Republic of Iraq Ministry of Higher Education And Scientific Research Al-Nahrain University College of Science Department of Chemistry



Indium, Tin and Antimony electro deposition from ionic liquid on copper substrate

A Thesis

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Summary

Room temperature ionic liquids gained massive growth in recent years for their distinguished characterization like non-volatile and designed media for variable chemical and industrial application. In addition, indium metal has applications in electronic and optoelectronic devices, tin and antimony metals have good corrosion resistance and optical properties respectively. Therefore ionic liquids of the type ammonium alum: urea (1:5 mole ratio) was used as a medium to investigate the behavior and possibility of obtaining pure metal and mixture of metals from anhydrous indium chloride, tin chloride dihydrate and anhydrous antimony chloride solutions or their mixture. This investigation was carried out with the assistance of XRD, SEM, EDAX, Cyclovoltammetric, potentiostatic, AFM to determine and characterize metal reactivity and deposition metal(s) particles.

Anhydrous indium chloride was found to be completely soluble up to 0.3 M in ionic liquid while suspended solutions of both tin chloride dihydrate and anhydrous antimony chloride were obtained at 0.3 M concentrations. The reduction of metal cations were in the sequence tin antimony and indium respectively showing a potential of -0.69 V, -0.8 V and -1.00 V respectively.

All metals either alone or their mixture gave a nanoparticles deposition layer on copper substrate.

A very smooth surface with maximum (Ra) of 34.6 nm obtained for indium and antimony after one hour from a potentiostatic deposition at -1.6 V.

Meanwhile, potentiostatic deposition on copper substrate for indium, tin, antimony or their mixture of (indium and tin) and (indium and antimony) all showed an increase of deposition quantities with time. The morphologies were also affected by deposition time and particles shapes were different from the initial deposited indium metal or its mixture with either tin or antimony at one hour from those at three hours.

Bulk deposition of indium was obtained at -1.00 V while tin was obtained at -0.7 V and antimony at -0.8 V.

However, only a mixture of indium with tin or indium with antimony were obtained with controlled deposited quantities by controlling the deposition potential. Thus, the deposition of indium and tin showed 80 wt.% of deposition related to tin and 20 wt.% to indium from a potentiostatic experiment at -0.8 V while at -1.1 V tin decreased to 59 wt.% and indium increased to 41 wt.% in contrast the mixture of indium and antimony showed 100 wt.% indium from potentiostatic experiment at -0.8 V while 79.5 wt.% indium and 20.5 wt.% antimony were obtained at -1.6 V.

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Abbreviation

Abbreviations	Name	
ACS	American Chemical Society	
[MMC ₃ Im] [Tf ₂ N]	1-2-dimethyl-3-propyl imidazolium bis(trifluorosulfonyl) imide	
$[MMC_{3}Im] [Tf_{2}N]$	1-2-dimethyl-3-propyl imidazolium bis(trifluorosulfonyl) imide	
[Py1,4]TFSA	1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) amide	
[BMP]Tf ₂ N	1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide	
[C ₄ MIm][BF ₄]	1-butyl-3-methy imidazolium tetrafluoro borate	
[C4MIm][BF4]	1-butyl-3-methy imidazolium tetrafluoro borate	
[BMIM]PF ₆	1-butyl-3-methylimidazolium hexafluorophosphate	
[BMIM]BF ₆	1-butyl-3-methylimidazolium hexafluorophosphate	
[BMIM]BF ₄	1-butyl-3-methylimidazolium tetrafluoroborate	
[C ₂ MIm][BF ₄]	1-ethyl-3-methyl imidazolium tetraflouro borate	
[C ₂ MIm][BF ₄]	1-ethyl-3-methyl imidazolium tetraflouro borate	
([EMIm]BF ₄	1-ethyl-3-methyl imidazolium tetrafluoroborate	

$[C_2MIm]^+$	1-ethyl-3-methylimidazolium	
[EMIM]Cl	1-ethyl-3-methylimidazolium chloride	
[EMIM]I	1-Ethyl-3-methylimidazolium iodide	
AlCl ₃	Aluminum chloride	
ASTM	American Society for Testing And Materials	
$[C_2H_5NH_3][NO_3]$	Ammonium nitrate	
SbCl ₃	Anhydrous antimony chloride	
InCl ₃	Anhydrous indium chloride	
AFM	Atomic force microscopy	
Tf_2N	Bis(trifluoromethylsulfonyl)imide	
C ₅ H ₁₄ ClNO	Choline Chloride	
CV	Cyclic Voltammogram	
EDAX	Energy dispersive X-ray analysis	
[EtNH ₃][NO ₃]	Ethyl ammonium nitrate	
PF ₆ -	Hexaflourophosphate anion	
Al(NO) ₃ .9H ₂ O	Hydrated aluminum nitrate	
AlK(SO ₄) ₂ .XH ₂ O	Hydrated aluminum potassium sulfate	
NH4Al(SO4) ₂ .12H ₂ O	Hydrated ammonium alum sulfate	
AlNH ₄ (SO ₄) ₂ .XH ₂ O	Hydrated ammonium alum sulfate	
ΙΤΟ	Indium tin oxide	
In(OH) ₃	Indium(III) hydroxide	

In ₂ O ₃	Indium(III) oxide	
ILs	Ionic Liquids	
RTILs	Room temperature ionic liquids	
Ra	Roughness	
SEM	Scanning electron microscopy	
Ag[BF ₄]	Silver tetrafluoroborate	
RSO ₃ H	Sulphonic acid	
[R ₄ N] [OH]	Tetraalkylammonium hydroxide	
[R ₄ N] [RSO ₃]	Tetraalkylammonium sulphonates	
BF_4	Tetraflouroborate anion	
SnCl ₂ .2H ₂ O	Tin Choride dihydrate	
$(CF_3SO_2)_2N^-$	Trifluoromethanesulfonate	
$CF_3CO_2^-$	Trifluroacetate	
([TMHA]TFSA Trimethyl-n-hexylammonium (trifluoromethylsulfonyl)ami		
UPD	Upper Potential Deposition	
XRD	X-Ray Diffraction	

Notations

Symbols	Name	Units
М	Molarity	M or mole/L
Ra	Roughness	nm
Wt.	weight	%
k	Conductivity	mS.cm ⁻¹
ρ	Density	g.cm ⁻³
μ	Viscosity	mPa.s



Introduction

1.1-History of Ionic liquids

The early history of ionic liquids started in 1888, when ethanol ammonium nitrate (m.p 52-55 °C) was reported by Gabriel^[1], Later in 1914 one of the earlier known room temperature ionic liquids was ethyl ammonium nitrate $[C_2H_5NH_3][NO_3]$, which had a melting point of 12 °C produced from the reaction of concentrated nitric acid with ethylamine.^[2]

In 1951, Hurly and Weirst stated that a room temperature ionic liquid could be prepared by mixing and warming 1-ethylpyridinium chloride with aluminum chloride ^[3]. In 1970s and 1980s, Osteryoung *e*t al. and Hussy *e*t al. moved broad studies on organic chloride-aluminum chloride ambient temperature ionic liquid and the first major review of room temperature ionic liquids was published. ^[4]

The ionic liquids based on aluminum chloride (AlCl₃) can be considered as the first generation of room temperature ionic liquids. The hygroscopic nature of AlCl₃ based ionic liquids has delayed the development in their use. In multiple science applications they have to be prepared and handled under inert gas atmosphere. A long these lines, the synthesis of air and water stable ionic liquids, which are considered as the second era of ionic liquids pulled in further eagerness for the utilization of ionic liquids in different fields.^[5]

In the year 1992, Wilkes and Zaworotko^[6] discovered the first air and moisture stable ionic liquids based on 1-ethyl-3-methylimidazolium $[C_2MIm]^+$ cation with either tetrafluoroborate $[BF_4]^-$ or hexaflourophosphate $[PF_6]^-$ as anions. Not like the chloroaluminate ionic liquids, these ionic liquids can be prepared and safely stored out off an inert atmosphere. Generally, these ionic liquids are water stable, however, the longtime exposure for a moisture to time may cause some changes in their physical and chemical properties^[6].

In 2006, Welton, Wasserscheid, MacFarlane Enders and Zien El Abedien^[7], entered in this field having a strong effect in offering the ionic liquids in numerous applications. Their focus was on the synthesis and characteristics of environmentally friendly ionic liquids as green solvents. They quantified and built up physicochemical characteristics for many ionic liquids with the point of giving information to start assessing the utilization of ionic liquids in a number of processes; in addition, they worked on the development of new materials from cellulose employing ionic liquids.

Wasserscheid is an active member of the ionic liquids community focused on the preparation and characterization of ionic liquids for use in the biphasic catalysis. For example, he managed to show that the use of hexaflorophosphate ionic liquids give selective biphasic oligomerization of ethylene to 1-olefins. Together with Welton; they modified important book entitled "ionic liquids in synthesis"^[8], which proffers the combination and physicochemical properties of ionic liquids in addition their utilization in catalysis, polymerization, organic and inorganic synthesis.

MacFarlane has made a new air and water stable ionic liquids to utilize such ionic liquids as pointers for detecting and displaying an environmental parameter like humidity. This process was managed by the color change of the ionic liquids where they are synthesized with either a colored cation or anion, so that the ionic liquids themselves are pointers. In addition, he has published many papers on the use of ionic liquids in electropolymerization and in the batteries ^[9, 10].

Most recently new ionic liquids based on aluminum chloride when it mixed with either urea or acetamide or trimethyl urea were prepared by Abood and co-workers in 2011^[11]. These ionic liquids are much stable than other chloroaluminate ionic liquids of i.e. imidazolium or pyridinium chloride, offering relatively lower costs, less sensitive, easily prepared ionic liquids with promising similar

properties in at least its catalytic properties for organic reactions and aluminum coating on metal substrate.

A new class of air and moisture stable ionic liquids based on choline chloride was prepared by Abbott and co-workers ^[12], a green chemistry of such ionic liquids were shown especially in the metal process such as metal winding coating, this process offered a safer conditions and a better quality for the manufacture.

Many sorts of choline chloride based ionic liquids with metal chlorides (hydrated or anhydrous) were synthesized also, each can be used as a part of particularly for their constituent metal covering such as chrome, nickel, copper, zinc*e*tc ^[13,14]. Researching of chloroaluminate was not stopped at swapping the imidazolium or pyridinium by the less sensitive boron tetrafluoride or phosphate hexafluoride ions.

Abood ^[15] managed to synthesized another kind of ionic liquid from alum sulfate in its place of aluminium chloride because of easier handling, less cost, greener and availability of these compounds in variable industrial applications like water purification. Alum of the type AlNH₄(SO₄)₂.XH₂O, AlK(SO₄)₂.XH₂O and Al(NO)₃.9H₂O^[16] with urea or acetamide offered room temperature ionic liquids with exceedingly air and moisture stable characterization. This is a green ionic liquid as it was expected to be used in variable fields such as metal coating since it offers good media for some insoluble compounds in aqueous media to dissolve easily in this ionic liquid such as metal oxides or silver sulfate.

1.2-Definition of Ionic liquids

Ionic liquids usually forms of ions only (an organic cation and inorganic anion), but this definition is different from the classic definition of a molten salt. The last

is a high-melting, highly viscous, and highly corrosive liquid, while an ionic liquid is liquid at a much lower temperature (< 100 °C) and has a lower viscosity.

Ionic liquids are known as environmentally friendly substitutes for volatile organic solvents, not only because of their low vapor pressures, but, more importantly, also because of their ability to act as catalysts. Furthermore, ionic liquids have several other good properties, including chemical and thermal stability, nonflammability, high ionic conductivity, and a wide electrochemical potential window^[17].

1.3-Significant importance of ionic liquids

In these days, there are more than 1000 of synthesized RTILs available in literature and the research in this field is ongoing ^[18, 19]. During the 1990s there were only 40 articles each year about ionic liquids ^[20], in 2002 there were about 500 articles and in 2005 there were more than 1500 articles. The research area of ionic liquids expanded further until it reached around 5,000 articles each year in 2010 and more than 6,500 articles in the year 2012 and in 2013 it's almost 7,000 articles related to ionic liquid per year ^[21].



Fig (1-1) Annual growth of the ILs publication from 2000 till 2014 updated by the ISI web of science.^[22]

1.4-Preparation of ionic liquids

There are multiple preparation methods to obtain an ionic liquids which can be summarized as:

1) Metathesis reactions ^[23]:

There are good candidates for the preparing of new ionic liquids for the first time. However, they can leave the ionic liquids contaminated with a small amount of halide particles that may react with solute. An example of it the preparation of [EMIm][BF₄] were stable ionic liquid prepared by

$$[\text{EMIm}]\text{I} + \text{Ag}[\text{BF}_4] \rightarrow [\text{EMIm}][\text{BF}_4] + \text{AgI} \qquad \text{at (12°C)}$$

2) Acid-base neutralization reaction ^[23]:

Tetraalkylammonium sulphonates is made by mixing equimolar amounts of the sulphonic acid and the tetraalkylammonium hydroxide, the surplus water was removed in vacuum.

 $RSO_{3}H + [R_{4}N] [OH] \rightarrow [R_{4}N] [RSO_{3}] + H_{2}O$

3) Direct combination of salts ^[23]:

Direct combination of a halide salt with a metal halide such as:

 $AlCl_3 + [EMIm]Cl \rightarrow [EMIm]^+ + AlCl_4^- (basic part)$

When a large amount of $AlCl_3$ was added, it gave $[Al_2Cl_7]^-$ this considered (acidic part), and the addition of farther $AlCl_3$ would form $[Al_3Cl_{10}]^-$, this reaction must carried out under dry and highly pure conditions.

4) Eutectic method ^[23]:

Another method for ionic liquid preparation

Cholin Chloride + Urea ____ [cholin chloride] [urea]

The imidazolium-based ionic liquids can be derived from a corresponding common precursor, the 1-alkyl-3-methylimidazolium halide, in general the chloride. This precursor is prepared by alkylation of methylimidazole. The alkylation is carried out in an autoclave, at 6 atmosphere of nitrogen and 90^oC without addition of solvent, if the chloroalkane is gaseous at room temperature (e.g. chloroethane), higher homologues can be prepared under atmospheric pressure. This precursor is then either used in a metathesis reaction, where the 1-alkyl-3-methylimidazolium halide is reacted with a Group 1 metal salts, in particular a sodium salt, or a silver salt of the desired anion, or in an acid-base neutralization reaction^[24]. This reaction is stoichiometric and therefore, equimolar amounts of waste MX or HX are produced. This could be circumvented by the

direct alkylation of 1-methylimidazole with alkyltrifluoromethanesulfonate or alkyl bis(trifluoromethanesulfonyl) amide, for example ^[25].



Figure (1.2): some common cations and anion in ionic liquids.

1.5- Properties of Ionic Liquids

1. Melting Point: Ionic liquids have a melting point below 100 °C and most of them are liquids at room temperature. The increase in anion size induce to a decrease in the melting point, for example, the melting point of $[C_2MIm]^+$ type ionic liquid with different anions such as $[BF_4]^-$ and $[Tf_2N]^-$ are 15 °C and -3 °C, respectively. Cations size and symmetry have a critical effect on the melting point of ionic liquids. Large cations and increased asymmetric substitution reduces the melting point value ^[26], a temperature of 75°C was observed for AlCl₃-acetamide^[27].

