ADVANCED ELECTRONIC MATERIALS

Supporting Information

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Transparent Electrodes for Efficient Optoelectronics

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1. Free carrier absorption in TCOs

In the NIR-IR part of the spectrum, the main source of optical loss in TCOs is parasitic absorption by free carriers in the conduction band. This effect is called free carrier absorption (FCA), which is well-described by the classical Drude theory in the NIR-IR range as follows.[1,2]

The collective oscillation of the free electrons with the electric field of the incident photons form plasmons with a frequency (ω_p) described by the classical Drude model as:

$$\omega_p = \sqrt{\frac{Ne^2}{m^*\varepsilon_\infty\varepsilon_0}}, \qquad \text{(S1)}$$

where N is the optical carrier concentration, e is the charge of the electron, m^* is the effective mass of the carriers and $\varepsilon_\infty\varepsilon_0$ is the permittivity of the material. The plasma wavelength at which the transmittance of the TCO is limited by FCA is then calculated from $\lambda_p = 2\pi\hbar/\omega_p$. For degenerated TCOs with $N_e \approx 10^{20}$ cm^{-3}, $\lambda_p \approx 1000$ nm. For metals ($N_e > 10^{22}$ cm^{-3}), λ_p blue-shifts to the deep-UV, i.e. $\lambda_p < 200$ nm.[3]

Following the Drude model, FCA absorption of TCOs can be expressed as a function of the electron carrier density and optical mobility as follows. For free electrons in metals and highly doped semiconductors, the complex dielectric function (ε) of the material is given by

$$\varepsilon = (n-ik)^2 = \varepsilon_\infty + \frac{\varepsilon_\infty{\omega_p}^2}{(\omega^2+i\omega\Gamma)} = \varepsilon_\infty\left[\left(1-\frac{{\omega_p}^2}{(\omega^2+\Gamma^2)}\right) - i\left(\frac{{\omega_p}^2\Gamma/\omega}{\omega^2+\Gamma^2}\right)\right], \qquad \text{(S2)}$$

where ε_∞ is the high-frequency dielectric constant, n is the refractive index, k is the extinction coefficient and Γ is the oscillator damping constant or a broadening parameter given by

$$\Gamma = {}^{e}/_{(\mu_{opt}m^*)}, \qquad \text{(S3)}$$

where μ_{opt} is the optical mobility. By separating the real and imaginary parts, we can obtain an expression for n and k in terms of N_e and μ_{opt}. For our case of low-to-moderate doping, it holds that $n \gg k$ so that only the imaginary part of Eq. (2) has to be taken and we obtain[1]

$$2nk = \frac{N_e e^2}{m^* \varepsilon_0}\left(\frac{\Gamma/\omega}{\omega^2+\Gamma^2}\right). \qquad \text{(S4)}$$

Considering the absorption coefficient, $\alpha = {}^{4\pi k}/_{\lambda}$ and $\omega \gg \Gamma$ for TCOs with high N_e (i.e., 10^{19}-10^{21} cm^{-3})[1,4], the photon loss due to free carrier absorption, or the free carrier absorption coefficient (α_{FCA}) can be written as [4,5]

$$a_{FCA} = \frac{\lambda^2 e^3 N_e}{4\pi^2 \varepsilon_0 c^3 n (m^*)^2 \mu_{opt}}. \qquad \text{(S5)}$$

2. Table of high performing n-type and p-type transparent conductors

In order to construct Figure 3 in the main text, we used a representative sample to the highest performing n-type and p-type TCOs in the literature. The candidate high performing p-type transparent conductors were selected from the table in the supplement of Woods-Robinson et al.[71] In Table S1, below, we list the properties of the candidate materials shown in Figure 3.

Table S1. Candidate n-type and p-type transparent conductors (oxides and other chalcogenides) used in Figure 3.

