

# Electrodeposition of indium phosphide from an ionic liquid for photovoltaics

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## 1. Introduction

Over the last two decades, low-temperature ionic liquids have received great attention due to their wide applications in different research fields and applications such as electrodeposition, organic synthesis and chemical separations [1-6]. These ionic liquids generally demonstrate wide electrochemical window, where metals with very negative standard potentials can be deposited [7-13]. In addition, they exhibit good chemical and thermal stability, along with a good electrical conductivity. These low melting temperature (< 100°C) ionic liquids are easier to work with compared to molten salts. Moreover, ionic liquids are nonvolatile and ideal replacement for traditional organic solvents that are volatile and flammable. However, the majority of the ionic liquids exhibit high sensibility to water or degradation by oxygen and needs a complex synthesis. It has recently been found that the principle of creating an ionic fluid by complexing a halide salt can be applied to mixtures of quaternary ammonium salts with an amide, carboxylic acid or alcohol moiety [14-19]. These mixtures are called Deep Eutectic Solvent (DES). They are also known as third generation ionic liquids. Such eutectic systems are easy to manipulate, nontoxic and biodegradable compared to room temperature ionic liquids. Furthermore, they demonstrate chemical inertness towards water and the production involves low costs and environmental risks. The present study reports the suitability of one of these DES mediums (1:2 choline chloride/urea) to synthesize InP. InP is a promising binary semiconductor having a direct band gap of 1.35eV for PV application [20, 21]. Polycrystalline InP thin film is used for solar cell for optimum use of the material. However, existing thin film deposition methods (PVD, CVD, MOCVD etc.) are expensive [22-24]. In

order to minimize cost, this work was aimed to investigate the possibility of producing InP electrochemically.

## 2. Experimental

Choline chloride (ChCl) (Sigma-Aldrich) and Urea (U) (Sigma-Aldrich) were used as received. The Deep Eutectic Solvent (DES) was formed by stirring ChCl and U together in a 1:2 molar ratio at 80°C until a homogeneous, colourless liquid was formed. Initially efforts were focused on direct electrodeposition of InP from DES. Indium sulfate ( $\text{In}_2(\text{SO}_4)_3$ ) (Sigma-Aldrich) was used as In precursor and P precursors included ammonium hexafluorophosphate ( $\text{NH}_4\text{PF}_6$ ) (Sigma-Aldrich), phosphorous acid ( $\text{H}_3\text{PO}_3$ ) (Sigma-Aldrich) and sodium hypophosphite ( $\text{NaPO}_2\text{H}_2$ ) (Sigma-Aldrich). Deposition condition ranged in current density from  $\text{mA}/\text{cm}^2$  to tens of  $\text{mA}/\text{cm}^2$ , in precursor concentration from millimolar to molar (including different combinations of phosphorus precursors, and different ratios between phosphorus precursors and indium precursors). Electrodeposition experiments were conducted on a standard single compartment, two-electrode system, using Molybdenum (Mo) foil as substrate and Titanium (Ti) mesh as anode. Ti mesh was ultrasonically cleaned in acetone, then in distilled water for 10 minutes and dried under nitrogen gas prior to use. Mo foil was first ultrasonically cleaned in acetone for 10 minutes, then pretreated for 20 minutes in 32% HCl, ultrasonically cleaned in water for 10 minutes and finally dried under nitrogen gas. The deposits were always washed with distilled water and dried under nitrogen. Work temperature was kept constant at 80°C to lower the viscosity and maintain high conductivity of the solvent. The crystallinity of the deposits was analysed by X-ray diffraction Philips PW 1830, in conventional

Bragg–Brentano configuration with Cu K $\alpha$  radiation of 1.5418 Å wavelength. The surface morphology of the deposits was examined by scanning electron microscopy (SEM, Zeiss EVO50), and the chemical composition was determined by energy dispersive spectroscopy (EDS).

An alternative method for synthesis of InP was also investigated. That was electrodeposition of pure In from DES and subsequent phosphorization in phosphine (PH<sub>3</sub>) gas. 50 mM In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution was employed for electrodeposition of pure In. Several samples were made at different current densities. The sample exhibited best morphology was selected for phosphorization. The sample was capped with 50 to 100nm of evaporated SiO<sub>2</sub> which was porous and allowed the diffusion of P. Temperature was maintained at 750° C and 97 torr. of 10% PH<sub>3</sub> in H<sub>2</sub> was used for 23 minutes. The whole process was done in LPCVD chamber. After phosphorization, XRD analysis was performed. Then Photoluminescence (PL) and Time-Resolved Photoluminescence (TRPL) properties were examined. PL was performed using a HeNe laser at a wavelength of 632.8nm with a 5µm spot size. The TRPL

excitation source was a tunable Mira 900-F Ti-sapphire laser set to 800nm, different incident light power were used, ranging from 150mW to 400mW. The time between pulses was ~12ns.