- 2. Density: Ionic liquids are denser than water with values between1to1.6g.cm⁻³, the increase in the alkyl chain length's in the cation causes a decrease in the densities. For example, the density in ionic liquids comprised of substituted imidazolium cation and CF₃SO₃⁻ anions decrease from 1.39 g/ml for [C₂MIm]⁺ to 1.33 g/ml for [C₂EIm]⁺, 1.29 g/ml for [C₄MIm]⁺ and 1.27 g/ml for [C₄EIm]⁺. The densities of ionic liquids are additionally influenced by the identity of anions ^[28].
- **3.** Viscosity: In general, ionic liquids are more viscous than molecular solvents and their viscosities are between 10 mPa.s to around 500 mPa s at room temperature ^[28]. The viscosity of ionic liquids is deduced by Van der Waals forces and hydrogen bonding. Electrostatic forces can also play an essential part. Alkyl chain lengthening in the cation causes an increase in viscosity, because of stronger Van der Waals forces between the cations inducing an increase in the energy required for molecular motion. Also, the ability of anions to form hydrogen bonding has an effect on viscosity ^[29].

- 4. Conductivity: Ionic liquids have sensibly great ionic conductivities compared with those of organic solvents/electrolyte systems (up to 10 mS cm⁻¹)^[30].but, concentrated aqueous electrolytes usually have a higher conductivity at room temperature. Based on the fact that ionic liquids are comprise solely of ions, it would be expected that ionic liquids have high conductivities. But this is not the case since the conductivity of any solution depends not only on the number of charges carriers, but also on the mobility of these charges. The dense constituent ions of ionic liquids reduce the ion mobility which causes a lower conductivity. The conductivity of ionic liquids of higher viscosity suffers from a lower conductivity. Increasing the temperature increases the conductivity and lowers viscosity ^[30].
- 5. Electrochemical window: The electrochemical window is an essential property and plays a major role in using ionic liquids as solvents for the electrodeposition of metals and semiconductors. The electrochemical window is the electrochemical potential range that the electrolyte is neither reduced nor oxidized at an electrode. This value determines the electrochemical stability of solvents. The electrochemical potential window is mainly dependent on the resistance of the cation to reduction and the resistance of the anion to oxidation. Its known in aqueous solution that the electrochemical window of water (about 1.2 V). in fact, ionic liquids have a fundamentally larger electrochemical windows, e.g. 4.15 V for [BMIm]BF₆ at a platinum electrode, 4.10 V for [BMIm]BF4 and 5.5 V for [BMP]Tf₂N at a glassy carbon electrode. For electrochemical application, the potential window of the electrolyte solution is one of the most important properties. The potential window is determined not only by the chemical structure of the materials in use, but also by the electrode

materials, sweep rate of the potential, temperature, atmosphere, solvent and impurities. The use of an alternate reference electrode to determine cathodic and anodic limits of an ionic liquid makes the circumstance even more complex ^[31].

6. Thermal stability: Ionic liquid is thermally stable up to a temperature of 450 °C. The thermal stability of ionic liquid is limited by the strength of their hetero atom-carbon and their heteroatom-hydrogen bonds^[32]. Wilkes *et al. stated that* 1-ethyl-3-methyl imidazolium the ionic liquids tetraflouro borate $[C_2MIm][BF_4],$ 1-butyl-3-methy imidazolium tetrafluoro borate [C₄MIm][BF₄], and 1-2-dimethyl-3-propyl imidazolium bis(trifluorosulfonyl) imide [MMC₃Im] [Tf₂N] are stable to temperature of 445 °C, 423 °C, and 457 °C, respectively^[33]. Thermogravimetric analysis shows high thermal stability for many ILs, generally up to 350 °C. Such high temperatures are only tolerated by majority of liquids for a short period of time. For example, after 10 h., even temperatures as low as 200 °C, [BMIm][PF6] and 1-decyl-3at methylimidazolium triflate show a considerable mass loss. Long time exposure to such high temperature will inevitably leads to decomposition. The ILs with $[C_2MIm][X],$ thermal stability are where X = $[Tf_2N]^$ low and $Br^{[34]}$. Phosphonium ILs with $[Tf_2N]^-$ or $[N(CN)_2]^-$ anions decompose completely to volatile products in a single step. The degradation products show that Hofmann's elimination process and/or dealkylation reactions occurred. On the other hand, ILs based on nitrogen cations does not fully decompose ^[35]. The begining of the thermal decomposition is furthermore similar for the different cations however, it appears to decrease as the anion hydrophilicity increases. It has been suggested that the stability dependency on the anion is in the order $[PF_6]^- > [Tf_2N]^- > [BF_4]^- > halides.$

An increase in cation size, at least from 1-butyl to 1-octyl, does not provide a large effect ^[36]. It's also know that most of the ionic liquids have a very low vapor pressures. This enables removing the water by a simple heating under vacuum. Water contents below 1 ppm are quite easy to obtain with most of the liquid ^[37].

- **7.** Low nucleophilicity and capability of providing weakly coordinating or noncoordinating environment ^[25].
- 8. Color: Ionic liquids are colorless such as $[BMIm]^+$ cation and a variety of anions like PF_6^- , BF_4^- , $CF_3CO_2^-$ and $(CF_3SO_2)_2N^-$, although they are not 100% pure. The color of lesser pure ionic liquids likely to range from yellow to orange. The formation of the color is because the use of raw materials with color or by additional heating during the synthesis of imidazolium salt^[38,39].
- 9. Hygroscopicity: Viscosity estimations states that the ionic liquids become less viscous with the increasing water content. Hydrolysis issues can also happen. Most of the ionic liquids have amazingly a low vapor pressure, which allows removing water via simple heating under vacuum^[39].
- **10. Hydrophopicity:** The degree of polarity can be changed by changing the length of the alkyl chain. The anion chemistry has a huge impact on the properties of ILs, however, little modification in the properties is expected between the same cation salts, so the actual differences can be significantly dramatically expected, for example, $[BMIm]PF_6^-$ is immiscible with water, whereas $[BMIm]BF_4^-$ is water soluble^[39].

1.6- Applications of ionic liquids

1-Homogeneous and heterogeneous catalyst

For some applications, ionic liquids experience the better benefit of both homogeneous and heterogeneous catalysts. Because of chosen ionic liquids could be immiscible with the reactants and products and the catalysts is still soluble.

This has the advantages of a solid for immobilizing the catalyst, with the advantages of a liquid for allowing the catalyst to mobilize freely ^[40].

2- Biological reactions media

Enzymes are stable in ionic liquids, enabling the probability of ionic liquids to be used in biological reactions. Synthesis of pharmaceuticals is an example of such application^[40].

Ionic liquid-water biphasic systems were studied and applied as new energystorage processes for condensation, separation, extraction and of biopolymers^[41].Mainly stabilization and solubilization of proteins in isolated hydrophobic ionic liquid phase more than aqueous phase could lead to the interesting application of ionic liquids for product separation systems and/or continuous enzymatic reaction.

3- Treatment of high-level nuclear waste

The ionizing radiation does not affect in ionic liquids, so they could be used to treat high-level nuclear waste^[42].

4- Removing of metal ions

In another application, Davis and Rogers designed and synthesized multiple novel ionic liquids to eradicate cadmium and mercury from the pollutant water. When these water immiscible with ionic liquids, they arrest the metal ions outside of water and insulate them in the ionic liquid^{[43].}
5- Purification of gases

Ionic liquids can selectively dissolve and remove gases and could be used for air purification on spaceships and submarines, it was found that aluminum chlorideurea ionic liquid effective in carbon dioxide capture ^[44]. RTILs had the capability as a designer solvents in the gas capturing and also used in CO_2/CH_4 and ethylene (C_2H_4) /ethane (C_2H_6) isolations. RTILs is used as a basis for development substituent strong absorption solvents. Generally, pattern ionic liquids with fluorine-constituent anions, like BF₄, PF₆, Tf₂N, TFA, provided the higher CO₂ absorption capacity. The highest CO₂ solubility was performed with the ionic liquid $[C_2MIm][NTf_2]$, with a molar fraction of 0.23 at 303 K. The large gas capacity of this ionic liquid might belong to the weaker interaction of anioncation, which allow a large interaction with ions of the liquid and the gas solute [45].

6- Synthesis of coordination complex

The reports of directed synthesis of coordination complexes in ionic liquids are oxo-exchange chemistry, the exposure of chloroaluminate ionic liquid to water leads to the formation of aluminum oxo- and hydroxo-containing species ^[46].

7-Electrochemical applications:

RTILs can provide high opportunities for overcoming the limitations faced in traditional chemical processes, specifically in electrochemistry. The wide electrochemical window, non-volatile, noncombustible, and heat resistance nature of RTILs is observed for applications in electrodeposition, batteries, fuel cells, electrosynthesis, electrocatalysis, and electrochemical biosensing^[47].

1.7- Electrodeposition

The electrodeposition is a deposition of metal on a surface by the activity of electric current. This process is achievable by making the substrate an anion in order to coat and immerse it into the selected solution of the selected metallic salt. The positive charges held by the metallic ions are thus attracted to the substrate (which is negatively charged), they give electrons to reduce the positive charge ions to metallic form. Electrodeposition is fundamental for a number of industries, for example electronics, optics, sensors, aerospace and automotive. The regular solutions, such as water, have a drawback, that it has a relatively small potential window, therefore the deposition of metals that have a high negative reduction potentials are hindered by oxygen and hydrogen being produced. RTILs are an excellent media for the electrodeposition of metals and semiconductors, and have a special potential to enhance electroplating. The use of ionic liquids introduces not only the ability to electrodeposit metals that would have been until today impossible to reduce in aqueous solutions, but also the ability to manage the redox chemistry and control metal nucleation characteristics.^[48]

1.7.1-Electrodeposition of metals and alloys

The electrodeposition of aluminum from the first-generation ionic liquids, as known "room-temperature molten salts" or "ambient temperature molten salts" is easy. ^[49-53] Also many relatively noble elements such as copper, silver, gold and platinum can be deposited from these first-generation ionic liquids. However, reactive elements such as silicon, lithium, germanium and others cannot be electrodeposited from these ionic liquids.

Lipsztajn and Osteryoung reported the first electrochemical deposition of Li from 1-ethyl-3-methyl-imidazolium chloride/AlCl₃^[54]. In addition, Li later was able to electrodeposit from 1-ethyl-3-methyl-imidazolium tetrachloroaluminate by

Piersma et al. on platinum, glassy carbon and tungsten using molybdenum and platinum foils as counter electrodes ^[55].

Sodium ^[55,56], indium ^[57], gallium ^[58] and antimony ^[59] were also electrodeposited from AlCl₃ based ionic liquids. After the introduction of air and water-stable ionic liquids in 1990s which have a wide electrochemical window that reaches up to 6V in addition to extremely low vapor pressures, many reactive elements such Li, Si, Ta, Ge, Nb and other elements can be electrodeposited as pure elements. These ionic liquids are usually called the second and third generation of ionic liquids. Zinc and zinc alloys were electrodeposited from ZnCl₂/[EMIm]Cl^[60-62].

Copper has been electrochemically deposited from multiple ionic liquids such as 1-ethyl-3-methyl imidazolium tetrafluoroborate([EMIm]BF₄),trimethyl-n-hexylammoniumbis(trifluoromethylsulfonyl)amide([TMHA]TFSA)and1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) amide ([Py_{1,4}]TFSA)^[63].

A very pure and adherent cadmium was electrodeposited from [EMIm] BF_4 containing CdCl₂ on tungsten ^[64].

In 2004 Abbott et al. reported the electrochemical deposition of chromium in a mixture of choline chloride and chromium(III) chloride hexahydrate also adding of LiCl leads to nanocrystalline black chromium films ^[66].

Palladium is well known for its absorption of hydrogen; hence, the deposition of palladium from aqueous solutions yields only to brittle deposits. The deposition from ionic liquids is known to prevent the hydrogen embrittlement, thus a compact adherent deposits of Pd and many of its alloys such as Pd–Ag^[67], Pd–Au^[68] and Pd–In^[69] could be electrodeposited from basic 1-ethyl-3-methylimidazolium chloride/tetrafluoroborate.

Antimony and its alloys can be electrodeposited from the same basic ionic liquid ([EMIm]Cl-BF₄)^[70].

The electrodeposition of silver from ionic liquids that are based on AlCl₃ has been reported in number of papers ^[71,72]. The electrodeposition of silver from 1-butyl-

3-methylimidazolium hexafluorophosphate([BMIm]PF₆) has also been reported [73].

The electrodeposition of aluminum on copper substrate from AlCl₃/urea ionic liquid has been reported by H. M.A.Abood and N. L.Dawood^[74] for different time, temperature , potential and mole ratio.

Dense and shiny deposits of Pt with a tiny particle size were reported from $[BMIm]BF_4$ and $[BMIm]PF_6$ ^[75]. The electrodeposition of Al from ionic liquids that are composed of more hydrophobic anions like $[TFSA]^-$ has also been studied ^[76,77]. Magnesium electrodeposition from [BMIm] BF₄ and 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate ($[Py_{1,4}]TFO$) was also reported ^[78-81]. Other reactive elements like lithium ^[82] was also deposited from $[Py_{1,4}]TFSA$.

1.7.2-Electrodeposition of semiconductors

Semiconductors are great interest in both fundamental and industrial applications due to their wide applications in different field such as electronics, optical devices and solar cells. Aqueous solutions are rarely used as suitable solvents for the electrodeposition of semiconductors as hydrogen evolution disturbs the deposition process. The electrochemical deposition of germanium from ([BMIm]PF₆) saturated with GeI₄, GeBr₄ and GeCl₄ was also reported in ^[83,84].

Nanocrystalline silicon which have a crystal diameters between 50 and 150 nm were electrochemically deposited from 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl) amide at room temperature ^[85].

Recently, silicon nanotubes and nanowires were obtained via the electrodeposition in ionic liquids at room temperature ^[86], Also the anion effect on the interfacial processes during silicon deposition from three different ionic liquids was also studied ^[87].

Ionic liquids can also be employed to get a compound semiconductors such as InSb^[88] and CdTe^[89].

1.8-Electrodeposition of indium

Indium is silvery-white, very soft, highly ductile, relatively rare post-transition metal with a bright luster ^[90]. The indium characteristics are mostly intermediate between both of its vertical neighbor's the gallium and the thallium.

Indium is a metal that have many useful applications like electronic and optoelectronic devices, solar cells, alkaline batteries, transparent conducting materials etc. the main use of Indium is as an alloy compounds that are binary (Al-In, Bi-In, Pb-In etc.), ternary (Al-Sb-In, Cd- Sn-In etc.), quaternary (Cd-Ge-Sn-In etc.) and quinary (Cd-Ge-Sn-Zn-In etc.) alloys [91]. Generally, the addition of a small quantity of indium can give the effect of hardening, strengthening, and corrosion resistance increase of the metal. Some indium alloys like as InSb^{[92-} ^{94]},InP^[95],InN^[96,97],InGaAs^[98],InSe^[99] are studied as a optoelectronic materials, magneto resistive materials and anodic materials of lithium battery. Chemical and physical characteristics of indium have been well known through multiple references ^[91,100]. Piercy et al. ^[101] and Losev et al. ^[102] reviewed basic electrochemistry of indium. Electrochemistry of indium has also been studied by many researchers since 1930. Most researches focused on the reduction and oxidation of indium ions and indium metal. It is known that the cathodic reduction of In³⁺ and the anodic dissolution of indium metal occur in two charge-transfer steps and In⁺ is an intermediate species during the electron transfer processes of In^{3+}/In^{0} .

