Electrochemically synthesized microcrystalline tin sulphide thin films: high dielectric stability with lesser relaxation time and efficient photochemical and photoelectrochemical properties

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Electronic Supplementary Information – I

Deposition Chemistry (Section 3.1)

When $SnSO_4$ is dissolved in water at low pH (c.a. 2.5), it dissociates as follows:

$$SnSO_4 \rightarrow Sn^{2+} + SO_4^{2-} \text{ ..... } (i)$$

Again, $Na_2S_2O_3$ dissociates in the aqueous medium to produce $S_2O_3^{2-}$ ions, which act as the source of sulphur for the deposition of tin sulphide.

$$Na_2S_2O_3 \rightarrow 2\,Na^{+} + S_2O_3^{2-} \text{..... } (ii)$$

For cathodic deposition:

$$2Sn^{2+} + 4e^{-} \rightarrow 2Sn^{0} \qquad E^0 = -\,0.1375\text{V} \text{ …… } (iii)$$

$$S_2O_3^{2-} + 6H^{+} + 4e^{-} \rightarrow 2S^0 + 3H_2O \qquad E^0 = +\,0.60\text{ V} \text{…….. } (iv)$$

Overall cathodic reaction may be cited as:

$$2Sn^{2+} + S_2O_3^{2-} + 6H^{+} + 8e^{-} \rightarrow 2SnS + 3H_2O \text{…… } (v)$$

Here, the formation of SnS film follows the conventional cathodic reduction pathways, where the Sn^{2+} and $S_2O_3^{2-}$ ions are reduced simultaneously on the cathode surface by taking up electrons to form the desired film. For stoichiometric SnS deposition, the overall cathodic reaction is an eight electron transfer process.

According to the Nernst equation, for the systems iii & iv:

$E_{(Sn^{2+}/Sn^0)} = E^0_{(Sn^{2+}/Sn^0)} + \left(\frac{RT}{2F}\right) \ln(a_{Sn2+})$ …… *(vi)*

$E_{(S2O3^{2-}/S^0)} = E^0_{(S2O3^{2-}/S^0)} + \left(\frac{RT}{4F}\right) \ln(a_{S2O3^{2-}}) + \left(\frac{3RT}{2F}\right) \ln(a_{H^+})$ …… *(vii)*

"E" and "a" denote standard electrochemical potential and the activities of the relevant ions of the bulk systems respectively , R is the universal gas constant, T is the absolute temperature, F is the Faradays constant.

Therefore, equation (v) reduces to,

$E_{(S2O3^{2-}/S^0)} = E^0_{(S2O3^{2-}/S^0)} - \left(\frac{3RT}{2F}\right) pH + \left(\frac{RT}{4F}\right) \ln(a_{S2O3^{2-}})$ …… *(viii)*

The above eqation signifies that pH and temperature would play a vital role for the electrodeposition of SnS thin film on TCO glass substrate.

Standard electrochemical potential (E_{cell}^0) will also be affected i.e. Formal potential of the above system at an optimum pH 2.5 and temperature will be:

$E_{(S2O3^{2-}/S^0)} = (0.60 - 0.0385 \times 2.5)V + \left(\frac{RT}{4F}\right) \ln(a_{S2O3^{2-}})$

$E_{(S2O3^{2-}/S^0)} = 0.5037V + \left(\frac{RT}{4F}\right) \ln(a_{S2O3^{2-}}) = \mathbf{E^F} + \left(\frac{RT}{4F}\right) \ln(a_{S2O3^{2-}})$ …… *(ix)*

Effective oxidising potential i.e formal potential of the thiosulphate – sulphur system now decreases to +0.5037 Volt, its reducing power also decreases.

For the overall cathodic reaction (v), applying Nernst equation at definite reaction conditions.

