Triethanolamine concentration effect on electrodeposited SnS properties

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ABSTRACT

SnS thin films were electrodeposited onto ITO-coated glass substrates using one-step potentiostatic electrodeposition in a bath solution consisting of tin chloride ($SnCl_2$) and sodium thiosulfate ($Na_2S_2O_3$) for different concentrations of triethanolamine complexing agent (TEA). For the kinetic study, the charge transfer coefficient α_c , the diffusion coefficient D, and the potential dependent cathodic rate K_c were deduced by analyzing cyclic voltammograms and potentiostatic current transients. The electrochemical study showed that the charge transfer controls the electrodeposition of SnS in the presence of TEA. The effect of triethanolamine addition on the structural, morphological, compositional, and optical properties was studied using XRD, SEM, EDX, Raman, and UV–visible techniques. All samples crystallize in the orthorhombic SnS phase. It was found that the addition of TEA not only affects the surface morphology of the films by reducing the grain size, but also slows down the deposition of tin and thus improves the stoichiometry of the film. The vibrational modes of the tin chalcogenides SnS, SnS_2, and Sn_2S_3 helped in the identification of the sample's chemical structure. All samples displayed low transmittance in the visible range, which decreases with the increase of the agent concentration. The band gap was identified to be direct and increases with TEA in correlation with structural parameters. The optimal properties and the stoichiometry were reached for the concentration ratio [Sn:TEA]=[1:1] and were found in good agreement with the calculated electrochemical parameters.

MATERIALS AND METHOD

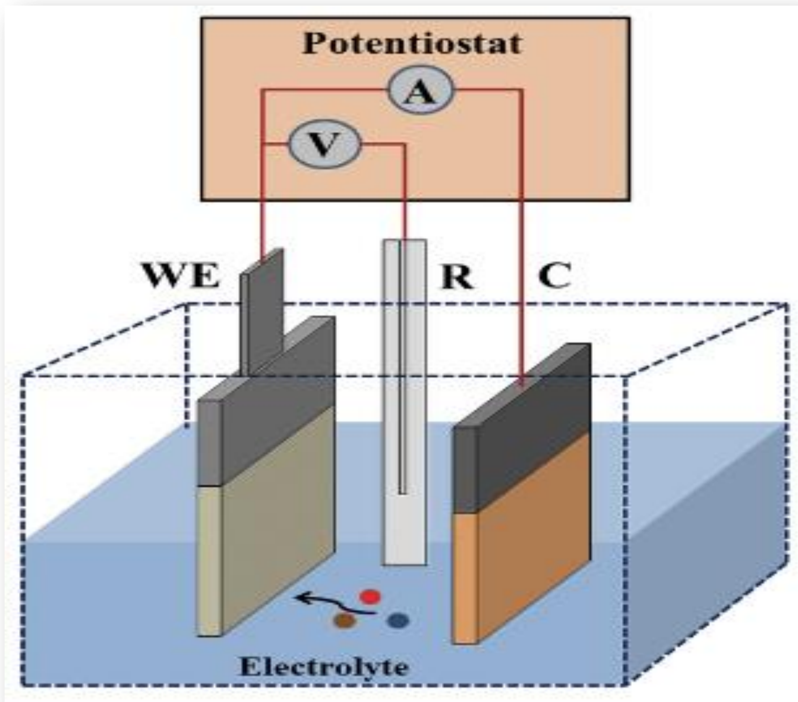
Electrochemical cell

- **R:** reference electrode **(SCE)**
- **C:** counter electrode **(Pt)**
- **WE:** working electrode **(ITO)**

Electrolyte

- Tin chloride: $SnCl_2$
- Sodium thiosulfate: $Na_2S_2O_3$
- Triethanolamine: **TEA**

