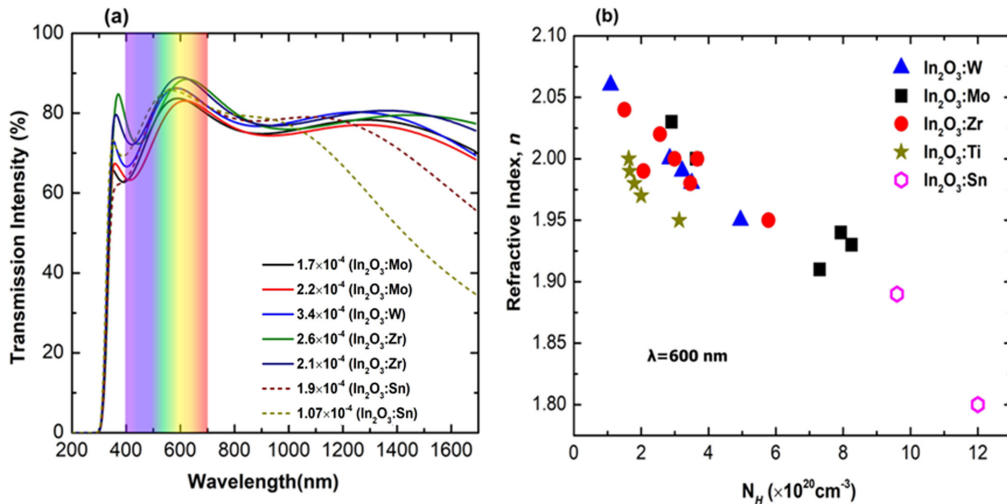


FIG. 9. (a) Optical transmission intensity of TM doped  $\text{In}_2\text{O}_3$  thin films with thickness,  $t = 150 \text{ nm}$  for different resistivity ( $\Omega\text{-cm}$ ),  $\text{In}_2\text{O}_3$  : Sn thin films obtained at similar condition are also shown. (b) Refractive index  $n$  at 600 nm wavelength of the  $\text{In}_2\text{O}_3$  thin films doped with various dopants obtained from SE Analysis.

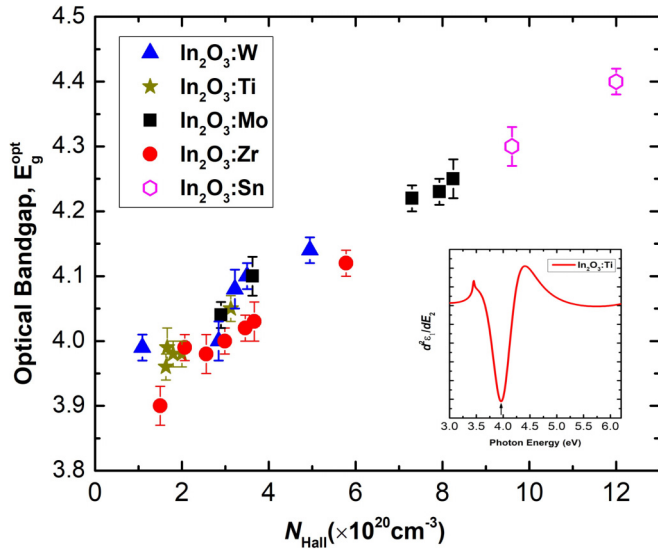


FIG. 10. Optical band gap of TM doped  $\text{In}_2\text{O}_3$  thin films vs  $N_{\text{Hall}}$  obtained from the second derivative of the real part of the dielectric function,  $d^2\varepsilon_1/dE^2$ . The inset shows  $d^2\varepsilon_1/dE^2$  of a  $\text{In}_2\text{O}_3:\text{Ti}$  sample as a function of photon energy with the black arrow indicating the optical band-gap energy value.

as dashed lines for comparison. The ITO films with  $\rho \sim 1.07\text{--}1.9 \times 10^{-4} \Omega \text{ cm}$  show clear decrease in long wavelength transmittance with a remarkable decrease in transmittance at  $\lambda > 1000 \text{ nm}$  for the ITO film with  $\rho \sim 1.07 \times 10^{-4} \Omega \text{ cm}$  due to the strong FCA [Fig. 8(b)] and the low  $\lambda_p$  [ $\sim 1.2 \mu\text{m}$  from Fig. 5(a)]. However, TM doped thin films with  $\rho$  as low as  $\sim 1.7 \times 10^{-4} \Omega \text{ cm}$  show negligible decrease in NIR transmittance. From Fig. 9(a),  $\text{In}_2\text{O}_3:\text{Mo}$  thin films with  $\rho \sim 1.7 \times 10^{-4} \Omega \text{ cm}$  (black line) show transmittance  $\sim 80\%$  up to  $1700 \text{ nm}$ . This is a remarkable improvement in the transmittance compared to ITO films with similar conductivity due to the higher mobility in  $\text{In}_2\text{O}_3$  : TM thin films.

To achieve the minimum light reflection and optimum transmittance in optoelectronic devices utilizing TCO, the refractive index of the TCO layer plays an important role. The refractive index of these  $\text{In}_2\text{O}_3$  : TM thin films at the visible wavelength of  $600 \text{ nm}$  is shown in Fig. 9(b). A monotonous decrease in the refractive index with increasing  $N_H$  of the films at the  $600 \text{ nm}$  is observed. In comparison, since ITO requires a higher  $N_H$  to achieve a comparably low resistivity as  $\text{In}_2\text{O}_3$  : TM, and thus values of the refractive index for ITO samples are much lower ( $n \sim 1.8\text{--}1.9$  compared to  $\sim 1.9\text{--}2.0$  for  $\text{In}_2\text{O}_3$  : TM). The higher refractive index for  $\text{In}_2\text{O}_3$  : TM is also a favorable attribute for optical coating applications [53].