$E_{cell} = E^0_{cell} + \left(\frac{RT}{8F}\right) \ln (a_{Sn^{2+}})^2(a_{S2O3^{2-}})(a_{H^+})^6/(a_{Sn^0})^2(a_{S^0})^2(a_{H2O})^3$ …… *(x)*

Ionic activities of Sn^0, S^0 and H_2O are all taken as unity. Therefore the above equation reduces to

$$E_{cell} = E^0_{cell} + \left(\frac{RT}{8F}\right) \ln(a_{H^+})^6 + \left(\frac{RT}{4F}\right) \ln(a_{Sn^{2+}})(a_{S2O3^{2-}}) \ldots\ldots\ldots\ldots\ldots\ldots \textit{(xi)}$$

According to Gibb's free energy, we can easily calculate final E^0 potential, stability constant and the feasibility of the involved chemical reactions.

$\Delta G^0_f = \Delta G^0_1 + \Delta G^0_2$ or, $- nFE^0_f = - nFE^0_1 + (- nFE^0_2)$

or, $E^0_f = 1/8\{- 0.275 + 2.4\} = 0.2656V = E^0_{cell}$

$$E_{cell} = \{0.2656 - 0.01926pH\}V + \left(\frac{RT}{4F}\right) \ln(a_{Sn^{2+}})(a_{S2O3^{2-}})$$

$$\text{or, } E_{cell} = \{0.2656 - 0.01926 \times 2.5\}V + \left(\frac{RT}{4F}\right) \ln(a_{Sn^{2+}})(a_{S2O3^{2-}})$$

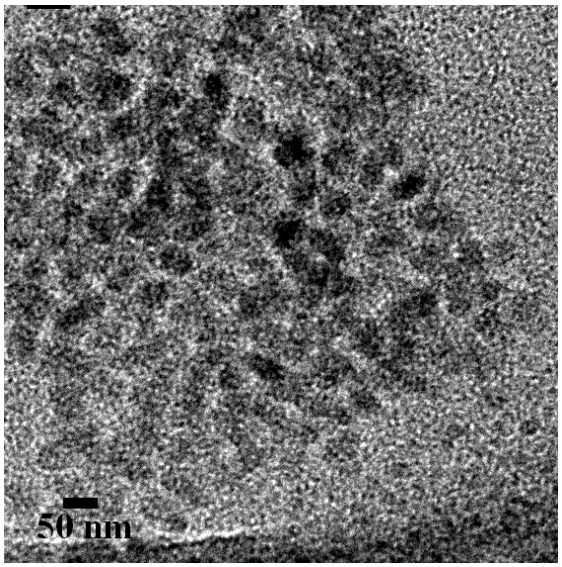
$$\text{or, } E_{cell} = 0.2175V + \left(\frac{RT}{4F}\right) \ln(a_{Sn^{2+}})(a_{S2O3^{2-}}) = \mathbf{E^F} + \left(\frac{RT}{4F}\right) \ln(a_{Sn^{2+}})(a_{S2O3^{2-}}) \ldots\ldots\ldots\ldots \textit{(xii)}$$

From the thermodynamic consideration, the overall free energy $\Delta G_{(cat)}$ for the formation of SnS by the cathodic reactions may be given as:

$\Delta G_{(cat)} = [\Delta G^{\circ}_{(eq.\ iii)} + \Delta G^{\circ}_{(eq.\ iv)}] = [-nFE^0_{(eq.\ i)} + (-nFE^0_{(eq.\ ii)}] = 96500 \times [-4 \times (-0.1375) + (-4 \times 0.60)]$ $= -17.8525 \times 10^4$ J. The high negative value of $\Delta G_{(cat)}$ indicates that the overall cathodic reaction leading to the formation of SnS is highly feasible.

At equilibrium condition, we know, $\Delta G_{(cat)} = -nRTlnK_{cat}$; where, K_{cat} is the equilibrium constant for the cathodic deposition, "R" is the gas constant in Joules and "n" is the number of electrons involved. Therefore, we have, $lnK_{cat} = 9.00705$. Such high value of equilibrium constant (K) is associated with the high stability of the cathodically deposited SnS film.

Electronic Supplementary Information – II



The low resolution transmission electron microscopy (TEM) image of the deposited SnS indicates crystallite size of about 50 nm. A small amount of the deposited SnS film was scrapped off and dissolved in ethanol followed by sonication for 1 hour. One drop of the sonicated sample was placed onto a copper grid for the TEM analysis. The black spots in the image are indicating the SnS crystallites.