Electrochemical deposition technique

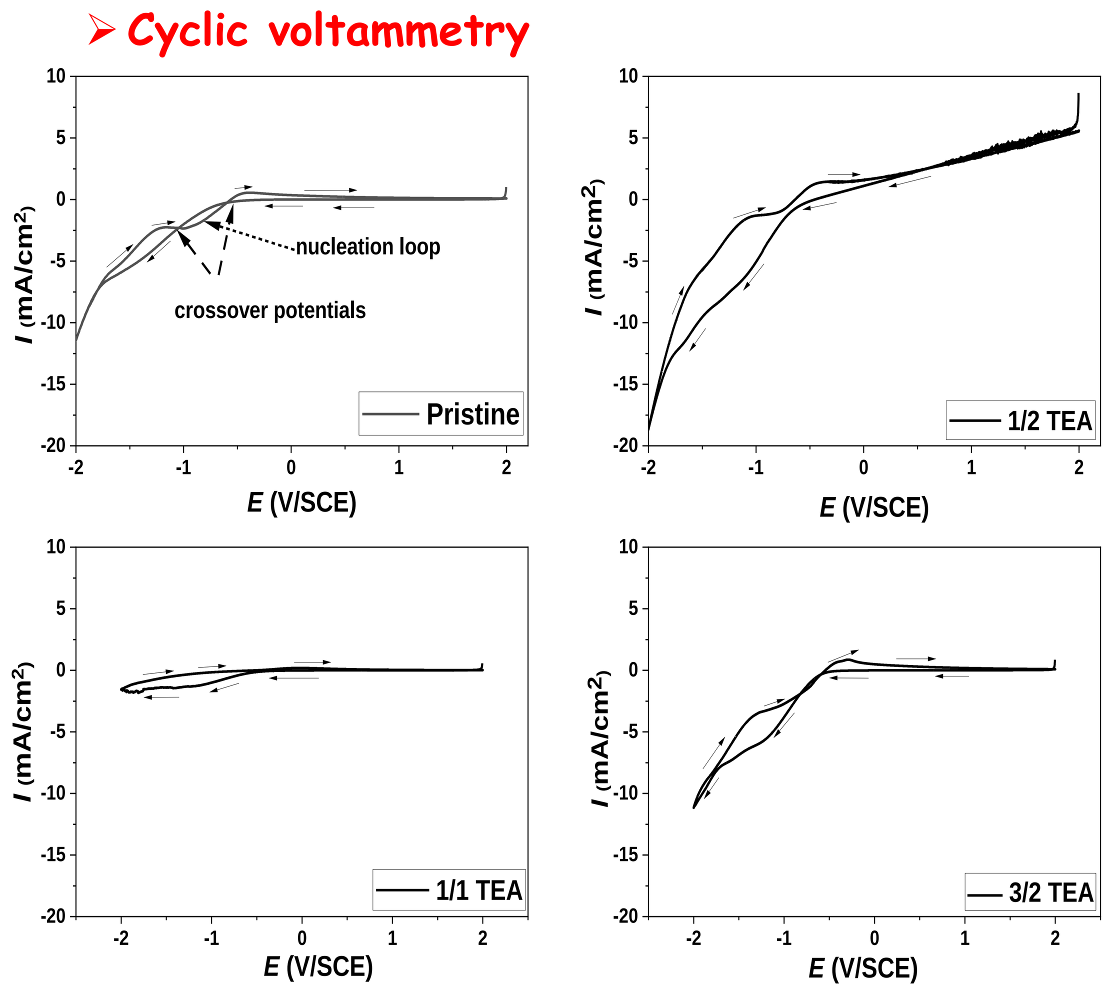


4 samples with different concentration ratios [Sn:TEA]

[1:0] [1:$\frac{1}{2}$] [1:1] [1:$\frac{1}{2}$]