Most of the existed indium is used to create indium tin oxide (ITO), which is a significant part of touch screens, solar panels flat screen TVs. This is because it's a good electricity conductor, Also, its transparent and strongly bounds to glass. Indium nitride, phosphide and antimonide are semiconductors used in transistors and microchips.

The indium metal sticks to glass, this property can be utilized to give a finish to mirrors in windows of high buildings, also as a protective film on goggles of welders, Also, because of its low friction it has been used as coat for ball bearings in racing cars (Formula one) racing cars.

1.8.1-Electrodeposition of indium from aqueous solutions

1. Cyanide solutions

Indium is a trivalent metal that, it can be electrodeposited from a cyanide solution. Gray ^[103] the first commercial indium baths were prepared by dissolving freshly prepared In(OH)₃ in an alkaline or a cyanide solution, a recommended procedure that continued in most modern formulations. The hydroxide best method of preparation is by precipitation from InCl₃ solutions using NH₄OH, after being washed it will dissolve in the alkaline cyanide solution. these baths are stabilized by the addition of a weak organic acids like glycine or, more often, by the means of sugars like D-glucose or dextrose. Uncomplexed solutions tend to hydrolyse with time and appear cloudy but it does not prevent operation since a satin finish is possible over wide ranges of current density. Insoluble anodes are always used, and the cathode initial efficiency is 100% drops rapidly to about 50%, thus the disadvantage for this solution, because of the inconveniently in preparation and its relative instability and the aging requirement before a consistent deposition is obtained. Mohler ^[104] did investigate many main variables that can potentially have an affect the cathode efficiency over wide range of limits but the recommended conditions give a value of around 50%. Specific versions of this solution using sorbitol and dextro as a complexants have been patented and it can be completely dehydrated to facilitate storage and transport.

It is known that indium forms complexes with hydroxide, dextrose and cyanide; their effects are believed to be synergistic, therefore the use of all three together can be recommended like the species $In(CN)_4^-$ and $In(OH)_4^-$ are present in solution. Mohler^[104] has suggested that decomposition and precipitation can occur by the reactions:

 $In(CN)_4^- \longrightarrow CN^- + In(CN)_3$

 $In(OH)_4^- \longrightarrow OH^- + In(OH)_3$

Addition of alkali appears to favour:

 $In(CN)_4^+ + 4OH^- \longrightarrow In(OH)_4^+ + 4CN^-$

2-Acid sulphate solutions

Sulphate electrolytes have been studied extensively and it's the most widely used commercially by virtue because of their relative simplicity, Although they are considered inferior to the cyanide solutions in throwing and "strike" characteristics. Generally used are the Soluble anodes (at about 100% efficiency) however, because the cathode's efficiency is usually between 60 - 80%, either a combination of insoluble and soluble anodes can be preferred, Alternatively the electrolyte must be periodically removed or diluted with water and a pH correction must be made. Early attempts to use the sulphate solution were relatively experimental and the formulations contained additives like hydroxylamine, pyridine, formic acid or tartrate ^[105]. The solution was stable and could be operated on relatively wide ranges of indium concentration. Consequently two separate investigations deduced an acceptable sulphate solutions used in metal finishing and engineering applications.

Fink and Lester ^[106] has used A1₂(SO₄)₃ and gelatin to improve levelling,

Even though the second did reduce the efficiency of cathode by around 20% when present to the extent of 7.5 mg 1^{-1} . The boric acid addition did reduce the deposit's grain size and did increase the efficiency of the cathode while the addition of

NaOH and H₃BO₄ together made the efficiency to pass the minimum and reducing the quality of the deposit.

Linford has managed to improve the solution further ^[107] who specified the pH's calibration and the concentrations indium. Control was also improved by the use of soluble and insoluble anodes or by split anode circuits.

Recent work ^[108] has shown that the cathode efficiency is extremly sensitive to changes in the current density, temperature and pH for a solution of Linford type. The deposition mechanism has been investigated for both solid cathodes and amalgamated mercury surfaces, however while the second offers the possibility of detailed analysis by using polarographic techniques they may not be characteristic of electroplating conditions.

Consideration of the available data suggests that the mechanism Changes overpotentials from low to high however, there is no evidence of any influence on the more practical deposit properties.

3-Fluoride solutions

While fluorides have been added to sulphate solutions for improving the conductivity and the rates of deposition they have also been considered individually or with fluosilicates and fluoborates ^[109].

In particular, the fluoborate solution has the advantage of simple formulation from stable concentrates, an increased efficiency of anode and cathode, low fluctuations in bath composition and a deposits that are fine-grained.

Both Narcus^[110] and Wild ^[111] have suggested improvements to formulation and conditions, specifically the use of NH₄BF₄ as a brightener and grain refiner. Benning shoff ^[112] has suggested that a "high speed" solution can be developed by further optimization, with cathode efficiencies about 100% and with deposits that are silk-like which are particularly suitable for printed circuit applications.

1.8.2-Electrodeposition of indium from ionic liquids

The indium electrodeposition by first group of the ionic liquid systems that has an interest is the chloroaluminate which is formed from dialkylimidazolium chlorides and aluminum chloride ^[113]. While the chloroaluminate ionic liquids have proven to be good solvents, their extreme reactivity towards air and moisture makes them hard to handle without an inert atmosphere is available. A waterstable ionic liquids were developed to accelerate the research and applications using ionic liquids^[114] by exchanging the chloroaluminate anion with other anions such as BF₄⁻, PF₆⁻, CF₃SO₃⁻, and ZnxCly ^{(2x-y)-}, that's because ionic liquids are aprotic solvents, complications associated with hydrogen evolution that often occur in aqueous bath are circumvented in the ionic liquids. Furthermore, ionic liquids exhibit a larger working temperature ranges than the aqueous baths.

The electrodeposition of indium (III) in the EMICI-BF₄.Indium is the component of multiple useful metal alloys and semiconductors such as Ag-In, Ni-In, InAs, and InSb.

Information about the electrochemical properties of indium itself is essential to the electrochemical production of indium-containing materials. many examples of the indium's electrodeposition that took place in aqueous solutions or high temperature molten salts can be found in the literature ^[115]. On the other hand, studies on the indium's electrochemistry in low-temperature ionic liquids are very limited; an InCl₃-EMIC ionic liquid electrolyte has been utilized for the indium's codeposition with antimony ^[116].

Recently it has been discovered that the principle of an ionic liquid preparation is by complexing a halide salt can be applied to mixtures of quaternary ammonium salts with an amide, carboxylic acid or alcohol moiety ^[117,118]. Deep Eutectic Solvent (DES) is what these mixtures are called. Such eutectic systems are easy to manipulate, they are not toxic and biodegradable in compare with room temperature ionic liquids. Besides, they show chemical inertness towards water and the production process is low cost and no environmental risks. The study also state the electrochemical behavior of indium in one of these DES mediums (1:2 cholinechloride/urea)and the results show the likelihood of electrodeposition of pure crystalline indium. The surface morphology of the deposits improves at higher current density, with a decrease of the surface roughness. Additional investigation can be done to enhance the surface's morphology of the deposit bearing in mind several applications of indium. Many articles are available that discusses the electrochemical production of indium^[119,120], while only few articles are available related to the electrodeposition of indium from ionic liquids ^[121].

1.9-Electrodeposition of tin

Tin is a ductile, soft and silvery white metal which can be deposited as a matte or bright finish. Tin coatings have been used to create a protective surface to resist air oxidation, and to enhance corrosion resistance and to improve solderability. The bright tin coatings can also provide a decorative finish that can be visually appealing even when it is become in contact to moisture and air. The electrodeposition of tin has a long history and a good summary of its established science and technology is discussed in the book by Jordan^[122], while the protective coatings for metals book by Gabe^[123] discusses a useful treatment of tin plate as a metallic coating. Tin is one of the very few metals fit for contact with foodstuffs during the cooking process. Pure tin and its alloys have received increasing focus as anode materials for Li-ion batteries as replacements to graphite mainly due to their high specific capacity and energy density. Tin has many applications. It can take a high polish and it could be used to coat other metals for corrosion prevention, like in tin cans, which are manufactured of tin-coated steel. Most of window glass is manufactured by floating molten glass on molten tin to

obtain a flat surface. Tin salts sprayed onto glass are used to produce coatings that are electrically conductive.Some tin compounds have been used as an anti-fouling paint for ships and boats, to prevent barnacles. Even so, these compounds are still deadly to marine life even at low levels, oysters especially. Its use has now been banned in most of countries.

1.9.1-Electrodeposition of tin from aqueous solutions

Electrodeposition of tin from aqueous solutions has been studied for at least a hundred years. Electrolytes for tin deposition can be acidic or alkaline. Tin is normally deposited from divalent stannous ions, Sn^{2+} in an acidic bath and via tetravalent stannate ions, $SnO4^{4-}$ in an alkaline one.

Alkaline baths are usually hydroxide based and acidic baths have sulphate or sulphonate based compositions. Alkaline baths can be operated without additives since the stannate ion appears as a soluble complex. In acidic baths, the addition of additives is required for electrolyte stability. A low maximum current density is achieved in alkaline baths and they may suffer from losses in current efficiency 'Acidic baths can offer faster deposition rates at ambient temperature but are more complicated to maintain^[124].

1.9.2-Electrodeposition of tin from ionic liquids

Xu and Hussey ^[125] investigated the electrochemistry of Sn(II) and Sn(IV) in acidic and basic [EMIm]Cl/AlCl₃) molten salt at 40°C. The electrochemistry of Sn(II) and Sn(IV) was studied at polycrystalline Pt and Au, And at glassy carbon (GC) electrodes. The Sn(II) reduction process is uncomplicated at Pt. The underpotential deposition of a Sn monolayer is observed at Au; an additional UPD process is attributed to surface alloy formation. The deposition of Sn on GC is complicated by nucleation. The formal potentials of the Sn(II)/Sn couple in the

66.7-33.3 and 44.4-55.6 mole percent melts are 0.55 ± 0.01 and -0.85 ± 0.03 V, respectively, vs. Al(III)/Al in the 66.7-33.3 mole percent melt. The electrochemistry of tin was examined by Huang and Sun in acidic and basic [EMIm]Cl/ZnCl₂ ionic liquid ^[126] at 90°C. The electrochemistry of tin at polycrystalline tungsten and at glassy carbon (GC) electrodes. The electrodissolution of Sn produces a Sn(II) solution, which can be either oxidized to Sn(IV) or reduced to Sn metal. The formal potentials of the Sn(II)/Sn(0) couple in the 40.0-60.0 and 25.0-75.0 mol % ionic liquids are 0.25 and -0.24Vrespectively, vs. Zn(II)/Zn in a 50.0-50.0 mol % ionic liquid. The formal potentials of the Sn(IV)/Sn(II) couple in the 40.0-60.0 and 25.0-75.0 mol % ionic liquids are 0.78 and 0.29 V, respectively. The electrodeposition of Sn from Sn(II) at both electrodes is complicated by nucleation. Tachikawa et al.^[127] researched the electrochemical behavior of Sn(II)/Sn species in a room-temperature ionic liquid, 1-butyl-1-methylpyrrolidinium

bis(trifluoromethylsulfonyl)imide(BMPTFSI). The anodic dissolution of Sn metal proceeded by a two-electron transfer reaction. Electrodeposition of Sn on a Cu substrate is possible in BMPTFSI containing Sn(II). The formal potential of the Sn(II)/Sn is -0.57 V vs. Ag/Ag(I). Morimitsu *et* al.^[128] studied the electrodeposition of tin in the 1-ethyl-3-methylimidazolium tetrafluoroborate molten salt containing free chloride ions (EMI·BF₄·Cl) originated from the mixture of EMIC and NaBF4 (60:40 mol%). The well defined redox waves for the electro deposition and dissolution of tin were observed on a platinum electrode at 30 °C.

Abbot et al ^[129] have described the electrolytic deposition of Sn and Zn/Sn alloys from a solution of the metal chloride salts in urea and ethylene glycol/choline chloride based ionic liquids. The deposition kinetics and thermodynamics differ from the aqueous processes and that qualitatively different phases, compositions and morphologies are obtained for the metal coatings in the different ionic liquid systems. The differences in electrochemical responses are rationalised in terms of the speciation of both Zn and Sn chlorides in the ionic liquids that have been identified using FAB mass spectrometry. Also they demonstrate that composite metal coatings, *e.g.* containing Al_2O_3 particles, can be obtained from these liquid systems by virtue of the stable liquid suspensions. This novel feature of these liquids is a function of their relatively high viscosity.

1.10-Electrodeposition of antimony

Antimony is a brittle silvery-white shiny metal with a high metallic

luster and a crystalline structure. It does not tarnish readily on exposure to air and is oxidized only slowly by moist air. Dilute HC1, HNO₃ and H₂SO₄ have no action on antimony 'In the absence of air concentrated HC1 and HF do not attack the element, but it is slowly attacked by strong aerated acids. Concentrated acids do not dissolve the metal but rather oxidize it to insoluble antimony trioxide or antimony pentoxide ^[184]. Alkalis have no action on antimony. Because of its high corrosion resistance and non-oxidizing properties, antimony might well be considered for a corrosion-resistant surface on many components where more critical metals are used such as hardware, domestic ware, automotive trim and radio and radar equipment and to cover brass and lead alloys which require a high degree of corrosion protection^[130].

1.10.1- Electrodeposition of antimony from aqueous solution

The use of fluoride solutions was proposed by Betts ^[131] who obtained smooth brittle untarnished deposits.Several other workers have proposed fluoride solutions for bright smooth antimony deposits with and without additives ^[132-134]. Solutions based on halides (chloride, bromide and iodide) which have been recommended for antimony plating ^[135,136] The fluoride solution has two distinct advantages over the other halide solutions in that (i) it does not hydrolyse to give insoluble basic salts and (ii) the deposit is not explosive. The Sulphide solutions ^[137] have been studied with respect to the electroforming and electrowinning of antimony.

While thick deposits of antimony were electroplated in fluoroborate baths ^[138] containing additives. A number of complex baths containing hydroxycarboxylic acids (both Aliphatic and alicyclic) ^[139,140] have been used for antimony plating. A Number of reports claimed for antimony plating from tartrate baths and citrate baths ^[141-144].Bespalko and Vdovenko ^[145] deposited a black powdery mixture of antimony and antimony trioxide from a pyrophosphate bath. It was reported that stirring the bath improved the nature of the deposit. A method of improving the adhesion of electrodeposited antimony by the preliminary anodic oxidation of steel (the basis metal) or by applying a layer of iron on steel, zinc or copper alloy has been patented^[146].Highly ductile, malleable and adherent antimony coatings have been obtained by roughening or etching the metal surface.