Electronic Supplementary Information – III

The total free energy of a system containing nanoparticles (NPs) is given by:

$$G_{total} = \mu_{NP\times}N_{NP} + \gamma\times S$$

Where, μ_{NP} is the chemical potential of the nanoparticles and N_{NP} is the total number of nanoparticles. γ is the interfacial tension (or the interfacial energy per unit area) and S is the surface area. Thus $\gamma\times S$ denotes the total surface energy of the system. We know; NPs have higher surface-to-volume ratio, making the total surface energy of the system significantly high. As every system has a tendency to lower down the free energy spontaneously, this $\gamma\times S$ part of free energy for a system consisting of nanoparticles also has a tendency to get lowered down by

means of forming larger grains (which reduces the value of S) from smaller crystallites by agglomeration. For this reason, from FESEM image analysis we see the grains to have somewhat larger size than the crystals.

Electronic Supplementary Information – IV

Goswami-Goswami model (Section 3.6.3.2)

$$\tan\delta = [\omega(1+\omega^2R^2C_p^2)\times\{R+r(1+\omega^2R^2C_p^2)\}]/[(\omega^2R^2C_p)\times(1+\omega^2R^2C_p^2)]$$

$$\text{or, } \tan\delta = (1/\omega RC_p)+(r/\omega R^2C_p)+\omega RC_p$$

$$\text{or, } \tan\delta = D(1+r/R)+\omega RC_p \ldots\ldots\ldots\ldots\ldots\ldots \textit{(a)}$$

Where, $D = 1/\omega RC_p$, angle frequency $\omega = 2\pi f$, R is the dielectric resistance and r being the resistance due to the electrodes and connecting wires. Eq. (a) gives the interpretation of tanδ in terms of the parameters ω, R, C_p and r. The minimum dielectric loss, which will occur at a frequency (ω_{min}), may be expressed as:

$$\omega_{min} = (1/rRC_p^2)^{1/2} \ldots\ldots\ldots\ldots\ldots\ldots \textit{(b)} \quad [\text{As } R >> r]$$

If $\omega R^2C_p >> r$ or $r/R << 1$, then Equation (b) reduces to:

$$\tan\delta = (1/\omega rC_p) + \omega rC_p = (D + \omega rC_p) \qquad \ldots\ldots\ldots\ldots\ldots\ldots \textit{(c)}$$

In case of smaller ω, $1/\omega RC_p >> \omega rC_p$, thus the second term of Equation (c) becomes negligibly small, giving an equation of the first term as:

$$\tan\delta = (1/\omega rC_p) = D \ldots\ldots\ldots\ldots\ldots\ldots \textit{(d)}$$

It is also possible that ω is considerably large, so that $1/\omega RC_p << \omega rC_p$, and elimination of the first term of equation (d) results in another expression,

$$\tan\delta = \omega rC_p \ldots\ldots\ldots\ldots\ldots\ldots \textit{(e)}$$

The treatments given in Eq. (d) & (e) can be correlated to the curves plotted in Figure 9, where the behavior of tanδ in the lower frequency region (2 – 60 kHz) can be explained by Eq. (d),

whereas, the behavior of the same in the higher frequency region (60 – 1000 kHz) can be explained by Eq. (e).

Electronic Supplementary Information – V

Impedance Measurement (Section 3.6.4)

The complex impedance Z* and dielectric constant ε* of this circuit can be written as,

$$Z^* = Z' - iZ'' \quad \text{(a)}$$

$$\text{and } \varepsilon^* = \varepsilon' - i\varepsilon'' \quad \text{(b)}$$

Where, ε′ and ε″ are the real and imaginary parts of the complex dielectric constant.

The dissipation factor or loss tangent, tanδ, is often used to characterize the dielectric loss of a material as:

$$D = \tan\delta = Z'' / Z' = \varepsilon''/ \varepsilon' \quad \text{(c)}$$

where ε′ is given by C/C_o, in which, C is the measured capacitance and C_o is the geometrical capacitance. C_o of a film is related to the vacuum permittivity ε_0, area A and thickness d as, $C_o = \varepsilon_0 A/d$.