RESULTS AND DISCUSSION

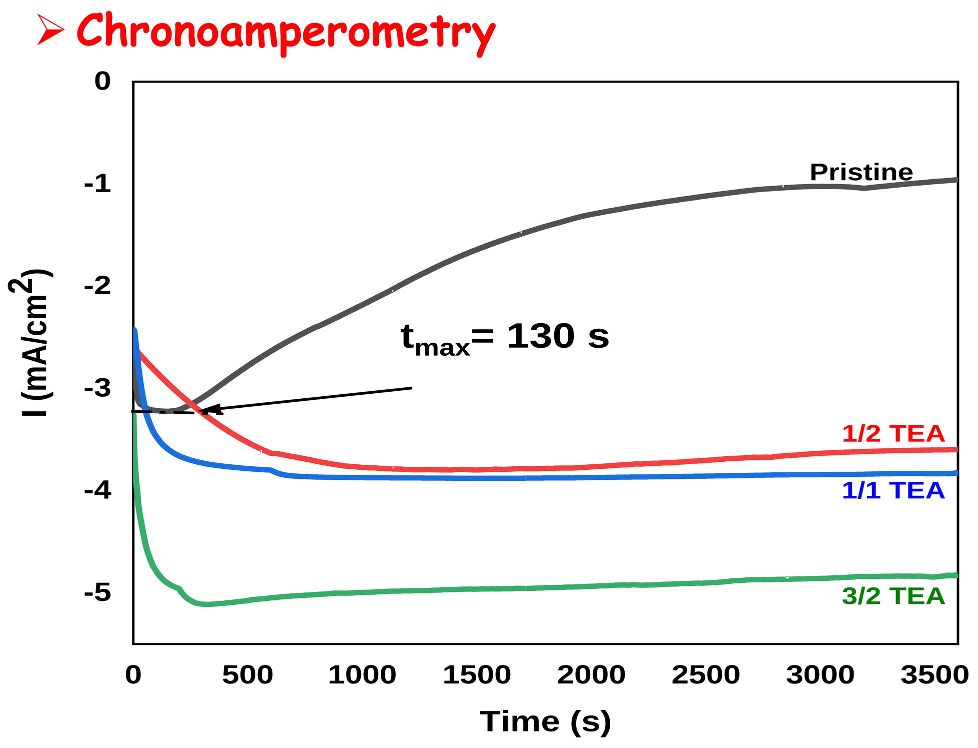
➢ Cyclic voltammetry



	Pristine	1/2 TEA	1/1 TEA	3/2 TEA
α_c	0.126	0.148	**0.089**	0.103
D(cm²/s)	2.63 10^{-7}	1.09 10^{-6}	**2.57 10^{-7}**	8.99 10^{-7}

The lowest α_c and *D* values were noted for the 1/1 TEA sample, confirming the effect of the complexation reaction to slow down the Sn electrodeposition

