SUPPORTING INFORMATION

Effect of Sol Stabilizer on the Structure and Electronic Properties of Solution-Processed ZnO thin Films

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Tafel plots obtained from ZnO films

Tafel plots for the ZnO films, formed by using various stabilizers, are shown in Fig. S1. Data was obtained by scanning the potential between –0.8 V (w.r.t. Ag/AgCl) to –0.025 V, in a 0.1 M KCl (aqueous) electrolyte, at room temperature. Samples were prepared by wrapping parafilm all around, except for a 0.5 cm × 0.5 cm area that was exposed to the electrolyte. This sealing of the edges by an insulator limited measurement and analysis errors due to points of high electric field concentration. Open circuit potential values were between –0.5 V and –0.3 V, implying that ZnO films exhibit blocking behavior in that potential range.

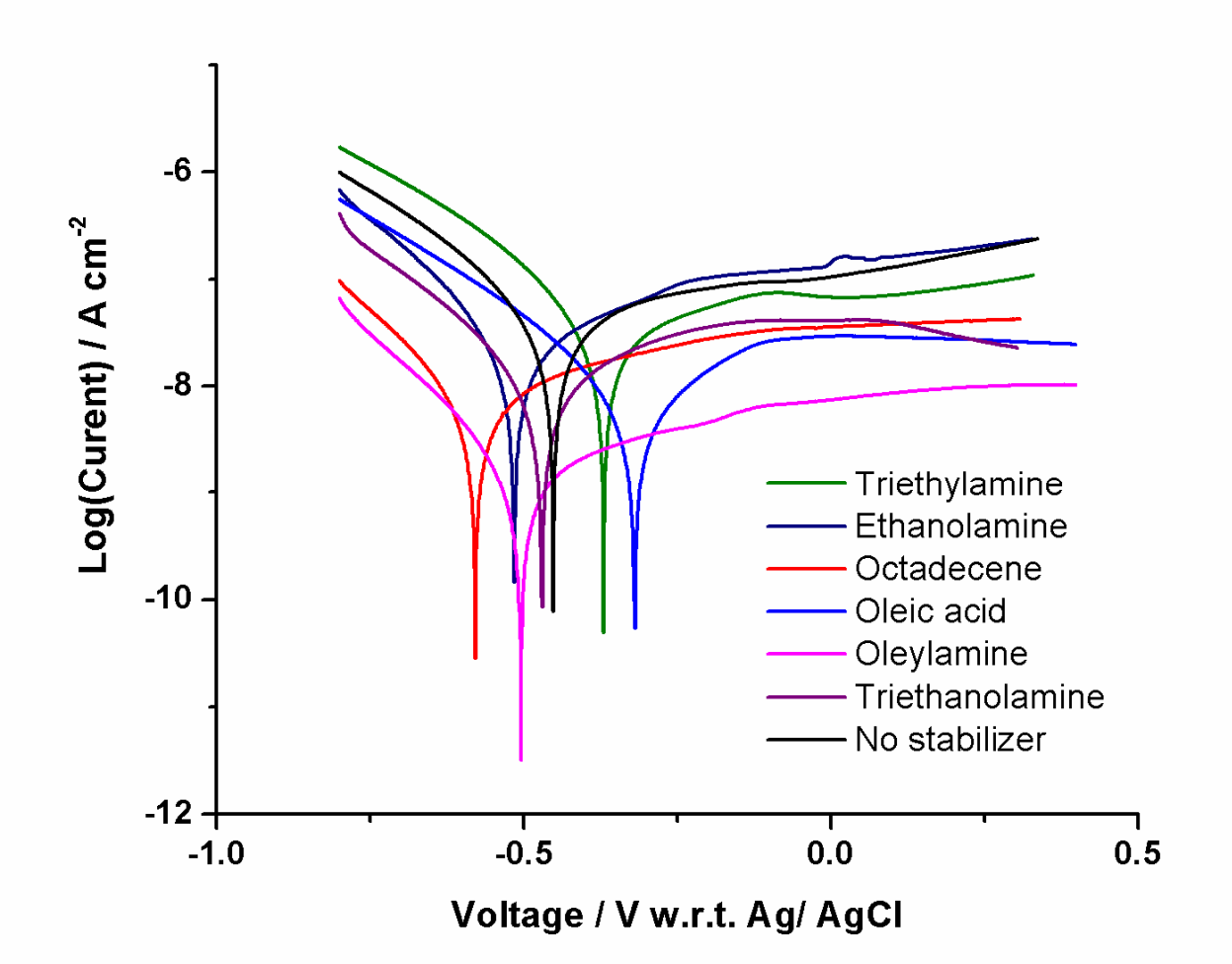


Fig. S1. Tafel plots for zinc oxide films grown with various stabilizers and also without stabilizer