1.10.2-Electrodeposition of antimony from ionic liquids

Habboush and Osteryoung were the first to describe the electrodeposition of a Group V metal from AlCl₃/1-butyl-pyridinium chloride-based ionic liquids. As antimony sources they used SbCl₃ or Sb-rods, dissolved by anodic dissolution ^[246]. For the composition AlCl₃:BuPyCl (0.8:1) a deposition of Sb was observed at -0.885 V and dissolution at -0.420 V and for the solution composed of AlCl₃:BuPyCl (1.5:1) a deposition of Sb occurred at +0.53 V and anodic dissolution at +1.11 V.

They remarked that $SbCl_2^+$ was the dominant species in the acidic ionic liquids. The reduction of this species on glassy carbon exhibited irreversible behavior. In the basic melts $SbCl_4^-$ and $SbCl_6^-$ were believed to be the dominant species. In basic media the reduction of Sb(III) to the metal on glassy carbon was also irreversible while its oxidation to Sb(V) showed quasi-reversible behavior. In another publication Lipsztain and Osteryoung used imidazolium-based ionic liquids to study the behavior of Sb(III) under conditions where the unbuffered properties of a neutral ionic liquid played an important role^[147].

Deep eutectic solvent mixture were formed between acetamide and antimony chloride (SbCl₃)^[148], which can be used for electrodeposition of antimony (Sb) films and its alloys, which are currently investigated for thermoelectric applications, are prepared by electrodeposition from aqueous electrolytes. However, this is challenging due to very low solubility of Sb in aqueous solutions .Mixtures of various mole fractions of SbCl₃ and acetamide were prepared in ambient environment and heated up to 90 °C. When cooled down to room temperature, liquid phase can be observed for the mixture with SbCl₃ mole fractions from 0.2 to 0.8. The mixture of 0.2 mole fraction of SbCl₃ had the lowest viscosity, SEM investigation shows that smoother morphology of Sb films is achieved mixtures with lower SbCl₃ mole fraction.

1.11-Electrodeposition of alloys

Electroplating of alloys from a solution containing different metal salts is generally straight forward. In principle, solid-solution phases (alloys) can be acquired by co-deposition where the composition of the alloy is determined by the ratio of metal ions in solution and the difference in redox potential.Copper–tin alloy electrodepositions are broadly used in manufacturing and are being used in the development of new materials. They are suitable for producing high energy outputs, such as can be found in rechargeable lithium batteries ^[149,150]. The majority of the literature about the coating and dissolution of this alloy was gathered in the early stages of alloy development. One issue connected with the

electrodeposition of these alloys from aqueous solution is the very toxic and corrosive species, such as thiocyanate or pyrophosphate.

1.11.1-Electrodeposition of indium-tin alloy

Ambient temperature molten salts have attracted much attention in recent years as the applications in lithium ion battery, supercapacitor or electroplating.EMI-BF4-Cl melts, composed of 1-ethyl-3-methylimidazolium cations, tetrafluoroborate anions and chloride anions, have some attractive properties such as a low melting point below room temperature, a low reactivity to air and moisture, a wide electrochemical window of *ca.* 3V, and a high solubility of metal chlorides ^[151].These features are appropriate to study the electrode reactions of various metal ions, which are difficult to dissolve in other ambient temperature melts except chloroaluminate melts. investigating the electrode reactions of metal ions such as Pb(II), Sb(III), In(III), Sn(II) ^[152], demonstrated that these metals and In-Sn alloys^[153] lead to possibility of electrodepositing from this melt.Indium-Tin alloy are available as bar, ingot, ribbon, wire, shot, sheet, and foil. Ultra-high purity and high purity forms also include metal powder, submicron powder and nanoscale, targets for thin film deposition, and pellets for chemical vapor deposition (CVD) and physical vapor deposition (PVD) applications.

Indium-tin is one of numerous metal alloys sold by American Elements under the trade name AE Alloys. American Elements produces to many standard grades when applicable, including Mil Spec (military grade); ACS, Reagent and Technical Grade; Food, Agricultural and Pharmaceutical Grade; Optical Grade, USP and EP/BP (European Pharmacopoeia/British Pharmacopoeia) and follows applicable ASTM testing standards.Typical and custom packaging is available. Primary applications include bearing assembly, ballast, casting, step soldering, and radiation shielding^[154].

1.11.2-Electrodeposition of indium-antimony alloy

InSb is one of the compound semiconductors that are widely used in many fields such as optoelectronic devices. Among the techniques for the growth of InSb, the electrodeposition would offer several advantages include low operating temperature, the ability to plate homogeneously on odd-shaped surfaces, simplified waste handling, and low cost. The electrodeposition of InSb has been studied in aqueous plating baths ^[155-157] either by direct codeposition of In and Sb or by sequential deposition of Sb and In. In some cases high-temperature annealing of the electrodeposits was required in order to obtain crystalline InSb. The electrodeposition of InSb in ambient-temperature ionic liquids is, however, limited to the work carried out in an InCl₃ based ionic liquid to which SbCl₃ was added .The authors^[158] reported that InSb and elemental In and Sb could be directly electrodeposited at 45°C. They claimed that the quality of the deposits could be improved by annealing at 350°C.

Aim of the present work

From the above stated works on the research studies involving the reduction of indium alone or with the presence of either antimony or tin received a little attention in ionic liquids in contrast to studies in aqueous solutions. Combining an electrolyte containing both ionic liquids and water in small ratio have not yet been investigated.

In present study we shall carry out the reduction of indium, antimony and tin metal from their metal chloride solutions in the ammonium alum:urea room temperature ionic liquid (1:5 mole ratio) as this ionic liquid possess the characterization of ionic liquid having water molecules within its structure and not present in free state as stated in previous work. The electrodeposition of indium with the presence of either antimony or tin is also to be covered in this study in an attempt to obtain metal mixture or alloys. The study will be under taken with the aids of different techniques such as, Cyclovoltammogram , Scanning Electronic Microscopy(SEM), Atomic Force Microscopy(AFM) , Energy Dispersive X-ray Analysis (EDAX) and X-Ray Diffraction (XRD)



Chapter Two Experimental part

2.1 Chemicals

All chemicals were used with the most available purity without further purification.

Table (2.1): The chemicals used in this work with their purities and suppliers.

No.	Chemical compounds	Formula	Purity %	Company
1	Anhydrous Indium chloride	InCl ₃	98	Thomas Baker
2	Anhydrous Antimony chloride	SbCl ₃	99	BDH
3	Tin chloride dihydrate	SnCl ₂ .2H ₂ O	97	BDH
4	Hydrated ammonium aluminum sulfate	NH ₄ Al(SO ₄) ₂ .12H ₂ O	99	BDH
5	Urea	NH ₂ CONH ₂	99.5	Thomas Baker
6	Acetone	CH ₃ COCH ₃	99.5	Thomas Baker
7	Hydrochloric acid	HC1	37	BDH
8	Sodium Hydroxide	NaOH	99	BDH
9	Copper metal	Cu	-	-
10	Stainless steel	-	-	-

2.2-Practical Method:

2.2.1-Preparation of Hydrated ammonium aluminum sulfate- urea ionic liquid:

A procedure for preparing ionic liquid was used as stated^[159] as following:

Hydrated ammonium aluminum sulfate $[NH_4A1 (SO_4)_2.12H_2O]$ and urea $[NH_2CONH_2]$ in a mole ratio of (1:5) were milled separately, well mixed and heated gradually to 85°C in a closed glass tube with continuous gentle stirring until the solid salts changed to colorless liquid.



Figure(2.1):Optical photograph of ammonium alum :urea room temperature ionic liquid, (1:5) mole ratio heated to 85°C for 3 hours.

2.2.2- Preparation of salts in ionic liquid

• Anhydrous indium chloride solution

A proper amount of $InCl_3$ (0.664g) was added to ionic liquid and stirred for 30 minutes at 85 °C to obtain a 0.3M indium chloride solution giving a clear colorless solution.



Figure(2.2): Optical photograph of 0.3M of InCl₃ in ammonium alum :urea room temperature ionic liquid ,(1:5)mole ratio heated to 85°C for 30 minutes.

• Tin chloride dihydrate solution

A proper amount (0.677g) to make a 0.3M SnCl₂.2H₂O solution in ionic liquid was weighted out and added to the ionic liquid, stirred for 30 minute showed a white suspended solution.



Figure(2.3): Optical photograph of 0.3M of SnCl₂.2H₂O in ammonium alum :urea room temperature ionic liquid, (1:5)mole ratio heated to 85°C for 30 minutes.

• Anhydrous antimony chloride solution

A proper amount (0.684g) to make a 0.3M SbCl₃ solution in ionic liquid was weighted out and added to the ionic liquid, stirred for 60 minutes when a white suspended solution was obtained.



Figure (2.4): Optical photograph of 0.3M of SbCl₃ in ammonium alum :urea room temperature ionic liquid (1:5)mole ratio heated to 85°C for 60 minutes.

• Solutions of anhydrous indium chloride with anhydrous antimony chloride and anhydrous indium chloride with tin chloride dihydrate

A 10ml of either SbCl₃ or SnCl₂.2H₂O solution in ionic liquid as described above was taken and mixed with 10ml of InCl₃ solution to make a mixture of both solutions and forming a white suspended solutions.



Figure(2.5): (a) Optical photograph of 10 ml of SnCl₂.2H₂O solution with 10 ml of InCl₃ solution. (b) Optical photograph of 10 ml of SbCl₃ solution with 10 ml of InCl₃ solution.

2.2.3-Pre-treatment of cathode and anode

In electrodeposition experiments, a copper metal sheet of (60*10*1)mm dimensions was used as a cathode, the stainless steel plate of (50*10*1)mm dimensions was used as an anode. Both electrodes pretreated when rubbed with sand paper followed by rinsing with deionized water, then plunged into 0.5% HCl, rinsed with deionized water after that immersed in 0.5% NaOH, finally were rinsed with deionized water and acetone sequentially.

2.2.4- Protocol of electrodeposition

A power supply (Thurlby 15V-4A, England power supply) to control the current and the potential of electrodeposition process, which was connected, to the electrode of copper as cathode and stainless steel as anode were immersed with 20mm depth in ammonium alum: urea room temperature ionic liquid which was used as electrolyte medium. The experiments have taken place in different potentials and times at temperature 30°C. An electrochemical reverse polarization at -1 V for two minute was the first step for each experiment and followed by:

- The electrodeposition of indium metal from anhydrous indium chloride occurred at different times (one, two, three and twenty four hours) at a potential -0.76 V and at different potentials (-0.76 V, -1.2 V and -1.6 V) at one hour.
- The electrodeposition of tin metal from tin chloride dihydrate occurred at different times (one, two and three hours) at a potential -0.7 V.
- The electrodeposition of antimony metal from anhydrous antimony chloride occurred at different times (one, two and three hours) at a potential -0.8 V.
- The codeposition of indium and tin metal(s) from anhydrous indium chloride and tin chloride dihydrate occurred at different times (one, two and three hours) at potentials -0.8 V and -1.1 V.
- The codeposition of indium and antimony metal(s) from anhydrous indium chloride and anhydrous antimony chloride occurred at different times (one, two and three hours) at potentials -0.8 V and -1.6 V.



Figure (2.6): Electrochemical cell used for electrodeposition

2.2.5-Post-treatment of electroplated specimens

The electroplated specimen when removed from the ionic liquid was immediately dipped in deionized water with stirring to remove ionic liquid and then rinsed with acetone and finally dried and stored for further analysis.

2.3-Instrument

2.3.1- Cyclic voltammogram (CV)

A three-electrode system comprising a platinum electrode(2mm) as the working electrode (WE), a platinum plate(1cm*1cm*0.5cm) as the counter electrode (CE) and a silver wire as the quasi reference electrode (RE) were used in the cyclic voltammogram. The platinum working electrode surface was freshly cleaned with water, polished with alumina and before each scan and rinsed with distilled water at each polishing step. The instrument for cyclic voltammogram (CV) was recorded using Digi-lvy- Dy2300 Bipotentiostat. The measurements were carried out in the laboratories of department of chemistry /college of science /Al-Nahrain University.

2.3.2- Scanning Electron Microscopy (SEM)

The surface morphology of specimens of metals coating on copper surfaces was investigated by using a high-resolution field emission scanning electron microscopy (INSPECT S50). The measurements were carried out in the laboratories of department of physics /college of science /Al-Nahrain University.

2.3.3- Energy Dispersive X-ray Analysis (EDAX)

The (X Flash 6110) Bruker EDX was used in conjunction with SEM. This was used to determine the composition of samples surface. This was carried out in the laboratories of department of physics / college of science / Al-Nahrain University.

2.3.4- Atomic Force Microscopy (AFM)

The surface topography of samples was analyzed by atomic force microscopy (AFM) (AA2000, Angstrom Advanced Inc.) contact mode. These were carried out in the laboratories of department of chemistry / college of science / Al-Nahrain University.

2.3.5- X-ray Diffraction analysis (XRD)

The crystalline and phase identification of samples were determined using X-ray Diffractometer (PAN analytical Philips, X Pert PRO MPD PW 3040) employing monochromatized radiation source of Cu-K α of 1.5408 °A. The voltage and current intensities were 8.5 kV*A. All samples were scanned in the range of 20° to 80° 2 θ with a step size of 0.01 and step time of 0.2 Sec. at room temperature 20 °C that was performed in physics department/college of science /Al-Nahrain University.



Chapter Three Results & Discussion

The possibility of electrodeposition in ionic liquid was investigated for different reasons, one of which is the possibility of using the room temperature ionic liquid formed between ammonium alum and urea in the mole ratio of 1:5, as electrolyte medium for metal electrodeposition. Hence ionic liquid solutions of metal chloride of indium, antimony, tin and their mixtures were first investigated cyclovoltammetrically to -2.00V which indicated that these metals and their mixture metal can be reduced and hence electrodeposited in this ionic liquid. Therefore time influence and potential variation guided the investigation to study the nature and morphology of the deposited metal(s).

Copper metal substrate was used as cathode in the potentiostatic electroreduction of metal cation or their mixtures in the ionic liquid, under the existence of air.Therefore, the pretreatment was very important to reduce impurities and oxide from the surface as shown in chapter two section(2.2.4).This pretreatment is important in order to strengthen the adherent of metal on the surface of cathode ^[160].An electrochemical reverse polarization at -1V for 2 minutes was also conducted. This protocol was found to clean the surface satisfactorly which dissolved a very thin layer of copper in the ionic liquid. Hence, the surface of cathode became clean and ready for electroreduction process with expected good adherence of coated metal on the surface.

3.1-Cyclic voltammogram of anhydrous indium chloride

InCl₃ solution in two concentrations of 0.1M and 0.3M showed only one signal of cathodic reduction started at -0.375V for 0.1M and at -0.425V for 0.3M revealing only small negative potential differences between the two indium chloride concentrations as shown in Figures (3.1). On the reverse potential, the

cyclovoltammogram of both concentrations showed one anodic broad curve at a maximum potential of -0.35 V for the 0.1 M and -0.425 V for the 0.3 M. This small differences might be related to mobility limitation at the high concentration (0.3M) than the low concentration (0.1 M). The broad oxidation signal could be related to slow metallic dissolution of In^0 to In^{3+} in viscous ionic liquid.