### 3. Results

XRD spectrum and EDX analyses of the deposits obtained from indium sulphate In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and phosphorous acid (H<sub>3</sub>PO<sub>3</sub>) solutions showed the presence of In only in all deposition conditions. Same results were obtained from indium sulphate In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and sodium hypophosphite (NaPO<sub>2</sub>H<sub>2</sub>) solutions. On the other hand, XRD patterns revealed presence of In only in all conditions while EDX analyses demonstrated presence of very small amount of P along with In for some deposits obtained from indium sulphate In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and ammonium hexafluorophosphate (NH<sub>4</sub>PF<sub>6</sub>) solutions. Fig. 1. shows XRD pattern and EDX spectrum of one of those deposits.

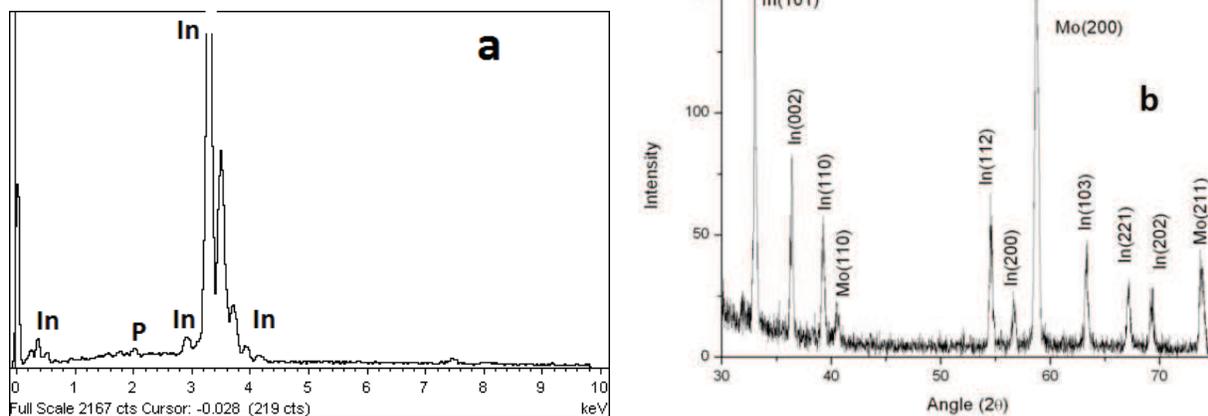


Fig. 1. (a) EDX spectrum and (b) XRD pattern of the deposit obtained from 10 mM In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution containing 1 M NH<sub>4</sub>PF<sub>6</sub> at current density 10 mA/cm<sup>2</sup>.

Atomic percentage of In and P is given in Table 1. Very small amount of elemental P was deposited. As the current density increases, the percentage of P decreases. Besides, higher concentration of P precursor (1.2M NH<sub>4</sub>PF<sub>6</sub>) doesn't exhibit any significant increase of P in the deposit.

Solutions containing very high amount of P precursor (NH<sub>4</sub>PF<sub>6</sub>>1.2M), became saturated and there was no deposition. On the contrary, when the concentration of (In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) was lower than 10 mM, there was no deposition in all conditions.

Table 1 Atomic percentage of elemental In and P obtained from solutions (10 mM In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution containing 1 M and 1.2 M NH<sub>4</sub>PF<sub>6</sub> respectively) at different current densities.

10 mM In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 1 M NH <sub>4</sub> PF <sub>6</sub>		10 mM In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 1.2 M NH <sub>4</sub> PF <sub>6</sub>		Current density(mA/cm <sup>2</sup> )
In%	P%	In%	P%	
98.7	1.3	98.6	1.4	5
98.9	1.1	98.9	1.1	10
99.1	0.9	99.2	0.8	20
99.7	0.3	99.5	0.5	50

Another set of experiment is related to the electrodeposition of high purity In for subsequent phosphorization in  $\text{PH}_3$  gas which is described in the experimental section. EDX analysis of the electrodeposits demonstrates that they are very pure deposits of In and there are no contaminants like Cl, O trapped in the deposits from deep eutectic solvent (Fig. 2).