Figure 10 shows the optical band gap  $E_g^{\text{opt}}$  of  $\text{In}_2\text{O}_3$  : TM thin films as a function of  $N_H$  obtained from the second derivative of the real part of the dielectric function from SE analysis,  $d^2\varepsilon_1/dE^2$ . The optical band gap of ITO is also shown for comparison. An example of using the  $d^2\varepsilon_1/dE^2$  method to obtain the optical band-gap energy for a  $\text{In}_2\text{O}_3:\text{Ti}$  sample is shown as the inset of Fig. 10 [57,58]. We found that using this method for determining the optical band gap for a degenerate semiconductor is more accurate

than the conventional Tauc plot method and results in values similar to the method proposed by Dolgonos *et al.* [59]. In general, the Tauc plot underestimates the optical band gap in these thin films. Figure S4 [26] shows a comparison of the optical band gap of  $\text{In}_2\text{O}_3$  : TM thin films obtained from Tauc method and the  $d^2\varepsilon_1/dE^2$  method. Figure 10 shows a trend of increasing  $E_g^{\text{opt}}$  with  $N_H$  for different dopants. This increasing  $E_g^{\text{opt}}$  with  $N_H$  is attributed to the Burstein-Moss shift and band-gap renormalization effects observed for degenerately doped semiconductors [60,61].

## V. CONCLUSION

Obtaining an ideal TCO with a high electrical conductivity and at the same time high transmittance over a wide spectral window (from UV to IR) posts a formidable challenge. This is because the high electron concentration required to achieve a high electrical conductivity in a TCO will also necessarily increase free carrier absorption and moves the plasma reflection wavelength to lower photon wavelength, and hence make the TCO not transparent in the NIR region. Transition metal doping in  $\text{In}_2\text{O}_3$  provides an alternative to mitigate this trade off since the mobility in  $\text{In}_2\text{O}_3$  : TM is improved and consequently a lower electron concentration is required to achieve a high conductivity comparable to the commonly used ITO. In this study, we explore the effects of free carriers on the transport and optical properties of TM (W, Zr, Mo, Ti) doped  $\text{In}_2\text{O}_3$  thin films grown at low temperature by magnetron sputtering followed by RTA processing. The sputtered thin films showed higher mobilities for all TM dopants compared to ITO. In particular, a mobility of  $75 \text{ cm}^2/\text{V}\cdot\text{s}$  is obtained for  $\text{In}_2\text{O}_3:\text{Ti}$  thin films with a carrier concentration of  $\sim 2 \times 10^{20} \text{ cm}^{-3}$ . Variable temperature measurements show a decrease in mobility with increasing temperature for high mobility  $\text{In}_2\text{O}_3$  : TM due to phonon scattering. Detailed optical properties of  $\text{In}_2\text{O}_3$  : TM films were studied by room temperature standard spectroscopic ellipsometry. Analyses of the SE data using dielectric function parameterization combining a Drude oscillator and several Tauc-Lorentz oscillators reveal the effects of free carriers on the complex dielectric function. Optical band gap shifts due to the Burstein-Moss and band-gap renormalization effects are also evident in these highly doped  $\text{In}_2\text{O}_3$  thin films. Several material parameters useful for describing the electronic and optical properties of these  $\text{In}_2\text{O}_3$  : TM films such as the plasma wavelengths  $\lambda_p$ , electron effective mass  $m^*$ , high-frequency dielectric constant  $\varepsilon_\infty$ , refractive index  $n$ , extinction coefficients  $k$ , and optical mobility  $\mu_{\text{opt}}$  were obtained from our SE analysis. In general, a decrease of the  $\varepsilon_\infty$  and an increase in the plasma energy are observed with increasing carrier concentration. From the fittings of the electron effective mass using the nonparabolic conduction band model, the electron effective mass at the bottom of the conduction band  $m_o^*$  for  $\text{In}_2\text{O}_3$  : TM are lower than that in ITO. Specifically,  $m_o^* \sim 0.11\text{--}0.14m_o$  is found for  $\text{In}_2\text{O}_3$  : TM compared to the reported  $m_o^* \sim 0.18\text{--}0.3m_o$  for ITO. This is consistent with recent theoretical studies which proposed that  $4d$  donor states of the TMs are resonance in the CB and do not disturb the CB dispersion of the host. For samples with high TM doping  $N_d > 2.5\%$ , the effective mass of  $\text{In}_2\text{O}_3$  : TM films increases more rapidly and deviates

significantly from the CB nonparabolic model, resulting in a drastic drop in the mobility. This is in agreement with previous studies on TM doped ZnO and CdO which showed that at high dopant concentration anticrossing interactions of the TM  $d$  states with extended CB states results in the restructuring of the CB and significantly flattens the CB. Our study provides a detailed understanding of the optical properties in high mobility transparent TM doped  $\text{In}_2\text{O}_3$  films. Using TM doping, we have achieved TCOs with conductivity comparable to ITO but with transmission extended to  $>1600$  nm into the NIR spectral region. These materials will be potentially important as transparent conductors for optoelectronic devices utilizing the NIR photons.

The data that supports the findings of this study are available within the paper and Ref. [26].

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