Ionic liquid of the present type contains water molecules in its composition ammonium alum: urea (1:5) mole ratio, this could be expected to limit the reduction range to -0.8V reduction potential of proton as fallow:

 $H^+ + e^- \longrightarrow 1/2H_2$ (3.1)

The absence of bubbles on the cathode within the visual observation limitation and therefore absence of gas evaluation could be related to the absence of such reduction of hydrogen cation or other reduced ionic species until -1.2V .It is worth noting that indium reduction

 $In^{3+} + 3e^{-} \longrightarrow In^{0} \dots (3.2)$

in aqueous solution with respect to standard hydrogen potential is less negative than the protonic reduction (eq.3.1), compare -0.8 V of H⁺ with -0.338V of In^{3+} which means that water molecules of ionic liquid would have no effect on the potential of indium reduction. The standard redox potentials values for indium as reported by Petr Vanysek^[161] illustrated in the following equations:

$In^{3+} + e^{-} \longrightarrow$	In^{2+}	-0.49V(3.3)
$In^{3+} + 2e^{-} \longrightarrow$	In^+	-0.443V(3.4)
$In^{3+} + 3e-$	In	-0.338V(3.5)

Although water molecules were present, the observed potential reduction of indium at -0.76V this indicated that indium hydroxide or indium oxide are not

formed otherwise the reduction would be expected to occur near -1.00 V as shown in the following equations reported by Petr Vanysek^[161]:

$In(OH)_3 + 3e^- \longrightarrow In + 3OH^-$	-0.99V(3.6)
$In(OH)_4 + 4e^- \longrightarrow In + 4OH^-$	-1.007(3.7)
$In_2O_3 + 3H_2O + 6e^- \longrightarrow 2In + 6OH^-$	-1.034(3.8)

The concentration effect on the onset of reduction potential was observed when solutions of 0.1M and 0.3M of InCl₃ were cyclovoltammetrically scanned and compared with that obtained from scanning a 0.3M solution of InCl₃ after potentiostatic electrodeposition experiment for one hour. Latter solution showed a reduction started at similar negative potential to that of the fresh 0.1M InCl₃ with very small signal of cathodic scan. In addition the onset reduction signal of 0.3M InCl₃ could be explained as a UPD of reduced In⁺³/In⁰ as shown in Figure (3.1). When the electroscanning was taken more negative (down to -1.6V) a large oxidation band was observed indicating clearly that the reduced indium metal cation was oxidized to In³⁺ in one step with slow indium dissolution due to viscous ionic liquid which limit the mass transportation. However, it is important to notice that at a potential of -1.0V two oxidations potentials a_1 and a_2 were observed related to the cathodic potential c_1 and c_2 related to UPD and bulk reduction of indium respectively. The reduction of indium cation to indium metal as seen in the scan to 1.2 V as shown in Figure(3.2), showed only one oxidation band that was related to the bulk oxidation a₂ which overcomed the band of the UPD oxidation a_1 . The one signal reduction step of In^{3+} to In^0 observed in this work was in contrast to that reported by other worker who found five reduction steps in ionic liquid although similar platinum working electrode was used. This might indicate an influence of ionic liquid type on the indium cation coordination and complex compound formed by the ionic liquid of the present work. However ,the working electrode might also influence the reduction process of indium as stated

by S.Zein El Abedin et al.^[162], who reported two reduction steps for indium when glassy carbon working electrode was used, yet giving one oxidation step for In⁰ to In^{3+} . The passivation behavior of indium in alkaline solutions suggested by Ts.Dobrovolska^[163] that was also reported in aqueous solution of pH=3.1 was related to alkalization during the cathodic process leading to the formation of insoluble indium oxides and hydroxides. This behavior was not observed in this ionic liquid and therefore oxide or hydroxide formation was excluded yet water molecules were present in the ionic liquid suggesting a weak interaction between oxygen of water with indium cation. In fact, the cyclovoltammogram of anhydrous indium chloride (0.3M) in ionic liquid showed only two cathodic reduction when scanned down to negative potential of -2.5V in this ionic liquid, as only two oxidation a_1 and a_2 on the reverse scan were observed related to c_1 and c_2 respectively. Indeed the first reduction potential (c_1) was relatively involving only small amount of reduced indium when potentiostatic reduction was conducted for one hour at -0.76 V that was related to under potential reduction of indium in a similar behavior to that reproted by S.Zein El Abedin and et al.^[162] and by Y.Traore et al.^[164]. Another differences of reduction behavior of anhydrous indium chloride (InCl₃) found in this work that it showed two positive reduction c_1 representing UPD and c₂ representing bulk reduction of indium while the above workers^[164]reported five reduction and oxidation processes of indium indicating the influence of ionic liquid type on the stability and probably complex formation in their ionic liquids differ from then formed in present ionic liquid.

Although, reversing the scan from -2.00 V showed only one curve of anodic oxidation of indium. The UPD and bulk depositions were studied by potentiostatic experiment at -0.76 V, -1.2 V and -1.6 V. These two processes were not found in aqueous solutions ^[165], RTIL^[166] or molten salts ^[167]. However ,working electrode materials might also represented a reasonable effect on the indium reduction as

only one signal was also reported if substrates of Mo^[167], glassy carbon ^[168], or indium ^[169]were used.



Figure (3.1): Cyclovoltammogram of 0.1 M and 0.3 M of InCl₃ solution in (1:5) ammonium alum: urea ionic liquid and 0.3 M InCl₃ after deposition at 50 mV scan rate using Ag wire (RE), Pt disc (WE) and Pt plate (CE) at 30°C.



Figure (3.2): Cyclovoltammogram of 0.3 M of InCl₃ solution in (1:5) ammonium alum: urea ionic liquid at 50 mV scan rate using Ag wire (RE), Pt disc (WE) and Pt plate (CE) at 30°C.

3.2-Electroreduction of indium in ammonium alum /urea ionic liquid:

The potentiostatic electroreduction of indium from the solution of $InCl_3$ in ammonium alum:urea room temperature ionic liquid was carried out for two concentrations of $InCl_3$ of 0.1M and 0.3M at 30°C. However, for both concentrations at -0.76 V when the solutions were heated up to 30°C a reducible indium was noticed only for the 0.3M $InCl_3$ solution. The experiments showed the effect of concentration and temperature on the electroreduction of In^{3+} to In^{0} which reveals the catalytic effect of temperature on the reaction. The absence of reduction process of indium in the 0.1M solution is also noticed in the cyclovoltommogram as shown in Figure (3.1) which showed reducible indium at lower negative potential in the case of 0.3M solution but not for the 0.1M solution.

In addition at the end of carrying potentiostatic reduction at -0.76 V on the 0.3M solution for one hour, this solution showed cyclovoltammetrically similar reduction potential (-0.475) to that of fresh 0.1M solution with similar absence of any oxidation wave, indicating depleting the solution from reducible indium species. Therefore, the electrodeposition was normally carried out at -0.76 V, -1.2 V and -1.6 V at 30°C on the 0.3 M InCl₃ solutions for all experiments to insure similar thermal condition. These potentials were chosen depending on the results of the cyclovoltammogram of 0.3M InCl₃ solution in ionic liquid as shown in Figure (3.2) which was scanned to -2.00V. This voltammogram showed that two reduction waves started at around -0.42V and around -1.00V. Therefore, the first potentiostatic reduction was carried out to illucidate the first reduction process and investigate the morphology of reduced particles at different deposition time. Another potentiostatic experiments were carried out to investigate the effect of increased potentials on the reduced indium cations and to investigate the second wave revealed in Figure (3.2). It is to be noticed that at the more negative potentials of the cyclovoltammetric experiment as shown in Figure (3.2) more than -1.6 V unstable curve was recorded indicating a production of gases, which were produced from reducing ionic liquid positive species. The following sections will illustrate the results obtained from the electroreduction of indium chloride in ammonium alum: urea room temperature ionic liquid at different potentials and time.

3.2.1-The effect of time on morphology of deposited indium at -0.76 V.

Long coating time was expected to influence the thickness of deposited metal and effected the aggregation of particles and their compaction .The effect of deposition time of indium at one, two, three and twenty four hours at -0.76V and 30°C was investigated in 1:5 mole ratio of ammonium alum: urea room temperature ionic liquid.

3.2.1.1- Scanning Electron Microscopy (SEM) of indium nanoparticles at different times

The surface morphologies of the deposits indium were examined with SEM and some typical micrographs are presented in Figure(3.3). These micrographs show crystal particles shaped with size ranging from 145nm to 362nm for deposited indium in one hour, from 155nm to 496nm for deposited indium in two hours, from 221nm to 500nm for deposited indium in three hours and from 254nm to 847nm for deposited indium in twenty-four hours. In the first, second and third hours the deposition of indium has appeared as layers of small particles. After twenty-four hours, the deposition of indium appeared as a flat layer of large particles shaped as a plate on top of the initial layer contains small particles of indium as shown in Figure (3.3.g). Also, it was found that the visual appearance of coating indium was dual, gray and silver after one , two , three and twenty-four hours respectively as shown in the corresponding optical photograph of the samples in Figure (3.3.b, d, f and h).
Chapter Three



(a)



(b)



(c)

(**d**)

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Chapter Three











Figure (3.3): SEM images of deposited indium on copper substrate in 1:5 mole ratio ammonium alum : urea room temperature ionic liquid, at -0.76 V, 30^{0} C after (a)1 h., (c) 2 h., (e) 3 h. and (g) 24 h. and the corresponding optical photograph of deposited indium on copper substrate showed after (b) 1 h., (d) 2 h., (f) 3 h. and (h)24 h.

3.2.1.2-Energy Dispersive X-ray Analysis(EDAX) of indium nanoparticles at different times

Energy dispersive x-ray analysis has been utilized to investigate the chemical composition of the sample, Figure (3.4) shows the typical EDAX spectrum of indium nanoparticles deposited on copper substrate. The peaks of indium nanoparticles have been appeared as M_{α} , $L_{(\alpha 1+\alpha 2)}$, $L_{\beta 1}$, $L_{\beta 2}$ and $L_{\gamma 1}$ at (0.4, 3.2, 3.4, 3.8 and 4)Kev which agreed with reported values published by B.G.Kumar and K.Muralidharan^[170] while the peaks of copper have been appeared as L_{α} , K_{α} and K_{β} at (0.9, 8.0 and 8.9)Kev which agreed with reported values published by R.A.Dar *et* al.^[171].The observed percentage of deposited indium increased with time as it increased from 7.5 At.% ,10.5 At. % , 21.9 At. % and 44.41 At.% at one , two ,three and twenty-four hours respectively. This indicated a linear correlation between the time and rate of indium deposition as shown in Table (3.1).



(a)

49



(b)



(c)

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(**d**)

Figure (3.4): EDAX spectra of deposited indium nanoparticles on copper substrate in 1:5 mole ratio ammonium alum: urea room temperature ionic liquid, -0.76 V, 30°C after different deposition time, (a)1h., (b)2h., (c)3h. and (d) 24h.

3.2.1.3-Atomic Force Microscopy (AFM) of indium nanoparticles at different times

AFM has been employed to investigate the topographic nature of the deposited indium particles in addition to the SEM results. Figure (3.5) demonstrate the 3-D images for one ,two , three hours and twenty fours samples which reveal an increase in roughness value (Ra) from (30.6nm) in one hour , (32.7nm) in two hours and (43.9nm) in three hours and (21.3nm) in twenty four hours of the deposited nanoparticles of indium is considered to be of smooth surface. When compare to superfinishing metal process and within the range of Fly cut or Ground aluminum^[172] which have Ra values of around100nm. In addition Ra of indium in this work are better than milled aluminum which has Ra value around 1000nm. The average height of those deposited indium have values of (179.61nm) in one hour increased to (183.98nm) in two hours then decreased to (161.82nm)

in three hours and then increased to (179.98nm) in twenty four hours as shown in Table (3.1).





(a)





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(**d**)

Figure (3.5): AFM images (contact mode) of indium nanoparticles deposited on copper substrate from 1:5 mole ratio ammonium alum :Urea room temperature ionic liquid at - 0.76V, and 30°C after different deposition time (a)1h.,(b)2h.,(c)3h. and (d) 24h.

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Table (3.1): Total grain, roughness, average size, average height,% of In coating , average diameter and particles range of deposited indium nanoparticles obtained from 1:5 mole ratio ammonium alum :Urea room temperature ionic liquid, - 0.76V, 30^oC, after different deposition time.

No.	Time	Total grain	Roughness (Ra) [nm]	Avg. size[nm ²]	Avg. Height [nm]	% of In from EDAX	Avg. Diameter [nm] from (AFM)	Particles range [nm] from(SEM)
1	1	293	30.6	13302.06	179.61	7.5	110.47	145 - 362
2	2	361	32.7	10854.90	183.98	10.5	95.09	155 - 496
3	3	749	43.9	86095.12	161.82	21.9	277.08	221 - 500
4	24	154	21.3	25440.55	173.19	44.41	179.98	254 - 847

3.2.2-Effect of the potential on the deposited indium morphology

The effect of cell potential on electrodeposition of indium was obtained at (-0.76 V, -1.2 V and -1.6 V) at one hour and a temperature of 30 $^{\circ}$ C in 1:5 mole ratio ammonium alum:urea room temperature ionic liquid.

3.2.2.1-Scanning Electron Microscopy (SEM) of indium nanoparticles at different potentials

To study the morphology of indium deposited, scanning electron microscopy (SEM) was employed. Figure (3.6) shows three SEM images of deposited indium films after applying a different cathodic potentials, -0.76 V,-1.2 V and -1.6 V, for one hour on copper substrate. It is worth noting that in the -1.6 V potential the deposition of indium nanoparticles was appeared as a layer of large shaped flat plate on top of a small particles layer of indium. While at -0.76 V the particles were only of a crystal shaped deposited on each other and -1.2 V. The particle size

ranged from 145nm to 362nm, from 250nm to 500nm and from 204nm to 633nm for electrodeposited indium at -0.76 V, -1.2 V and -1.6 V respectively as shown in Figure (3.6.a, c and d). Also, it was found that the visual appearance of electrocoated indium was dull at -0.76 V and gray at -1.2 V and -1.6 V as shown in the corresponding optical photograph of the samples in Figure (3.6.b, d and f).



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(b)

Chapter Three



(**c**)



(**d**)



Figure (3.6): SEM images of deposited indium nanoparticles on copper substrate from 1:5 mole ratio ammonium alum: urea room temperature ionic liquid, (a) -0.76 V, (c) -1.2 V and (e) -1.6 V. the corresponding optical photograph of deposited indium nanoparticles on Copper substrate showed at (b) - 0.76 V, (d) -1.2 V, and (f) -1.6 V.