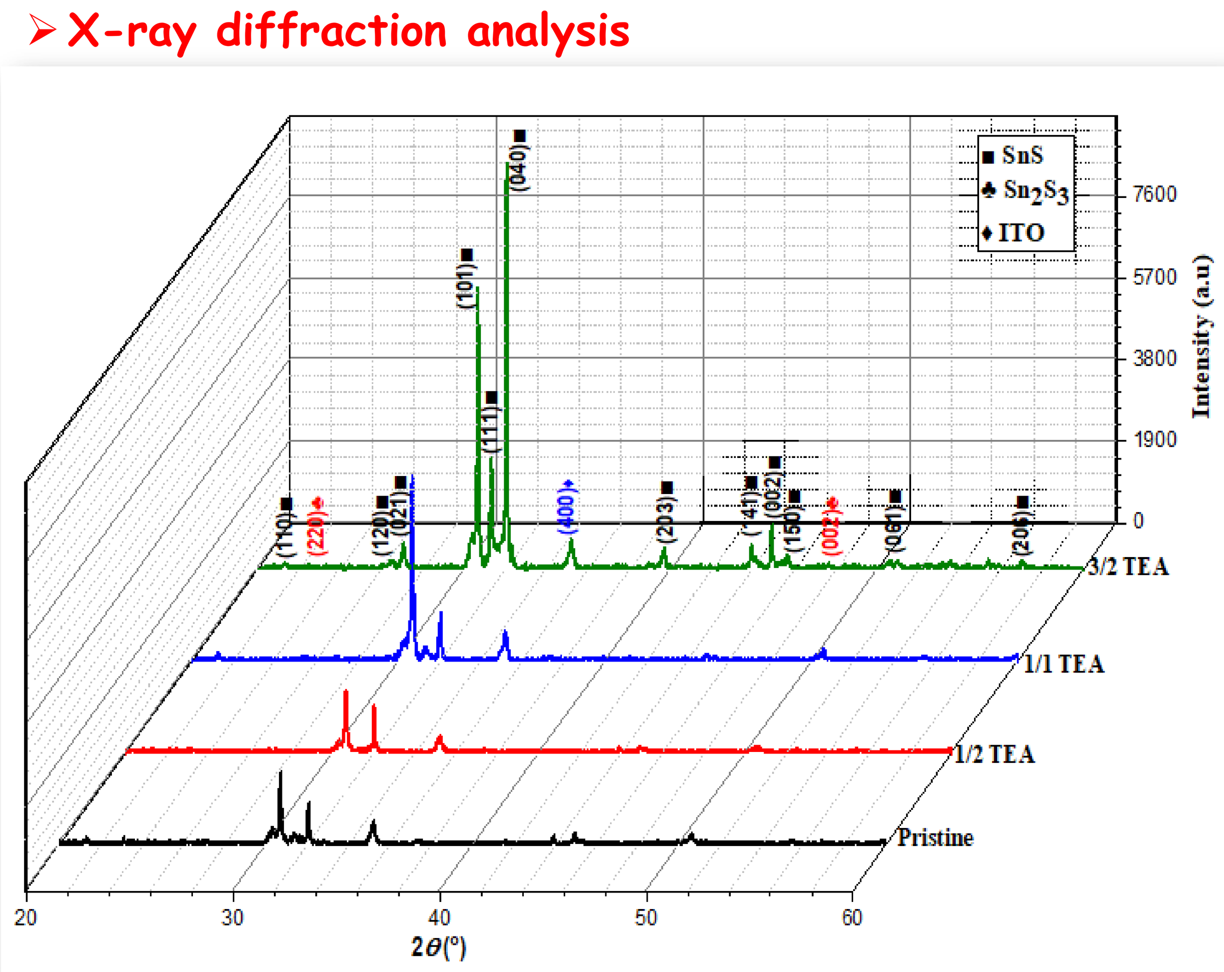
➢ Chronoamperometry



	Pristine	1/2 TEA	1/1 TEA	3/2 TEA
K_c	0.76	0.89	**0.69**	1.03

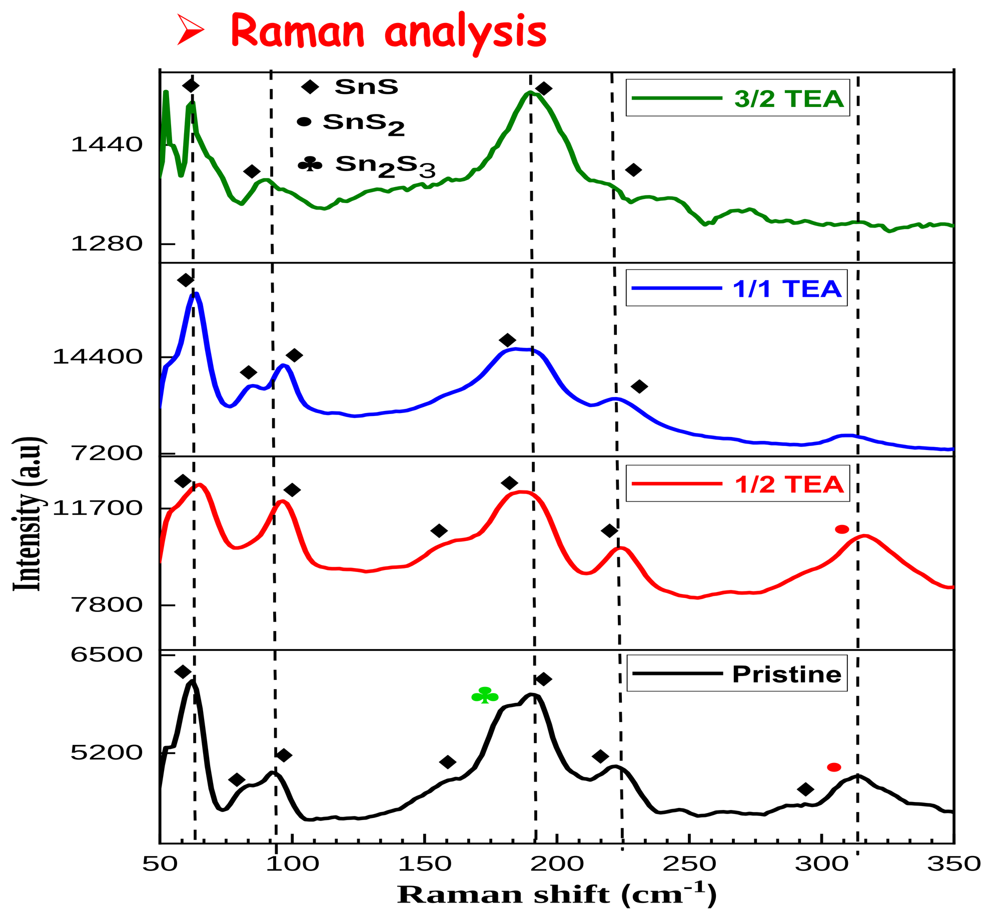
TEA affects the kinetic parameters (I_{max} . T_{max})
Adding TEA with high concentration slows the reduction reaction rate K_c