	Material	Deposition Method	Max Processing Temperature (° C)	Conductivity σ (S cm^{-1})	Optical Absorption Coefficient α (cm^{-1}) (averaged over 400-700 nm)	σ/α (Ω^{-1})	Reference
n-type	In_2O_3:Ce:H (ICO)	Sputtering + anneal	200	2700	132	20.45	6
	In_2O_3:H (IOH)	Atomic layer deposition (ALD)	100	2860	514	5.56	7
	In_2O_3:H (IOH)	Sputtering + anneal	200	3150	168	18.75	8
	In_2O_3:Zn (IZO)	Sputtering	60	2500	453	5.52	9
	In_2O_3:Sn (ITO)	Sputtering	300	3000	500	6.00	10
	In_2O_3:Sn (ITO)	Sputtering + anneal	200	960	880	1.09	11
	SnO_2:F (FTO)	APCVD	400	1900	1550	1.23	12
	ZnO:B	CVD	178	576	100	5.76	13
	ZnO:Al (AZO)	Sputtering	200	750	1135	0.66	14
	CdO:In	Sputtering	200	2500	2500	1.00	15
	$Zn_6Sn_{28}O_{66}$ (ZTO)	Sputtering	150	365	1300	0.28	16

	$Zn_6Sn_{28}O_{66}$ (ZTO)	Sputtering + anneal	500	600	800	0.75	[17]
	TiO_2:Nb	Pulsed laser deposition (PLD)	500	2170	875	2.48	[18]
p-type	$CuAlO_2$	Laser ablation (PLD)	700	<1	21000	4.76E-05	[19]
	$CuAlO_{2+x}$	DC sputtering	200	5	21000	2.38E-04	[20]
	$CuCrO_2$:Mg	RF sputtering	750	220	42000	5.24E-03	[21]
	Cu_xCrO_y	Spray pyrolysis	345 ± 10ºC	12	79000	3.50E-04	[22]
	$CuScO_{2+x}$	Sputtering	900	30	83000	3.60E-04	[23]
	$CuYO_2$:Ca	Sputtering	900	8	50000	1.61E-04	[24]
	Co_3O_4:Ni_3O_4 "$NiCo_2O_4$"	RF sputtering	400	333	190000	1.76E-04	[25]
	MoO_3:In	Tube furnace	727	400	22000	1.84E-02	[26]
	$LaCrO_3$:Sr	Molecular beam epitaxy (MBE)	700	54	170000	3.14E-04	[27]
	ZnO:Rh_2O_3	RF sputtering	25	21	27000	7.70E-04	[28]
	Zn-Co-O	Pulsed laser deposition (PLD)	25	1.9	40000	4.76E-05	[29]
	$Zn_x(CuAlS_2)_{1-x}$	Conventive Self Assembly (CSA)	500	63.5	16000	3.91E-03	[30]
	$BaCu_2S_2$	RF sputtering	264	17	16000	1.05E-03	[31]
	Cu-Zn-S	Pulsed laser deposition (PLD)	550	54	51000	1.06E-03	[32]
	$Cu_xZn_{1-x}S$	Pulsed laser deposition (PLD)	25	42	28000	1.34E-03	[33]
	ZnS:Cu_yS	Chemical bath deposition (CBD)	80	1000	102000	9.79E-03	[34]

3. Table of selected TCO, graphene and metal work functions.

Table S2. TCOs, graphene and metal work functions as reported in literature.

TCO	Work function (eV)	Ref	Metal	Work function (eV)	Ref
ZnO:Al (AZO)	3.5 - 4.5	[35-36-37]	Ag	4.3 - 4.7	[42]
In_2O_3	4.8 – 5	[38]	Al	4 - 4.5	[42]
In_2O_3:Sn (ITO)	4 – 5	[35-36-37]	Au	5 - 5.5	[42]
SnO	4.5 - 5	[36-38]	Cu	4.5 – 4.7	[42]

SnO:F (FTO)	4.5 – 5	[35-36-37]	Pt	5 – 6	[42]
SnO:Sb (ATO)	4.5 - 5	[35-36]	Mg	3 – 4	[42]
$Zn_2In_2O_5$ (IZO)	4.9	[35-36-37]	Li	2 – 3	[42]
$ZnSnO_3$ (ZTO)	4.7 - 5.3	[35-36-37]	Zn	3 - 4	[42]
In_2O_3:Ga (IGO)	4.9 - 5.4	[35-36]	Sn	4.2 - 4.4	[42]
In_2O_3:Sn:Ga (GITO)	4.9 - 5.4	[35-36]	Ca	2.8 – 3	[42]
12 CaO·7 Al2O3 (C12A7)	2.4	[39]	W	4.5	[42]
Graphene	4.5 - 5	[40,41]			

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