3.2.3.2-Energy Dispersive X-ray Analysis(EDAX) of indium nanoparticles at different potentials

EDAX investigation of the chemical composition of samples obtained at (-0.76 V, -1.2 V and -1.6 V) potentials shown at Figure (3.7). From the EDAX spectrum, it indicated indium nanoparticles deposited on copper substrate. So, that the peaks of indium nanoparticles and peaks of copper have been mentioned in section (3.1.2). From these results it was observed that the percentage of deposited indium nanoparticles increased with increasing potential as it increased from 7.5 At.% to 10.22 At.% and to 15.85 At.% at -0.76V, -1.2V and -1.6V respectively.



(a)



(b)



(c)

Figure (3.7): EDAX spectra of deposited indium nanoparticles on copper substrate in 1:5 mole ratio ammonium alum: Urea room temperature ionic liquid, at different deposition potentials, (a) -0.76 V, (b) -1.2 V and (c) -1.6 V.

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Table (3.2) potentials, % of indium coating and particles range of deposited indium nanoparticles obtained in 1:5 mole ratio ammonium alum: urea room temperature ionic liquid.

No.	Potential (volt)	% of In from EDAX	Particles size [nm] from SEM
1	-0.76	7.5	145 - 362
2	-1.2	10.22	250 - 500
3	-1.6	15.85	204 - 633

It was found that the shape of the second layer that was appeared at -1.6 V for one hour has the same appearance of a second layer appeared at -0.76 V for twenty four hours. This might be said that the deposited large amounts of indium particles reached a limit on the copper substrate that was capable of forming a flat plate layer as shown in Figure (3.3.g) and (3.6.e).

3.3- X-Ray Diffraction (XRD) of indium nanoparticles

The XRD patterns from several electrodeposits prepared at a potential of -0.76 V for three hours and twenty four hours and electrodeposition at a potential -1.6 V for one hour are shown in Figure (3.8). In these experiments, the deposited metal shown clear XRD patterns that are consistent with tetragonsl crystal system of indium. The peaks that corresponds to the indium appeared at scattering angles (20) of 32.995, 36.361 and 39.165 were observed. The lattice parameters of the unit cell of indium sample are calculated as a=3.250 and c=4.944, in good agreement with the known lattice parameter for bulk indium (a=3.251 and c =4.954), which indicates that the nanoparticles have the same crystal structure as

that bulk indium^[173]. In addition, three peaks at 43.50° , 50.72° and 74.8° that correspond to the copper substrate were observed.



(a)



(b)



(c)

Figure (3.8): XRD of indium electrodeposits on copper substrate from anhydrous indium chloride solution in ammonium alum: urea room temperature ionic liquid at 30 °C (a) at -0.76 V and 3 h. ,(b) at -1.6 V and one h. and (c) at -0.76 V and 24 h.

3.4-Cyclic Voltammogram of tin chloride dihydrate

The cyclicvoltammogram of a suspended solution of 0.3 M of $SnCl_2.2H_2O$ was carried out to elucidate the electrochemical behavior of Sn^{2+} in ammonium alum: urea room temperature ionic liquid. This cyclovoltammogram is shown in Figure (3.9) which indicated a current flow at about -0.54 V versus quasi-silver wire reference electrode. When this solution was scanned at 50mV/sec toward the reductive values, a fast increase in current indicated an increase in the deposition rate of tin metal on the platinum working electrode. The maximum reduction peak of tin was recorded at -0.69 V against quasi silver wire where the rate was decreased until a reduction potential of -1.0 V. When a reverse scan was applied, indicated a decrease in the reduction rate until an oxidation of tin to tin(II) was recorded at -0.50 V against quasi silver wire with fast dissolution of tin. At a

maximum potential of -0.205 V versus quasi silver wire, the rate of current was decreased sharply indicates a very fast diffusion of tin into the ionic liquid reaching zero current at around -0.1 V. The standard redox potentials values for tin in aqueous solution is -0.14 V as reported by Petr Vanysek^[161]. This redox process can be summarized as:

 $\operatorname{Sn}^{2+} + 2e^{-} \longrightarrow \operatorname{Sn}$ reduction(3.9) $\operatorname{Sn} \longrightarrow \operatorname{Sn}^{2+} + 2e^{-}$ oxidation(3.10)

During the reverse scan, however, the current looped with that occur during the reduction scan in overpotential process revealing a nucleation process of tin on the platinum working electrode. The well defined redox process of the cyclovoltammogram indicated a reversible process of tin in this ionic liquid. The one signal reduction step of Sn^{2+} to Sn^0 observed in this work was in contrast to that reported by Pulletikurthi Giridhar *et* al.^[174] who reported the cyclovoltammogram of $SnCl_2$ in $[Py_{1,4}]$ TfO ionic liquid on polycrystalline gold electrode exhibits four reduction peaks(c_1 - c_4) similarly the cyclovoltammogram of $SnCl_2$ in $[Py_{1,4}]$ DCA ionic liquid on polycrystalline gold electrode shows three reduction peaks(c_1 - c_3) in the forward scan. Four oxidation peaks (a_1 - a_4) were clearly observed in the backward scan of the cyclovoltammogram on polycrystalline gold electrode for both reported ionic liquids and the difference between ionic liquids reduction peaks was related to the different nature of these ionic liquid.



Figure (3.9): Cyclovoltammogram of 0.3 M SnCl₂.2H₂O saturated Solution in ammonium alum: urea ionic liquid at 50m V scan rate using Ag wire(RE), Pt disc (WE) and Pt plate (CE) at 30°C

3.5-Electroreduction of tin in ammonium alum /urea room temperature ionic liquid:

The potentiostatic electroreduction of tin from the suspended solution of 0.3M SnCl₂.2H₂O in ammonium alum:urea room temperature ionic liquid at 30°C with a negative potential of -0.69. This potential was obtained from the cyclovoltammogram which indicated a maximum rate at around -0.69 V. See Figure (3.9).

3.5.1-Scanning Electron Microscopy(SEM) of tin nanoparticles

The SEM micrograph indicates the surface morphology of electrodeposited tin layer on copper substrate obtained at one, two and three hours at -0.7 V and 30°C. The deposited tin particles were shaped like a plate with some particles that of

spherical nodules with particles sizes ranged from 242nm to 484nm, 220nm to 441nm and 189nm to 472nm at one, two and three hours respectively as shown in Figure (3.10) and Table (3.3). At one hour the particles size was larger than those obtained at two hours, while at three hours the particles became more compact than they were at the one and two hours. The visual appearance of coated copper with tin was gray, at first ,second or third hours as shown in the corresponding optical photograph of the samples in Figure (3.10.b, d and f).which might be related to the particle shapes which disperse light allowing very small light reflection.



(a)

(b)

Chapter Three



(**c**)



(**d**)



(e)

(**f**)

Figure (3.10): SEM images of deposited tin nanoparticles on copper substrate from 1:5 mole ratio ammonium alum: urea room temperature ionic liquid, at -0.7 V and 30° C after different deposition time (a)1h., (c) 2h. and (e)3h., the corresponding optical photograph of deposited tin nanoparticles on copper substrate showed at (b) 1h., (d) 2h. and (f) 3h.

3.5.2-Energy Dispersive X-ray Analysis(EDAX) of tin nanoparticles

The obtained deposited samples were analyzed by EDAX to determine the elemental composition of the deposited metal. The EDAX analysis indicated the presence of small amounts of tin 3.9 At.% at one hour. However, the EDAX analysis showed that with an increase in deposition time, the amount of tin deposited increased to 11.19 At.% and 31.4 At.% at two and three hours respectively, as shown in Table (3.3). The peaks of tin have been appeared as $M_{\alpha}Sn$ and $L_{\alpha}Sn$ at (0.4 and 3.4) Kev. which agreed with reported values published by A.Chaurasia *et* al. ^[175] as shown in Figure (3.11)



(a)

65



(b)



(c)

Figure(3.11):EDAX spectra of deposited tin nanoparticles on copper substrate from 1:5 mole ratio ammonium alum:urea room temperature ionic liquid at -0.7 V and 30°C after different deposition time, (a)1h., (b)2h. and (c)3h.

3.5.3-Atomic Force Microscope(AFM) of tin nanoparticles

Atomic force microscopy has been used for surface observation and have provided information about the topography of coated tin particles. the values of roughness and average height for tin nanoparticles after different deposition time were (21.8nm and 163.85nm),(15.1nm and 140.53nm) and (9.61nm and 72.14nm) at one , two and three hours respectively, as shown in Table (3.3) and AFM images Figure (3.12).These values clearly indicate that the electrocoated tin on copper substrate is being smoother with time as the height of plated tin particles decreases with time, although having almost similar diameter. This also appears from the optical topographic investigation of the three samples which indicate a more compact deposition of tin at the three hours than the two or the one hour deposition.



(a)

(b)



(c)

Figure (3.12): AFM images (contact mode) of tin nanoparticles deposited on copper substrate from 1:5 mole ratio ammonium alum: urea room temperature ionic liquid at -0.7V, and 30°C after different deposition time (a)1h.,(b)2h.,(c)3h.

Table (3.3): Total grain, roughness, average size, average height, average diameter,% of Sn coating and particle size ranging of deposited tin obtained from 1:5 mole ratio ammonium alum: urea room temperature ionic liquid at -0.7 V and 30^{0} C, using different deposition time.

No.	Time	Total grain	Roughness (Ra) [nm]	Avg. size[nm ²]	Avg. Height [nm]	% of Sn from EDAX	Avg. Diameter From (AFM)	Particles size [nm] From(SEM)
1	1	684	21.8	5681.77	163.85	3.9	85.05	242-484
2	2	913	15.1	4265.30	140.53	11.19	73.69	220-441
3	3	733	9.61	5348.30	72.14	31.4	82.52	189-472

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3.5.4- X-Ray Diffraction (XRD) of tin nanoparticles

Due to the small amount of deposited tin on the surface of copper substrate, the x-ray diffraction was not helpfule to analysis the deposited tin and only indicated the peaks of copper as shown in Figure (3.13)



Figure (3.13): XRD of tin electrodeposits on copper substrate in ammonium alum: urea room temperature ionic liquid at three hours and 30 °C.

3.6-Cyclic Voltammogram of anhydrous antimony chloride The cyclovoltammogram of a suspended 0.3 M saturated solution SbCl₃ in the ionic

Every ovortaining rain of a suspended 0.5 M saturated solution $SDC1_3$ in the folice liquid with scan rate of 50mV is shown in Figure(3.14) when the potential was scanned negatively from the rest potential a rise in current was recorded with increasing the negative potential started at -0.5 V (c₁) potential showing another increases at -0.8 V (c₂). The first cathodic potential (c₁) is similar to the ionic liquid cathodic reduction. The current of the second cathodic reduction (c₂) increased with increasing the negative scanning potential, yet it did not show a metal potential reduction probably overlapping with the reduction of the positive ionic liquid species. However, when the scan was reversed to the positive potential, no curve was recorded for an oxidation. This might indicate an irreversible process of the reduction of Sb³⁺/Sb that occurred on the working electrode.



Figure (3.14): Cyclovoltammogram of saturated solution (0.3 M) SbCl₃ in ammonium allum: urea (1:5) ionic liquid and ionic liquid alone at 50 m V scan rate using Ag wire (RE), Pt disc (WE) and Pt plate (CE) at 30°C.

3.7-Electroreduction of antimony in ammonium alum /urea room temperature ionic liquid:

The potentiostatic electroreduction of antimony from the suspended solution of $0.3M \text{ SbCl}_3$ in ammonium alum:urea room temperature ionic liquid at 30°C and - 0.8 V was as deduced from the cyclovoltammogram. The experiments showed the effect of deposition time on the electroreduction of Sb^{3+} to Sb^0 .

3.7.1-Scanning Electron Microscopy (SEM) of antimony nanoparticles

The surface morphology of antimony electrodeposits was examined by SEM and the resulting micrographs are illustrated in Figure (3.15). The SEM of the deposit surface showed the morphology of the deposited antimony as a plate shaped particle with some particles like nodules at one and two hours, while at three hours the particles were of sand–like shaped. The particles size was found to range from 154nm to 462nm, from 227nm to 455nm and from 217nm to 435nm at one, two and three hours respectively, as shown in Table (3.4). This indicated no effect of the deposition time on the morphology of deposited antimony giving almost similar range of nanoparticle size The visual appearance of coated antimony was black as shown in Figure (3.15.b, d) and f). Which might be related to the particle shapes, which disperse light allowing very small light reflection.

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(a)





(c)



(**d**)

-



Figure (3.15): SEM images of deposited antimony nanoparticles on copper substrate from 1:5 mole ratio ammonium alum: urea room temperature ionic liquid at -0.7 V and 30° C after different deposition time (a)1h., (c) 2h. and (e) 3h., the corresponding optical photograph of deposited antimony nanoparticles on copper substrate showed at (b)1h., (d) 2 h. and (f) 3 h.

3.7.2-Energy Dispersive X-ray Analysis (EDAX) of antimony nanoparticles

The EDAX spectrum of antimony nanoparticles deposited on copper substrate has been used to investigate the chemical composition of the sample. The peaks of antimony metal have been appeared as M_{α} and L_{α} at (0.4 and 3.6) Kev which agreed with reported values published by H.P.S.Chauhan *et al.* ^[176] as shown in Figure (3.16).The EDAX analysis confirmed the presence of small amounts of antimony as 3.47 At.%, 3.95At.% and 4.47At.% at one ,two and three hours respectively as shown in Table (3.4). This indicated probably a limited soluble amount of SbCl₃ in the ammonium alum: urea ionic liquid and imply a very slow rate of SbCl₃ dissolution in ionic liquid sine only limited percentage of antimony was deposited at the two or the three hours of depositions compare 3.47 At.% at one hour with 3.95 At.% and 4.47 At.% at two and three hours respectively.



(a)



(b)

ſ



(**c**)

Figure(3.16):EDAX spectra of deposited antimony nanoparticles on copper substrate from 1:5 mole ratio ammonium alum:urea room temperature ionic liquid at -0.8 V and 30°C after different deposition time, (a)1h., (b)2h. and (c)3h.

3.7.3-Atomic Force Microscope(AFM) of antimony nanoparticles

AFM images of the coating antimony samples are shown in Figure (3.17). The roughness value (Ra) was (19.0nm) at one hour, decreased to (15.9nm) at two hours, while at three hours the roughness value increased to (26.9nm). These values indicated a very smooth surfaces comparable to superfinishing metal process and within the range of Fly cut or Ground aluminum^[172] which have Ra values of around100nm and better than milled aluminum which has Ra value around 1000nm. The average height of those deposited antimony have values of (154.53nm) at one hour decreased to (120.18nm) at two hours then increased to (159.33nm) at threehours. These values indicated that the electrocoated antimony on copper substrate varies with time as agreed to the result obtained from SEM.

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(a)

(b)



(c)

Figure (3.17): AFM images (contact mode) of antimony nanoparticles deposited on copper substrate from 1:5 mole ratio ammonium alum :urea room temperature ionic liquid at -0.8V, and 30°C after different deposition time (a)1h.,(b)2h.,(c)3h.

Table (3.4): Total grain , roughness, average size, average height,% of Sb coating and particle size of deposited antimony obtained from 1:5 mole ratio ammonium alum:urea room temperature ionic liquid at -0.8 V, 30° C, using different deposition time.