Z′ and Z″ may be expressed as:

$$Z' = R_b + [R_g/(1+(\omega R_g C_g)^2)]+[R_{gb}/(1+(\omega R_{gb} C_{gb})^2)]+[R_e/(1+(\omega R_e C_e)^2)] \quad \text{(d)}$$

$$Z'' = [(\omega R^2_g C_g)/(1+(\omega R_g C_g)^2)]+[(\omega R^2_{gb} C_{gb})/\{1+(\omega R_{gb} C_{gb})^2\}]+[(\omega R^2_e C_e)/(1+(\omega R_e C_e)^2)] \quad \text{(e)}$$

Electronic Supplementary Information – VI

Hall Measurements

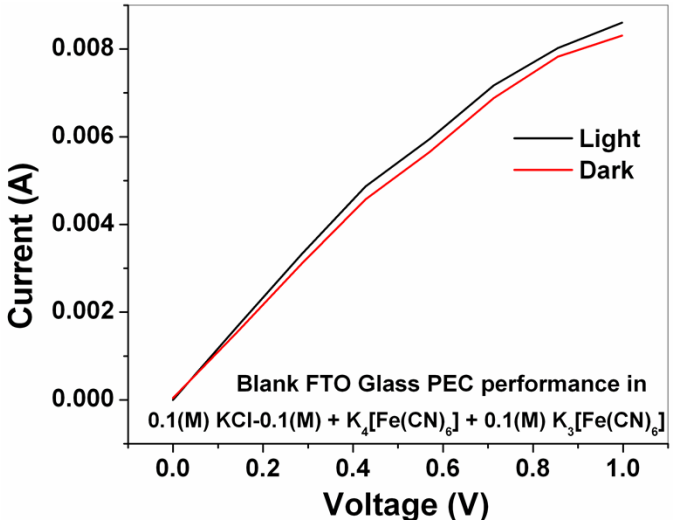
The Hall measurement of deposited SnS film was carried out under a fixed magnetic field of 0.55 Tesla to investigate the type of carrier, concentration of carrier and their mobility. The positive value of Hall coefficient indicates the p-type conduction of the deposited SnS films. Since, SnS is a p-type semiconductor, the majority carriers i.e. holes arise due to the metal (Sn)

deficiency in the film matrix. The carrier concentration was found to be in the order of 10^{11} cm^{-3} and the hall mobility was 10^2 $cm^2V^{-1}s^{-1}$. Hall measurements revealed that the SnS film deposited by this technique has p-type conductivity with moderately low carrier concentrations, which may arise from slight deviations from stoichiometry leading to native point defects such as Sn^{+2} vacancies and enriching the dielectrically stability as well as low dielectric loss. A low carrier concentration facilitates charge distribution at the p-n junction in solar cells since the depletion width, covered by built in electric field, extends through most of the absorber layer. This in turn, makes the material a good candidate for photocatalysis and photoelectrochemical performances. As the deposited SnS films were thicker (~2.5 μm), it is expected that the bottom conducting layer will have lesser influence on the properties of the film, which is also reflected in the obtained values of carrier concentration and mobility. Our observed carrier concentration for SnS film was 10^{11} cm^{-3}, which is significantly lower than the standard carrier concentration of FTO, i.e. 10^{20} cm^{-3}.

Table:

Magnetic field	Hall coefficient (cm^3 C^{-1})	Hall Mobility (cm^2 $V^{-1}s^{-1}$)	Carrier Conc. (cm^{-3})	Magneto Resistance (Ω)	Resistivity (Ω-cm)
0.55 Tesla	1.042×10^7	2.152×10^2	5.989×10^{11}	2.782×10^9	4.842×10^4

Electronic Supplementary Information - VII



Dark and light I – V characteristics of blank FTO glass in presence of the redox couple 0.1(M) $K_4[Fe(CN)_6]$ and 0.1(M) $K_3[Fe(CN)_6]$ in 0.1(M) KCl. The curve indicates basically no photoelectrochemical performance by the FTO glass.