Charge carrier concentration measurement using EIS

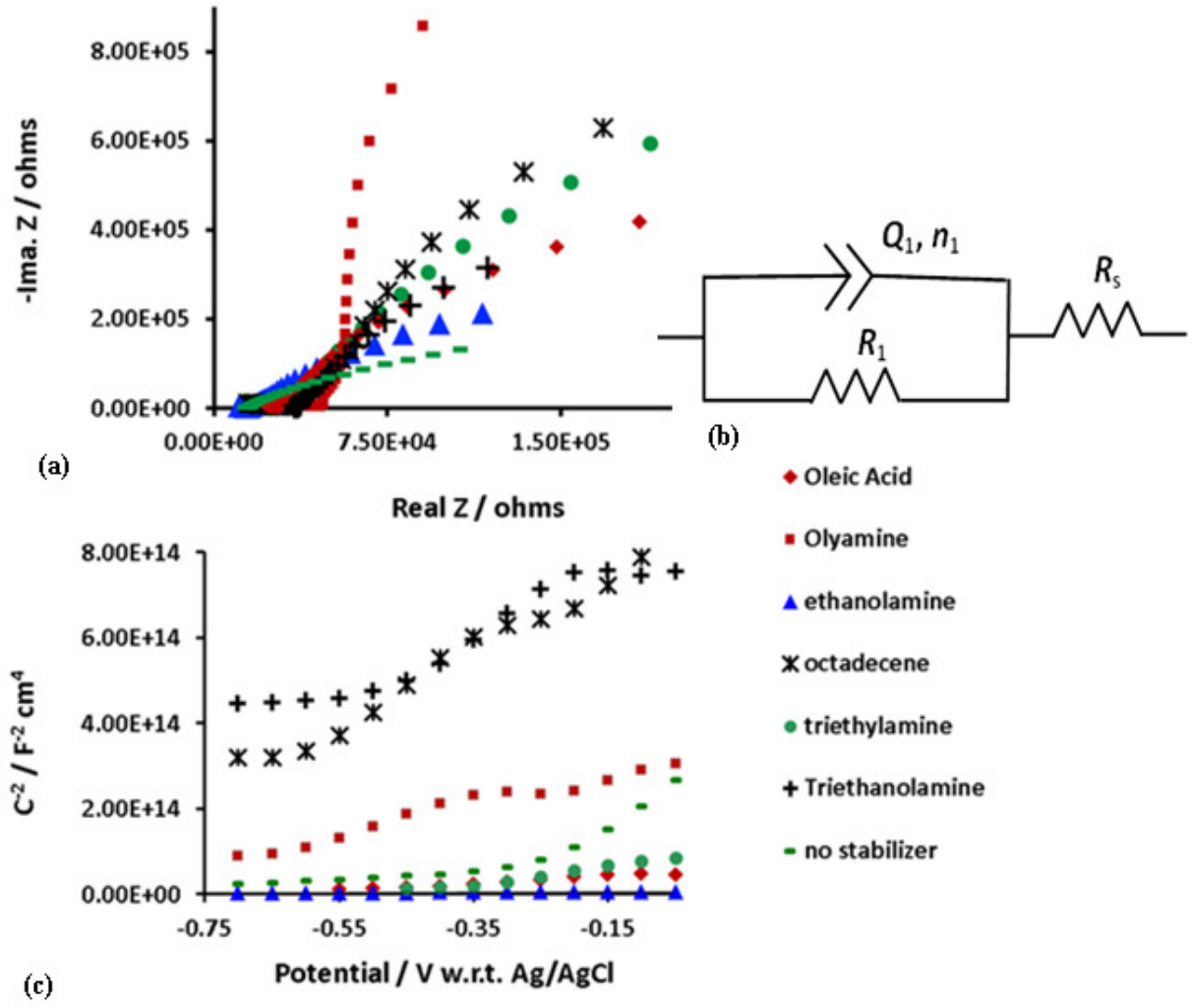


Fig. S2 Nyquist plots (a), equivalent circuit model (b) and Mott Schottky's plot (c) for zinc oxide films grown with various stabilizers and also without stabilizer.