No.	Time	Total grain	Roughness (Ra) [nm]	Avg. size[nm²]	Avg. Height [nm]	% of Sb from EDAX	Avg. Diameter [nm] from AFM	Particles size[nm] from SEM
1	1	593	19.0	6585.75	154.53	3.47	91.57	154-462
2	2	523	15.9	7434.35	120.18	3.95	97.29	227-455
3	3	1058	26.9	3626.52	159.33	4.47	67.95	217-435

3.7.4- X-Ray Diffraction (XRD) of antimony nanoparticles

Due to the small amount of deposited antimony the surface of copper substrate, the x-ray diffraction was not helpfully to analysis the deposited metal and only to indicated the peaks of copper as shown in Figure (3.18)



Figure (3.18): XRD of antimony electrodeposits on copper substrate in ammonium alum: urea room temperature ionic liquid at three hours and 30 $^{\circ}\mathrm{C}$

3.8-Cyclic voltammogram of anhydrous indium chloride with tin chloride dihydrate

A mixture of 0.3 M InCl₃ and 0.3 M SnCl₂.2H₂O showed a saturated solution in ammonium alum: urea ionic liquid at 30°C. This solution was studied cyclovoltammetrically as shown in Figure (3.19). This Figure contains three cyclovoltammograms of 0.3 M InCl₃ and 0.3 M SnCl₂.2H₂O both alone in ammonium alum : urea ionic liquid as described in section (3.1) and (3.3)respectively. As the mixture was scanned in the negative direction at a scan rate of 50 mV/sec. The cyclovoltammogram of the mixture on working electrode exhibits two reduction peaks in the forward scan and two oxidation peaks in the backward scan. The first reduction $peak(c_1)$ is at a potential around -0.7 V expected to be responsible for reduction of tin as compared with red curve which have a reduction peak for tin in ammonium alum : urea ionic liquid at a potential of -0.69 V as shown in section (3.3) and the second reduction peak is at a potential around -1.1 V, most probably belongs to the reduction of bulk indium formed in cathodic part as compared to -1.0 V of 0.3 M InCl₃ in ammonium alum: urea ionic liquid as stated in section (3.1). While the two oxidation peaks appeared in backward scan, the first oxidation peak (a_1) at a maximum potential of -0.45 V and the second oxidation peak (a_2) appeared at a maximum potential of -0.047 V. It could be noticed that a UPD, as in InCl₃ alone, wave is seen in the cyclovoltammogram of the mixture and the reduction waves but it was occurred at a more negative than the reduction of indium chloride alone in ammonium alum : urea ionic liquid .While the second reduction wave was almost close to that of indium in the mixture or alone. However, the reduction wave of tin chloride dehydrate in the mixture was a more negative potential than the metal chloride alone in ionic liquid. To study these reductions a potentiostatic experiments were

important to evaluate the nature of the reduced metal(s) at their reduction waves. This will be covered in the following section.



Figure(3.19): Cyclovoltammogram of InCl₃ and SnCl₂.2H₂O alone and in mixture at 0.3 M each in ammonium alum : urea at scan rate of 50 m V using Ag wire (RE) , Pt disc (WE) and Pt plate (CE) at 30°C.

3.9-Electroreduction of a mixture of anhydrous indium chloride and tin chloride dihydrate in ammonium alum: urea room temperature ionic liquid

The potentiostatic electroreduction of indium and tin from a saturated mixture solution containing 0.3 M anhydrous indium chloride and 0.3 M tin chloride dihydrate in ammonium alum : urea room temperature ionic liquid is to obtain a codeposition mixture of these two metals for their important usage in bearing assembly, ballast, casting, step soldering, and radiation shielding^[154]. The reduction was carried out at two potentials -0.8 V and -1.1 V. These potentials were chosen depending on the results of the cyclovoltammogram of 0.3 M InCl₃ and 0.3 M SnCl₂.2H₂O mixture solution in ionic liquid

3.9.1-The effect of time on the morphology of codeposition of indium and tin from ammonium alum: urea ionic liquid at -0.8 V and -1.1 V

The visual appearance of co-electrodeposited indium and tin on copper substrate was found visually to be gray at one, two and three hours as shown in Figure (3.20.b, d and f). The surface morphology of co-electrocoated indium and tin on copper substrate at a potential of -0.8 V was examined by Scanning Electron Microscopy (SEM) as presented in Figure (3.20). The samples of co-electrocoated indium-tin were found to form smooth coating and well adhered on copper substrate. The particles were in nano size with sand - like shape of a particle size ranged from 143 to 429nm, from 107nm to 454nm and from 156nm to 444nm at one ,two and three hours respectively, as shown in Table (3.5).



(a)

(b)

Chapter Three











(e)

(**f**)

Figure (3.20): SEM images of codeposited Indium-tin nanoparticles on copper substrate from 1:5 mole ratio $[NH_4Al (SO_4)_2.12H_2O]$: urea ionic liquid, -0.8 V ,30°C after (a)1 h, (c) 2 h and (e) 3 h, and the corresponding optical photograph of codeposited Indium-tin nanparticles on copper substrate showed at (b) 1 h. ,(d) 2 h. and (f) 3 h.
The co-electrodeposition at -1.1 V showed visually gray samples similar to those obtained at -0.8 V after one, two and three hours as shown in Figure (3.21.b, d and f). The shape of the co-electrodeposited particles were homogeneous with two layers, at one hour of electrocoated indium-tin nanoparticles. The first layer contained smaller particles with crystal-like shape, while the particles of the second layer were larger with prism shape, the particles ranged from 169nm to 424nm for both layers. At two hours, the first layer contained smaller particles with crystal-like shape, while the second layer gave larger particles with random shape. The particles ranged from 154nm to 462nm for both layers. At three hours, the first and second layers contained particles with crystal-like shape but different in the size of particles, which ranged from 179nm to 446nm for both layers. as shown in Figure (3.21) and Table(3.5).



(a)

(b)













Figure (3.21): SEM images of codeposited Indium-tin nanoparticles on copper substrate from 1:5 mole ratio [NH₄Al (SO₄)₂.12H₂O]: urea ionic liquid, -1.1V, 30^{0} C after different deposition time (a)1 h., (c) 2 h. and (e) 3 h. and the corresponding optical photograph of codeposited Indium-tin nanoparticles on copper substrate showed at (b) 1 h, (d) 2 h and (f) 3 h.

3.9.2-Energy Dispersive X-ray Analysis of indium-tin nanoparticles

The electrocoated samples on copper substrates at -0.8 V and -1.1 V from the mixture solution of 0.3 M InCl₃ and 0.3 M SnCl₂.2H₂O were examined by Energy Dispersive X-ray Analysis (EDAX). Figure (3.22) represent the sample obtained at -0.8 V which showed that a nano particles of indium and tin were deposited on copper with the peaks of indium and tin have appeared as $M_{\alpha}Sn$, $M_{\alpha}In$, $L_{\alpha}In$ and L_{α} Sn at (0.4 , 3.2 and 3.4) respectively which agreed with reported values published by B.G Kumar and K.Muralidharan^[170] and reported values published by A. Chaurasia *et* al.^[175]. The percentage of codeposited indium-tin nanoparticles from -0.8V were estimated to be (2.62 At.% and 0.64 At.%), (4.13 At.% and 4.85 At.%) and (3.51At.% and 5.91 At.%) at one , two and three hours respectively.as shown in Table (3.5). The rate of deposited indium from the mixture was found to be smaller than when the indium was deposited from 0.3 M indium chloride solution alone in ionic liquid. This could be induced by the presence of tin chloride.



(a)

85



(b)



(c)

Figure(3.22):EDAX spectra of codeposited indium-tin nanoparticles on copper substrate from 1:5 mole ratio[NH₄Al(SO₄).12H₂O]:Urea ionic liquid, -0.8V,30°C after different deposition time, (a)1h., (b)2h. and (c)3h.

At a potential of -1.1 V, the percentage of codeposited indium-tin nanoparticles were shown to be (5.12 At.% and 3.58 At.%), (13.05 At.% and 14.5 At.%) and (32.58 At.% and 28.4 At.%) at one, two and three hours as shown in Table(3.6). The percentage of codeposited indium-tin nanoparticles was found to be around two times at the two hours and about three times at the three hours than the deposition percentage at one hour. The EDAX peaks of indium and tin metals from -0.8V is smaller compared with those obtained from -1.1V as shown in Figure (3.23), this agree with the large percentage of codeposited indium and tin with a normal increase in codeposited indium-tin with increasing deposition potential.



(a)

87



(b)



(c)

Figure(3.23):EDAX spectra of codeposited indium-tin nanoparticles on copper substrate from 1:5 mole ratio[NH4Al(SO4).12H2O]:urea room temperature ionic liquid, -1.1V,30°C after different deposition time, (a)1h., (b)2h. and (c)3h.

3.9.3-Atomic Force Microscope (AFM) of indium-tin nanoparticles

AFM images of electrocoating indium-tin on the copper substrate at a potential of -0.8V are shown in Figure (3.24). The average height of the electrocoated indiumtin nanoparticles increased gradually with time, the average height 167.18nm, 176.63nm ,177.58nm at one , two and three hours respectively. The roughness values were found to be 25.2nm, 31.2nm and 23nm at one, two and three hours respectively. The roughness values was consider to be closely similar and indicated a very smooth surfaces as compared with reported values published by P.Young *et* al.^[172] which have Ra values around 100nm for superfinishing metal process and within the range of Fly cut or Ground aluminum and very much better than milled aluminum which has Ra value around 1000nm.





(a)

(b)



(c)

Figure (3.24): AFM images (contact mode) of indium-tin nanoparticles codeposited on copper substrate from 1:5 mole ratio [NH₄Al(SO₄)₂.12H₂O]:urea ionic liquid at - 0.8V, and 30°C after different deposition time (a)1h.,(b)2h.,(c)3h.

At the potential of -1.1 V, the codeposited indium-tin nanoparticles on copper substrate are shown in Figure (3.25). The roughness values were 38.4nm, 15.6nm and 29.6nm at one ,two and three hours respectively The average height of the electrocoated indium-tin nanoparticles were 203.06nm,139.11nm and 167.78nm at one, two and three hours respectively as shown in Table (3.6)

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(a)

(b)



(c)

Figure (3.25): AFM images (contact mode) of indium-tin nanoparticles codeposited on copper substrate from 1:5 mole ratio [NH₄Al(SO₄)₂.12H₂O]:urea ionic liquid at – 1.1V, and 30°C after different deposition time (a)1h.,(b)2h.,(c) 3h.

Table (3.5): Total grain, roughness, average size, average height, average diameter,% of(In &Sn) coating and particle size of codeposited indium-tin obtained from 1:5 mole ratio $[NH_4Al(SO_4).12H_2O]$:urea room temperature ionic liquid, -0.8 V, 30^oC, using different deposition time.

No.	Time	Total grain	Roughness (Ra) [nm]	Avg. size[nm²]	Avg. Height [nm]	% of In from EDAX	% of Sn from EDAX	Particles Diameter [nm] from AFM	Particles Range [nm] from SEM
1	1	416	25.2	9390.63	167.18	0.64	2.62	91.85	143-429
2	2	374	31.2	10447.32	176.63	4.13	4.85	95.46	107-454
3	3	462	23	8411.65	177.58	3.51	5.91	92.84	156-444

Table (3.6): Total grain, roughness, average size, average height, average diameter, % of (In &Sn) coating and particle size of deposited indium-tin obtained from 1:5 mole ratio [NH₄Al(SO₄).12H₂O]:urea room temperature ionic liquid, - 1.1 V, 30^{0} C, using different deposition time.

No.	Time	Total grain	Roughness (Ra) [nm]	Avg. size[nm²]	Avg. Height [nm]	% of In from EDAX	% of Sn from EDAX	Avg. diameter [nm] from AFM	Particles range [nm] from SEM
1	1	362	38.4	10845.28	203.06	5.12	3.58	117.51	169-424
2	2	486	15.6	8000.81	139.11	13.05	14.5	100.93	154-462
3	3	320	29.6	12250.18	167.78	32.58	28.4	124.89	179-446

From the above results of the electroreductions of the mixture of anhydrous indium chloride and tin chloride dihydrate in ammonium alum: urea ionic liquid would explain the cyclovoltammogram as shown in Figure (3.19). Hence the first reduction peak would be explained as a reduction of tin metal mainly .while the second wave was indicated as a coreduction of both metals indium and tin. This also shown the percentage of codeposition of these metals can be controlled with the limit of this experiment between 80% for tin and 20% for indium at -0.8 V to 41% for tin and 59% for indium at -1.1 V , both for one hour. In addition, it can also be seen that the limit of electrodeposition of these two metals in ammonium

alum: urea ionic liquid would influence the percentage of codeposition of metals as shown in Table (3.5) and (3.6).

3.9.4- X-Ray Diffraction (XRD) of indium and tin nanoparticles

Due to the small amount of codeposited indium-tin metals on the surface of copper substrate, the x-ray diffraction was not helpfully to analysis the deposited metals and only to indicated the peaks of copper as shown in Figure (3.26)



Figure (3.26): XRD of indium-tin codeposits on copper in ammonium alum: urea room temperature ionic liquid at three hours and 30 °C.

3.10-Cyclic voltammogram of a mixture of anhydrous indium chloride with anhydrous antimony chloride

A mixture solution of 0.3 M InCl₃ and 0.3 M SbCl₃ showed a suspended solution in ammonium alum: urea ionic liquid at room temperature. This solution was studied cyclovoltammetically as shown in Figure (3.27). As this solution was scanned negatively from zero potential, it showed one curve of a reduction characterized with very small rate of current as shown in the blue curve in Figure (3.27), compared to the faster reduction rate observed with indium chloride alone in the same ionic liquid as shown in the blue curve in Figure (3.27). The reduction potential started at -0.76 V and the scan was carried out until -1.6 V. The small rate of reduction probably was due to the initial deposition of antimony as shown in the red curve in Figure (3.27), which could prevent the nucleation of indium on the electrode. A more expected reason could be related to the mobility of indium cations, which were hindered by the suspended antimony chloride as the latter was found to be sparingly soluble in the ionic liquid. The slow reduction wave of the mixture observed to be coupled with a slow oxidation wave. This was observed when the scan was revered to the opposite direction when a slow oxidation wave was recorded in blue curve in Figure (3.27) with a very small rate of dissolution of metals into the ionic liquid. Again, the latter might also be effected by the suspended antimony chloride suspended solution.



Figure (3.27): Cyclovoltammogram of InCl3 and SbCl3 alone and mixture in ammonium alum : urea ionic liquid at 0.3 M with scan rate of 50 m V , Ag wire (RE) , Pt disc (WE) and Pt plate (CE).

3.11-Electroreduction of a mixture of anhydrous indium chloride and anhydrous antimony chloride in ammonium alum: urea room temperature ionic liquid

The task of potentiostatic reduction of metals from the mixture of 0.3 M anhydrous indium chloride and 0.3 M anhydrous antimony chloride which was suspended solution in ionic liquid is to investigate the probability of obtaining a codeposition of these two metals for their important usage in transistors and microchips^[177]. However, the electrode position was carried out as in indium chloride solution alone in the ionic liquid as shown in (section 3.2) at two potentials -0.8 V and -1.6 V in the ionic liquid at 30°C for one, two and three hours.