The morphology of the pure In deposits was investigated with SEM. At lower current density (Fig. 3(a) and (b)), the micrograph shows polygonal shaped grains having an average grain size of  $6\ \mu\text{m}$ . At higher current density (Fig. 3(c)) the deposit exhibits nodular morphology with rounded grains; the average grain size is  $2\ \mu\text{m}$  with increasing coverage of the substrate. Grains become fine at higher current density which reflects an increase in the indium nuclei density with increasing deposition current density.

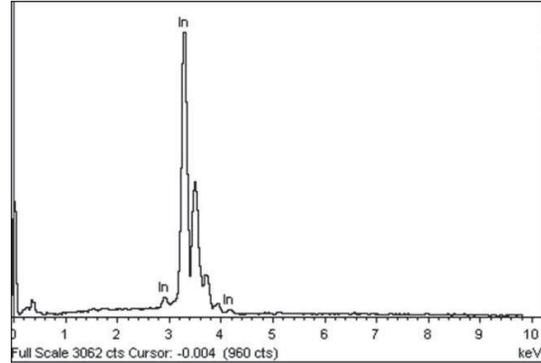


Fig. 2. EDX spectrum of In deposit obtained from 50 mM  $\text{In}_2(\text{SO}_4)_3$  solution at current density  $10\ \text{mA}/\text{cm}^2$ .

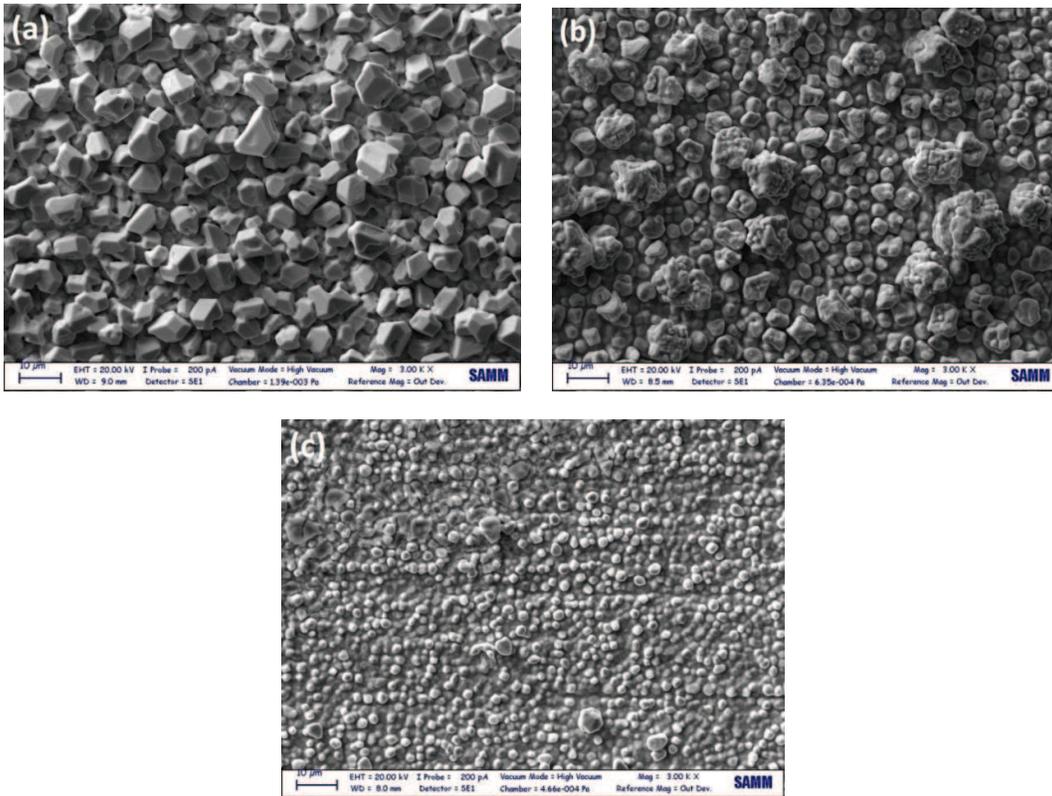


Fig. 3. SEM micrographs of the In deposits obtained from 50 mM  $\text{In}_2(\text{SO}_4)_3$  solution on molybdenum at current density (a)  $10\ \text{mA}/\text{cm}^2$ , (b)  $30\ \text{mA}/\text{cm}^2$ , (c)  $50\ \text{mA}/\text{cm}^2$ .

The sample which showed better morphology (deposited at current density  $50\ \text{mA}/\text{cm}^2$ ) was selected for

phosphorization. XRD pattern of the phosphorized sample confirms formation of InP (Fig. 4.).