Section S1: Chemistry of the sol formation process

Triethanolamine, ethanolamine and triethylamine cause hydrolysis and generate OH^- ions, as per *equation (1)*:

In *equation (1)*, "R" denotes triethanolamine, ethanolamine, and triethylamine

$$R + H_2O \leftrightarrow [R]^+ + OH^- \qquad \textit{equation (1)}$$

Zn^{2+} from zinc acetate precursors react with OH^- ions forming $Zn(OH)_2$ ions, as per *equations (2), (3) and (4)* **[1 to 4]**:

Formation of zinc hydroxide:

$$Zn(CH_3COO)_2 + (OH)^- \rightarrow HO\text{-}Zn\text{-}CH_3COO + CH_3COO^- \qquad \textit{equation (2)}$$

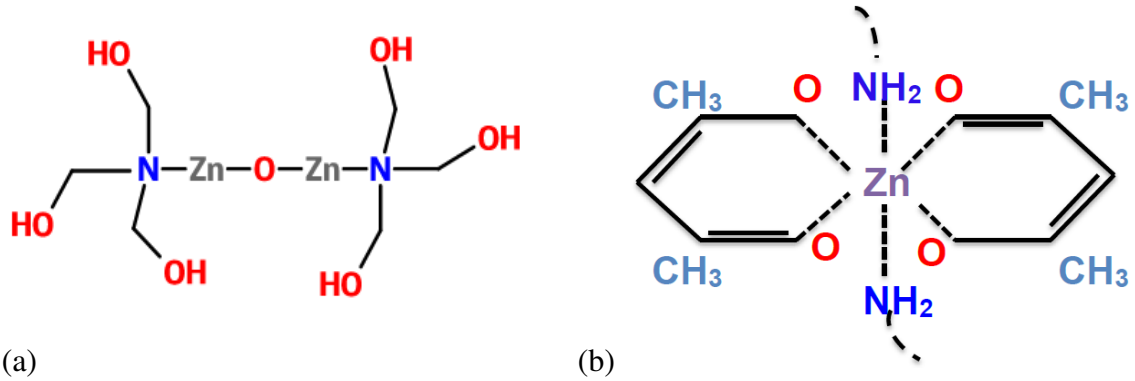
$$3HO\text{-}ZnCH_3COO + (OH)^- \rightarrow Zn(OH)_2 + CH_3COO^- \qquad \textit{equation (3)}$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \qquad \textit{equation (4)}$$

$Zn(OH)_2$ precursors decompose to ZnO under hydrothermal conditions as per *equation (5)*

$$Zn(OH)_2 \rightarrow ZnO + H_2O \qquad \textit{equation (5)}$$

ZnO forms complexes with amine bearing (primary amines) organic stabilizers [**6**] (e.g. triethanolamine, ethanolamine and triethylamine). For example, as shown in Fig. S3 (a), triethanolamine forms a complex with ZnO



(a) (b)

Fig. S3 (a) Representative structure of Zinc oxide – triethanolamine complex **[5]**, and (b) zinc acetate – oleylamine complex **[7]**

With oleylamine, zinc acetate forms a [Zn(acetate)$_2$]–oleylamine complex (pictorial schematic shown in Fig. 2 (b)), which thermally decomposes to yield ZnO **[7, 8]**.

With stabilizers like oleic acid and octadecene, ZnO(OH) species, generated by hydrolysis reaction, react to form complexes. An example reaction for oleic acid in shown in *equation (6)* **[8],** where, the zinc oxide – oleic acid complex yields ZnO at temperature above 400 $^{\circ}$C **[9]**

$$ZnO(OH)_x + {}_yHOOC(CH_2)_7CH{=}CH(CH_2)_7CH_3 \rightarrow \textbf{\textit{heat at 80 }}^{\circ}\textbf{\textit{C}} \rightarrow$$

$$Zn(OH)_{x-y}ZnO[OOC(CH)_7CH{=}CH(CH_2)_7CH_3]_y + yH_2O \qquad \textit{equation(6)}$$

Section S2: Effect of sol-stabilizer on crystallographic orientation

Preferred crystalline orientations are attained because of capping of growth of certain crystal planes and promoting the growth of others by stabilizers. Amine bearing small alkyl chain stabilizers, such as ethanolamine, triethanolamine and triethylamine function as complex forming agents that stabilize positively charged Zn^{2+} ions, and promote preferred crystalline orientation of ZnO along the c-axis by aiding polymerization of ZnO chains. This phenomenon is favored by the fast enough rate of hydrolysis, in order to generate ZnO to feed the formation process of orientated network of ZnO chains **[2]**. These stabilizers also provide a dense matrix for oriented crystal growth **[10]**. Other authors **[11]** state that amine bearing stabilizers (such as triethanolamine) aid in oriented agglomeration (by collision, rotation and oriented attachment) of ZnO and their growth.