➢ X-ray diffraction analysis



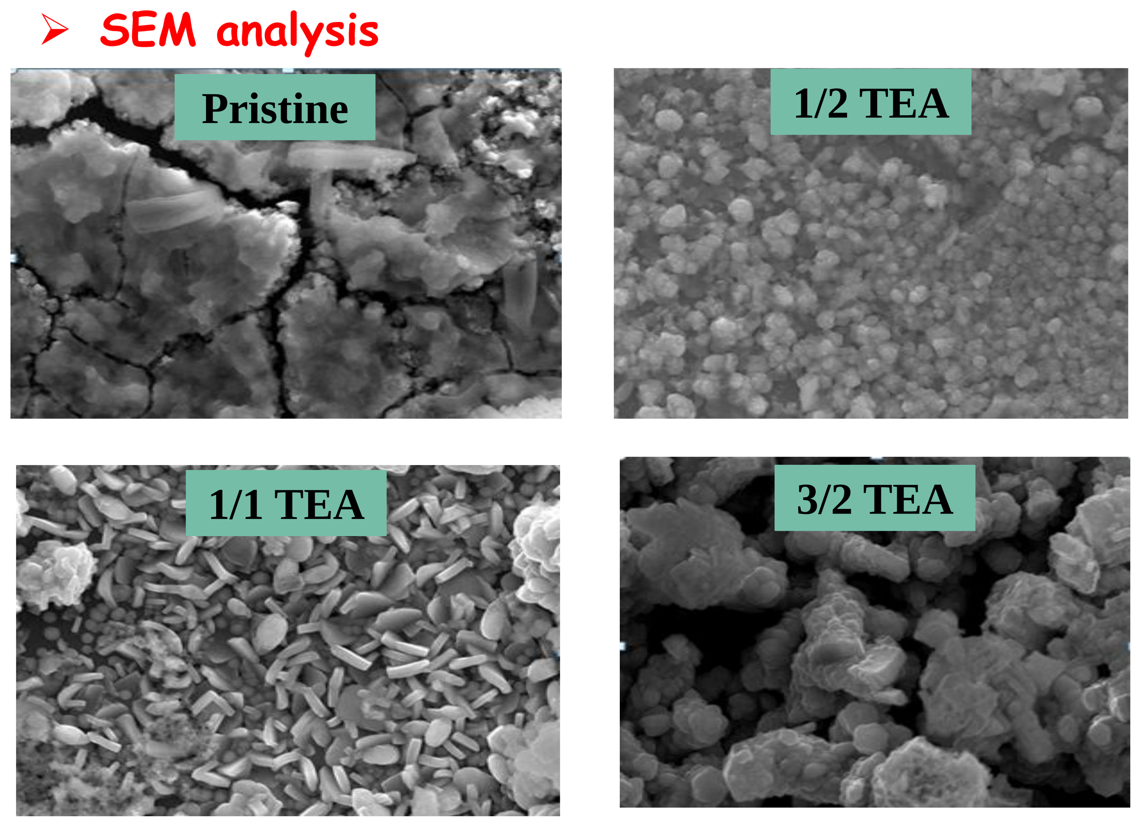
TEA has no significant effect on lattice parameters.
However, it decreases the crystallites size.
The (040) direction is unfavorable for SnS films since it limits the charge transport.

➢ Raman analysis



Secondary phases disappeared using higher concentration of TEA

➢ SEM analysis



TEA improves the compactness and film's morphology up to 1/1

➢ EDX analysis

	Pristine	1/2 TEA	1/1 TEA	3/2 TEA
Sn/S	1.49	1.40	**1.08**	0.84

TEA chelating agent reduces the deposition rate of tin ions
Stoichiometric film was deposited using 1/1 TEA

➢ UV-visible analysis

Sample	Pristine	1/2 TEA	1/1 TEA	3/2 TEA
Band gap energy (eV)	1.26	1.32	**1.39**	1.15
Crystallites size (nm)	71.54	64.30	**58.49**	96
Microstrain ε $x10^{-3}$	1.61	2.01	**2.01**	1.21

The blue shift could be attributed to the quantization effect or to the presence of microstrains in the films

CONCLUSION

In this work, the one-step chronoamperometric deposition at the potential -1 V vs SCE is used for the potentiostatic electrodeposition of tin sulfide in a mixture of $SnCl_2$ and $Na_2S_2O_3$ aqueous solutions. The effect of triethanolamine chelating agent on various properties of the electrodeposited SnS thin films was investigated. The optimum properties and the desired stoichiometry were achieved using the concentration ratio [Sn:TEA] = [1:1].