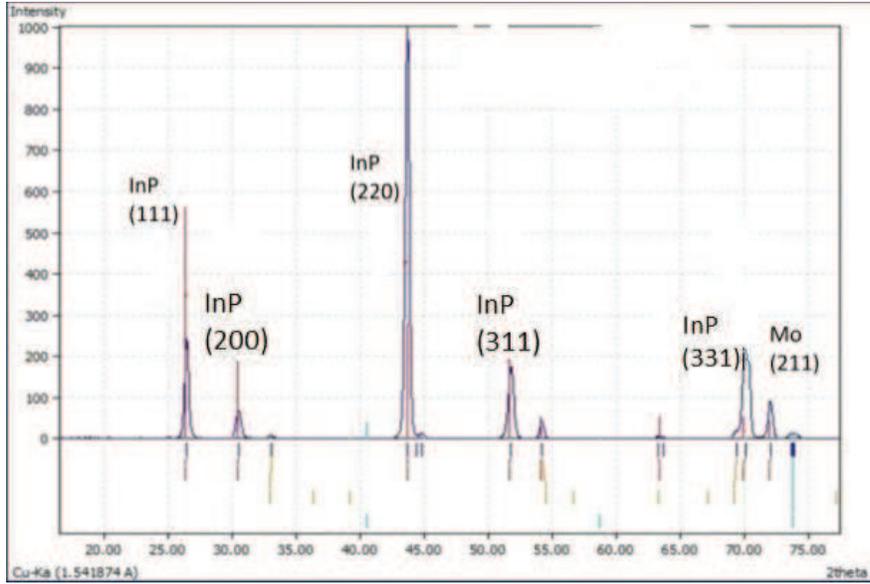


Fig. 4. XRD pattern of the phosphorized sample.

Fig. 5. shows PL of the phosphorized sample which is compared with another sample where In was deposited by vaporization and subsequently phosphorized. It is evident from the Fig. 5. that two graphs have the same behavior for their PL which is different from behavior of a single crystal of InP.

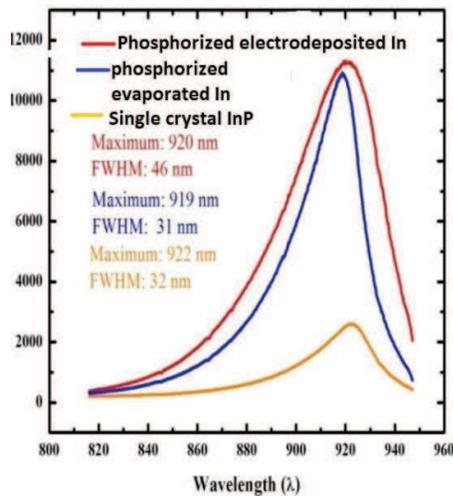


Fig. 5. PL of three InP samples which are prepared with evaporated indium (blue color trend), electrodeposited Indium (red color trend) and single crystal InP as a reference.

Another optical characterization experiment TRPL of the two samples (evaporated In and electrodeposited In) shows that exciton lifetime of evaporated In sample is 2.2 ns and of electrodeposited In is 2.3 ns (Fig. 6.).

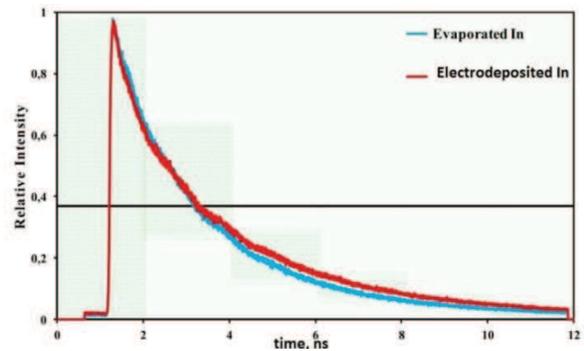


Fig. 6. TRPL of two InP samples which are prepared with evaporated indium (blue color trend), electrodeposited Indium (red color trend).

This result indicates that very pure crystalline In is obtained from the DES.

#### 4. Conclusions

Initially efforts were focused on direct electrodeposition of InP from DES. From EDX analyses on some samples presence of In and very small amount of P was observed in the deposited layer, while XRD spectra demonstrated presence of In only. Another set of experiment was related to the electrodeposition of high purity indium in DES for subsequent phosphorization in  $\text{PH}_3$  gas through which InP was synthesized. Pure crystalline In was obtained from the DES medium. PL and TRPL experiments revealed promising results for this film's potential application as a solar cell.

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