Also notable is that stabilizers such as oleic acid and oleylamine have long alkyl chains that form complexes, which cap surfaces of the Zn^{2+} species restricting growth in certain directions. For instance, the coordinated complex formed by oleylamines are located at the top and at the bottom, which have chains of alkyl groups that interact by Van der Waal's forces, promoting formation of oriented two-dimensional ZnO crystals **[12 - 14]**. In case of octadecene, preferred crystalline orientation is not observed because it is not a coordinating solvent, and therefore no one crystal plane was favored as a growth direction **[15]**

Table S1. Ranking order of films based on value of material parameters and correlation to actual surface area

Ranking based on ratio of actual to geometric surface area	**Photo to dark current ratio**	**Lifetime (s)**	**Bulk mobility ($cm^2 V^{-1} s^{-1}$)**	**Doping (cm^{-3})**
Ethanolamine (13.8)	Ethanolamine (90)	No stabilizer (42.3)	No stabilizer (23)	Ethanolamine (4.7E18)
Triethanolamine (8.4)	No stabilizer (62.9)	Ethanolamine (38.03)	Octadecene (11)	No stabilizer (9.4E16)
No stabilizer (6.5)	Triethanolamine (40)	Triethanolamine (34)	Triethanolamine(10)	Triethanolamine (7E16)
Triethylamine (4.67)	Triethylamine (4.8)	Triethylamine (32.34)	Triethylamine (2)	Triethylamine (7E16)
Octadecene (2)	Octadecene (4.3)	Octadecene (25)	Ethanolamine (7.8E-3)	Octadecene (3.5E16)

Section S3: FTIR analysis

FTIR spectra for the ZnO films is shown in Fig. 3. There we found that residual organic complexes are present on the resultant ZnO films. The peak intensities are similar for all the ZnO films and therefore we conclude that these organic residues contribute equally to the resistivity of the films. Peak at 482 cm^{-1} corresponds to ZnO. [**2, 16-19**]. Intense peak at 670 cm^{-1} corresponds to CH_2 [**5**], and those at 1010, 1100 and 1140 cm^{-1} may be ascribed to C–N bonds [**20-24**]. Peak at 1365 and 1490 correspond to C-O [**2**] and those at 1580, 1610 and 1700 correspond to C=O [**2, 24**]. Peak at 2380 cm^{-1} is due to absorption of atmospheric CO_2 [**24, 25**].

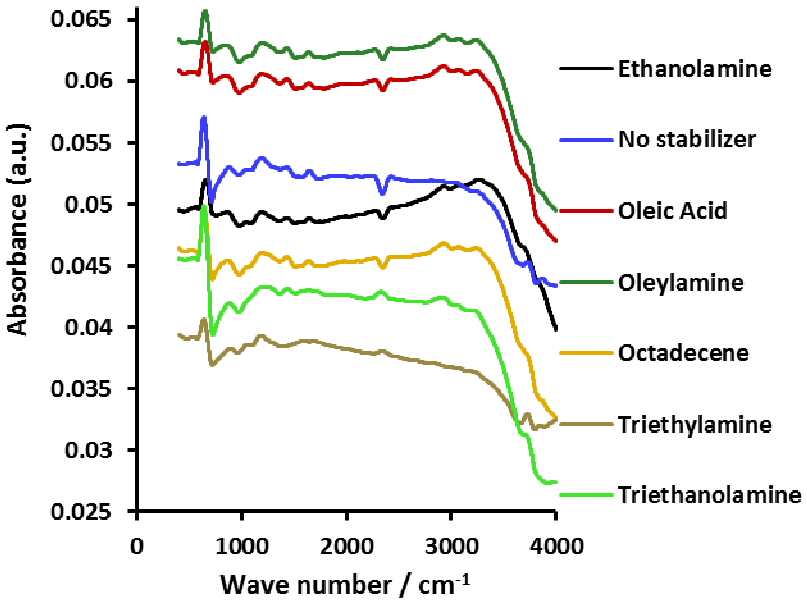


Fig. S4. Plots of FTIR data of ZnO films formed with various stabilizers

Table S2. Assignment of chemical groups the FTIR peaks exhibited by the ZnO films

Peaks Position (cm^{-1})	Assignment	Reference(s)
482	ZnO	2, 16-19
670	C-H_2	2
1010	C-N	20-24
1100	C-N	20–24
1365	C-O	23
1490	C-O	23
1580	C=O	19, 23
1610	C=O	23
1700	C=O	2, 24
2300	O=C=O	23, 25
2950	C-H	2
3600	O-H	2, 23

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