3.11.1-The effect of time on the morphology of codeposition of indium and antimony from ammonium alum:urea ionic liquid at - 0.8 V and -1.6 V

The visual appearance of coated samples on copper substrate was silver at one, two and three hours as shown in Figure (3.28.b, d and f).and the surface morphology of electrocoated layer on copper substrate at a potential of -0.8 V was examined by scanning electronic microscopy as presented in Figure (3.28). At one hour, the particles were nano size of sand- like shaped with particles size ranged from 181nm to 399nm, while at two hours the particles size ranged from 268nm to 446nm. However, at three hours the deposition formed a large particles in addition to deposited particles size ranged from 110nm to 442nm as shown in Table (3.7).





(a)

(b)

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(c)







(e)

(**f**)

Figure (3.28): SEM images of deposited indium nanparticles on copper substrate in 1:5 mole ratio ammonium alum: urea room temperature ionic liquid, -0.8V, 30^oC after (a)1h., (c)2h. and (e) 3 h., and the corresponding optical photograph of deposited indium nanparticles on copper substrate showed at (b) 1h., (d) 2h. and (f) 3h.

However, the electrodeposition at -1.6 V visually appearance as gray after one, two and three hours as shown in Figure (3.29.b), d) and f). The shape of particles at one hours were homogeneous with two layers with, first layer contained smaller particles with sand-like shape. While the particles of the second layer were larger

with flat-plate shape. The particles size ranged from 195nm to 469nm for both layers. At two hours, the coating on the substrate was the substrate with needle shape and the particles size ranged from 183nm to 441nm. However, at three hours, the particles were of sand shapes but with a particles size ranged from166nm to 491nm, as shown in Table (3.8). The flat shape particles electrodeposited from the mixture of 0.3 M $InCl_3 - 0.3$ M $SbCl_3$ at -1.6 V in ammonium alum : urea ionic liquid was found to be similar to that obtained from the electrodeposition of 0.3 M InCl₃ alone in the same ionic liquid and similar potential (-1.6 V). This might indicate the deposition from the mixture also containing indium metal and not effected by the presence of antimony in the solution. In fact, the percentage of indium in the deposition layer was found 15.77% while the deposition of antimony was only 4.08%. The latter percentage of antimony was similar to that obtained at -0.8 V for anhydrous antimony chloride alone in ionic liquid at one hour. While indium percentage was close to that obtained at -1.6 V for one hour with similar shape. However, the electrodeposition metals at two hours shows a different particles shape (needle) with increased amount of both metals to 25.72% and 8.12% of indium and antimony respectively. The third hours gave only small increase in the concentration of indium, probable due to depleted solution and the limitation of electrodeposited indium metal while antimony showed expectedly zero percentage as the latter had limited solubility in the ionic liquid.

Table (3.8) indicate that it could be possible to electrodeposit both metals in the percentage indicated in the table and it seems that indium would be deposited in much larger amount (up to 28.14%) than antimony (up to 8.12%) at -1.6 V However, the particles size of all deposition were of nano size with smallest lower range of 166nm at three hours but with almost similar large size of between 441nm-491nm.

Chapter Three



(a)



(b)



(**c**)



(**d**)



Figure (3.29): SEM images of codeposited indium-antimony nanoparticles on copper substrate in 1:5 mole ratio ammonium alum: urea room temperature ionic liquid, -1.6V, $30^{\circ}C$ after (a)1h., (c) 2h. and (e) 3 h., and the corresponding optical photograph of codeposited indium-antimony nanoparticles on copper substrate showed at (b) 1h., (d) 2h. and (f) 3h.

3.11.2-Energy Dispersive X-ray Analysis (EDAX) of codeposited indium-antimony nanoparticles

The electrodeposited samples on copper substrates at -0.8 V and -1.6 V from the mixture solution of 0.3 M InCl₃ and 0.3 M SbCl₃ were examined by Energy Dispersive X-ray Analysis (EDAX). Figure (3.30) represent the sample obtaining at -0.8 V which showed that a nanoparticles of indium were the only deposited metal on copper with the peaks of indium nanoparticles have appeared as M_{α} , $L(_{\alpha1}+_{\alpha2})$, $L_{\beta1}$, $L_{\beta2}$ and $L_{\gamma1}$ at (0.4 , 3.2 , 3.4 , 3.8 and 4)Kev which agreed with reported values published by B.G.Kumar and K.Muralidaran^[170] while the peaks of copper have been appeared as L_{α} , K_{α} and K_{β} at (0.9 , 8.0 and 8.9)Kev which agreed with reported values published by R.A.Dar *et* al.^[171].The percentage of deposited indium nanoparticles increases with time as it was 5.11 At.% at one hour and increased to 60.48 At.% and 74.21 At.% at two and three hours respectively as shown in Table (3.7). The deposited indium from the mixture was

found to be larger than when the indium was deposited from 0.3 M indium chloride solution alone in ionic liquid. It was found to be around six times at the two hours (compare 60.48 At.% with 10.5 At.%) and about five times at the three hours(compare 74.21 At.% with 21.9 At.%) although it was at the first hour with similar metal percentage rate from indium solution alone. This could be induced by the presence of antimony chloride, yet the latter was not deposited at this potential in contrast to the small deposition of antimony (4.81 At. %) from 0.3 M antimony chloride alone in ionic liquid.



(a)

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(b)



(c)

Figure(3.30):EDAX spectra of deposited indium nanoparticles on copper substrate in 1:5 mole ratio ammonium alum:urea room temperature ionic liquid, -0.8V,30°C after (a)1h., (b)2h. and (c)3h.

At the potential of -1.6 V, the EDAX have indicated that both indium and antimony nanoparticles were deposited on copper substrate. The peaks of indium and antimony have been appeared as $M_{\alpha}Sb$, $M_{\alpha}In$, $L_{\alpha}In$ and $L_{\alpha}Sb$ at (0.4, 3.2 and 3.6) respectively which agreed with reported values published by B.G.Kumar and K.Muralidharan^[170], H.P.S.Chauchan *et* al.^[176]. The percentage of codeposited indium-antimony nanoparticles were showed to be (15.77At.% and 4.08 At.%), (25.72 At.% and 8.12 At.%) and (28.14 At.% and 0.00At.%) at one, two and three hours as shown in Figure (3.31) and Table (3.8). At first hour, the amount of the electrodeposited indium from the mixture was similar to that obtained from indium chloride solution alone in ionic liquid at similar time (compare Table 3.1 with Table 3.8). In addition it showed, an increase with time but with a much slow rate than at -0.8 V. The latter could be related to the codeposition of antimony metal with indium. The codeposited antimony nanoparticles also increased with time from 4.08 At.% to 8.12 At.% but showed 0.00 At.% at three hours probably due to depleted solution.



(a)

104

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(b)



(c)

Figure (3.31): EDAX spectra of codeposited indium-antimony nanoparticles alloy on copper substrate in 1:5 mole ratio ammonium alum:urea room temperature ionic liquid, -1.6 V, 30°C after (a)1h., (b)2h. and (c)3h.

3.11.3-Atomic Force Microscope (AFM) of indium-antimony nanoparticles

AFM images of electrocoating indium on the copper substrate at a potential of -0.8V are shown in Figure (3.32). The roughness values were found to be 31.2nm, 23nm and 25.2nm at one, two and three hours respectively, which is considered as convergent values. The average height of the electrocoated indium nanoparticles were 176.63nm, 177.58nm and 167.18nm at one, two and three hours respectively as shown in Table (3.7). The roughness values were considered to be comparable and indicated a very smooth surfaces as compared with reported values published by P.Young *e*t al.^[172] which have Ra values around 100nm.



(a)

(b)



(c)

Figure (3.32): AFM images (contact mode) of indium nanoparticles deposited on copper substrate in 1:5 mole ratio ammonium alum:urea room temperature ionic liquid at –0.8V, and 30°C after (a)1h., (b)2h. and (c)3h.

At a potential of -1.6 V, the electrocoated indium-antimony at different time on copper substrate are shown in Figure (3.33). The roughness values were 34.6nm, 25.2nm, and 30.2nm at one, two and three hours respectively. The average height of the electrocoated indium-antimony nanoparticles alloy were 187.13nm, 173.68nm and 177.09nm at one, two and three hours respectively as shown in Table (3.8)



(b)

(a)



(c)

Figure (3.33): AFM images (contact mode) of indium-antimony nanoparticles deposited on copper substrate in 1:5 mole ratio ammonium alum: urea ionic liquid at -1.6V, and 30°C after (a)1h., (b)2h. and (c) 3h.

Table (3.7): Total grain, roughness, average size, average height, average diameter,% of In coating and particle size of deposited indium obtained in 1:5 mole ratio ammonium alum: urea room temperature ionic liquid, -0.8 V, 30^oC, using different deposition time.

No.	Time	Total grain	Roughness (Ra) [nm]	Avg. size[nm ²]	Avg. Height [nm]	% of In from EDAX	Avg. diameter [nm] from AFM	Particles range [nm] from SEM
1	1	374	31.2	10447.32	176.63	5.11	115.33	181-399
2	2	462	23	8411.65	177.58	60.48	103.49	268-446
3	3	416	25.2	9390.63	167.18	74.21	109.35	110-442

Table (3.8): Total grain, roughness, average size, average height, % of (In&Sb) coating and particle size of codeposited indium-antimony obtained in 1:5 mole ratio ammonium alum: urea room temperature ionic liquid, -1.6 V, 30^oC, using different deposition time.

No.	Time	Total grain	Roughness (Ra) [nm]	Avg. size[nm ²]	Avg. Height [nm]	% of In from EDAX	% of Sb from EDAX	Avg. diameter [nm] from AFM	Particles Range [nm] from SEM
1	1	166	34.6	23630.40	187.13	15.77	4.08	172.89	195-469
2	2	167	25.2	23476.34	173.68	25.72	8.12	173.46	183-441
3	3	220	30.2	17819.56	177.09	28.14	0.00	150.63	166-491

3.11.4- X-Ray Diffraction (XRD) of indium –antimony nanoparticles

Due to the small amount of deposited antimony on the surface of copper substrate , the x-ray diffraction was not helpfully to analysis the deposited metal and only to indicated the peaks of copper as shown in Figure(3.34)



Figure (3.34): XRD of indium-antimony codeposits on copper in ammonium alum: urea room temperature ionic liquid at three hours and 30 °C.

Conclusions

From the obtained results for this work, it may conclude that:

- 1. Ammonium alum: urea ionic liquid in the mole ratio of 1:5 was found to be a good electrolyte medium to carry out redox reaction of indium, tin, antimony or mixture of indium with either tin or antimony.
- 2. In³⁺ was reduced to In⁰ at a bulk deposition potential of 1.00 V and oxidized from In⁰ to In³⁺ and dissolute back in ionic liquid.
- 3. Sn²⁺ was also founed to be reduced to Sn⁰ at -0.69 V and dissolved back into ionic liquid.
- Sb³⁺ was found to be reduced to Sb⁰ metal at-0.8 V but note oxidized to Sb³⁺
- 5. Both In/Sn and In/Sb were codeposited as a mixture with different wt.% depending on reduction potential.
- 6. All deposited metal or their mixture were of a nano scale size with very smooth surfaces and good adhesion on copper substrates.
- Deposited indium metal was of tetragonal crystal system of (a=3.251 and c=4.954).

Future Work

- It is necessary to increase the solubility of tin chloride dihydrate (SnCl₂. 2H₂O) and anhydrous antimony chloride (SbCl₃) by either heating the solution or using stable metal salt that is soluble in the ionic liquid.
- 2. Investigating the morphology of the deposition of metals at different potentials.
- 3. Carrying an investigation to concentrate on the possibility of obtaining an alloys from above metals by focusing on the cyclovoltammogram to determine the right potential of alloy formation, if occurred.

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الخلاصة

اكتسبت السوائل الايونية المستقرة في درجة حرارة الغرفة نموا هائلا خلال السنوات الأخيرة للوصف المتميز التابع لها مثل عدم التطاير وكوسط مصمم للتطبيقات الكيميائية والصناعية بالإضافة الى ذلك عنصر الانديوم له تطبيقات في الأجهزة الالكترونية والضوئية، معادن القصدير والأنتيمون لها مقاومة جيدة للتآكل وفي الخصائص البصرية على التوالي. وقد استخدم السائل الايوني شب الامونيوم: يوريا بنسبة مئوية (1:5) كوسيلة للتحقيق في سلوك وإمكانية الحصول على المعدن النقي ومزيج من المعادن من كلوريدات الانديوم اللامائية ، كلوريدات القصدير ثنائي الماء و كلوريدات الأنتيمون اللامائية وقد أجريت هذه الدراسة بمساعدة تحليل حيود الأشعة السينية (XRD) , المجهر الماسح الالكتروني (EDAX), المتشنتة (EDAX) لتحديد ووصف فعالية المعادن وترسب جسيمات المعدن.

كل العناصر اما لوحدها او كخليط أعطت طبقة مترسبة من الجسيمات النانوية على ركيزة النحاس.

تم الحصول على سطح أملس جدا مع الحد الأقصى للخشونة بحوالي 34.6تابع للانديوم والأنتيمون بعد ساعة واحدة من الترسب الكهربائي بفولتية 1.6 V-.

وفي الوقت نفسه، الترسب الكهربائي على ركيزة النحاس للانديوم ,القصدير والانتيمون أو خليط من (الإنديوم والقصدير) و (الإنديوم والأنتيمون) كلها أظهرت زيادة في كميات الترسيب مع مرور الوقت. وقد تتأثر المورفولوجيا أيضا بسبب وقت الترسيب واشكال الجسيمات كانت مختلفة من بداية الترسيب التابع للانديوم او خليطه مع القصدير او الانتيمون في ساعة واحدة من تلك في ثلاث ساعات.

تم الحصول على ترسب الجزء الأكبر من الإنديوم في V 1.00- بينما حصل على القصدير في V 0.7 -والأنتيمون في V 0.8-

ومع ذلك، فقط تم الحصول على خليط الإنديوم مع القصدير أو الإنديوم مع الأنتيمون مع السيطرة على الكميات المترسبة بالسيطرة على فولتية الترسيب لهذا ترسب الإنديوم والقصدير اظهر %wt. 80 من الترسب تابعة للقصدير و wt.% 20 للإنديوم من تجربة ثابتة الفولتية في V 0.8- في حين بفولتية

1.1V- انخفضت نسبة القصدير إلى %wt. وازدادت نسبة الانديوم الى % 41 wt في المقابل

خليط من الإنديوم والأنتيمون اظهر %.wt 100 تابعة للانديوم من التجربة بفولتية V 0.8- بينما تم الحصول على %.wt 79.5 wt انديوم و %.wt 20.5 أنتيمون بفولتية V 1.6-.



جمهورية العراق وزارة التعليم العالي والبحث العلمي جامعة النهرين كلية العلوم قسم الكيمياء

الترسيب الكهربائي للانديوم القصدير رالانتيمون على

النحاس من السائل الايوني

رسالة مقدمة إلى كلية العلوم/ جامعة النهرين كجزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

من قِبَلْ الطالبة أزل أسامة أحمد بكالوريوس ٢٠١٤

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رمضان.۱٤۳۸

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