

# Morphology of Electrodeposited Aluminium Metal from Aluminium Chloride-Urea Room Temperature Ionic Liquid (RTIL) at Variable Parameters

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**Abstract:** *Electrodeposition of aluminium on copper substrate from aluminium chloride / urea ionic liquid (AlCl<sub>3</sub>: Urea) as electrolyte was conducted at variable conditions. Protected by layer of decan on the top of the liquid under statistic air. The deposit microstructure was monitored by changing temperature, mole ratio, potential and deposition time. The surface morphology of deposited aluminium was investigated by visual microscop Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Energy Dispersive X-ray analysis (EDAX). The effect of changing parameters on the morphology and microstructure of deposit was systematically studied. Results showed that the appearance and the deposit microstructure changed as a function of temperature mole ratio, time and potential. Current density also found to increase with previous parameters except time.*

**Keywords:** ionic liquids, electroplating, deposition aluminium metal. Aluminium chloride /urea ionic liquids, RTIL

## 1. Introduction

Aluminium coating play an important role in modern industries as a light material in automotive, ship, planes, food and packaging industries as well as for decorative purposes. The high corrosion resistance of Al against chemical and atmospheric attack due to the formation of oxide layers as a result of exposure to air makes it valuable coating material for many metals. The good adherence, slightly self-corrosive, silverish in color and easily polished, coating with high reflectivity of light and heat so it can be used for solar energy utilization, the thermal insulation of buildings and the development of various optical devices [1].

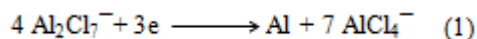
Hall-Héroult process is still the main industrial method for primary aluminum production. Aluminium can be recovered in this method from ores but this method is not suitable to coat other metals by aluminium because the electrolysis is carried out at 1000 °C, a temperature at which cryolite (Na<sub>3</sub>AlF<sub>6</sub>) and aluminium are in the liquid state [2]. (In crude aluminium production energy costs is the key factor. The Hall- Héroult process is known to be highly energy consuming, the high temperatures necessary for keeping the cryolite molten is responsible for this large electricity demand. Typical cells use a potential of 4 to 5 volts and a current of 300,000 amperes. Although the introduction of this process since 1886s, the significant improvements in energy efficiency have been made but the continually increasing cost of electricity did not allowed for major cost reductions of the production process [3]).

Currently, there are several methods available for aluminium plating such as hot dipping [4,5], thermal spraying [6], sputter deposition [7,8], vapor deposition [9,10] and electrodeposition [11],but all of these methods except electrodeposition are expensive, performed at elevated temperatures which may damage the specimens,

low dissolving capability of Al salts, high volatility, flamability and not suitable to get a thin aluminium films. However, it was reported that electrodeposition was employed successfully to get a thin aluminium film with higher purity and lower porosity, the coating has a good corrosion resistance and the thermal stress can be avoided since electroplating process can be carried out below 180 °C [12]. Aluminium cannot be electrodeposited from an aqueous solution because of its reactivity ( $E^{\circ} = -1.67$  V vs. normal hydrogen electrode NHE). The electrodeposition process would be restricted by hydrogen evolution at the cathode surface; consequently, aluminium can only be electrodeposited from non-aqueous aprotic electrolytes such as molten salts and organic solvents. Many of these electrolytes are sensitive to air and moisture so that the electrodeposition process must be carried out in inert atmosphere such as argon or nitrogen gas [12]. Many high temperature inorganic molten salts like NaCl-KCl [13], AlCl<sub>3</sub>-NaCl [14,15] and AlCl<sub>3</sub>-NaCl-KCl [16-18] have been investigated for the electrodeposition of Al, yet these have many disadvantages such as narrow electrochemical window, low dissolving capability of aluminium salt, highly corrosive natures and high experimental temperature which lead to high energy consumption caused to the necessity to find novel electrolytes have mild operating condition.

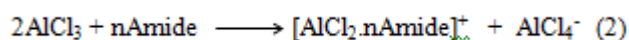
Over the last decades, aluminium coating from room temperature ionic liquid (RTIL) has received considerable attention. RTILs have many fascinating properties, including excellent thermal and chemical stability, negligible vapor pressure, low melting point, high electrical conductivity, broad liquid range, wide electrochemical window (4.5-6v), and ability to dissolve various organic, inorganic and organometallic compounds [19]. These attractive properties make RTILs play a vital role in the electrochemistry field.

Chloroaluminate ILs are the most frequently studied systems [20-23]. These ILs are mixtures of aluminium chloride and an organic halide (RX) and display adjustable Lewis acidity depending on the molar ratio of  $\text{AlCl}_3$  to RX [24]. Previous research show that electrodeposition of Al can only be performed under the Lewis acidic condition, in which the electroactive  $\text{Al}_2\text{Cl}_7^-$  ions are the only reducible species from which aluminium can be electrodeposited [25] according to the following reaction:



The electrodeposition was performed on various substrates such as tungsten [27], platinum [21,26], gold [21,26], copper [27], glass carbon [21] and mild steel [28]. However, chloroaluminate ionic liquids suffered from the highly reaction with moisture and thus the process required strict controlled inert conditions.

Few years ago it was reported that the addition of simple amide (urea or acetamid) to anhydrous  $\text{AlCl}_3$  caused the formation of a liquid of the form  $[\text{AlCl}_2 \cdot n\text{Amide}]^+ \text{AlCl}_4^-$ , the materials thus produced is liquid over a wide temperature range [29]. IL is relatively insensitive to moisture and has the properties of ionic liquid. This is shown to be a suitable medium for the electrodeposition of aluminium in the mole ratio ranged between 1: 1 to 2: 1  $\text{AlCl}_3$ : Urea respectively. The reaction that occurs to produce the aluminium based ionic liquid is:



Lewis acid nature of this liquid was also studied [30], and said that the positive Lewis acidic species can undergo an acid-base reaction with added Lewis basic ions such as Cl.

The aim of this work was to use this ionic liquid to investigate the deposition of aluminium metal on copper substrate and investigated the effect of changing parameters such as temperature, mole ratio, potential and deposition time on the morphology of deposited aluminium with the aid of Scanning Electron Microscopy SEM, Atomic Force Microscopy AFM, Energy dispersive x-ray analysis EDAX.

## 2. Experimental Work

### 2.1 Chemicals and General Procedure

Anhydrous aluminium chloride, (98% obtained from Fluka) and urea, (99.5% obtained from THOMAS BAKER) were used to prepare the aluminiumchloride: urea ionic liquid within 2: 1 to 1: 1 mole ratios to insure the formation of the ionic liquid [29]. A layer of decane can be added on the top of the liquid making protective top layer from air. Cathode copper metal sheet of (60mm $\times$ 10mm $\times$ 1mm) with an immersed part of 20mm length in ionic liquid, and an anode of aluminium mesh with (30mm diameter) were used. The cathode was rubbed with sand paper followed by rinsing with deionised water, then plunged in to 0.5% NaOH, and rinsed with water

then immersed in 0.5% HCl and rinsed with deionized water and acetone sequentially. The anode was abraded with iron brush followed by rinsing with deionized water and dipped it in to 0.5% NaOH, deionized water, 0.5% HCl, deionized water and finally rinsed with acetone. After deposition, specimen when removed from the ionic liquid was directly treated by dipping it in toluene until all ionic liquid was removed and then rinsed with n-propanol (99.5% obtained from BDH), acetone (99.5% obtained from BDH ) respectively and finally dried and stored for further analyses.

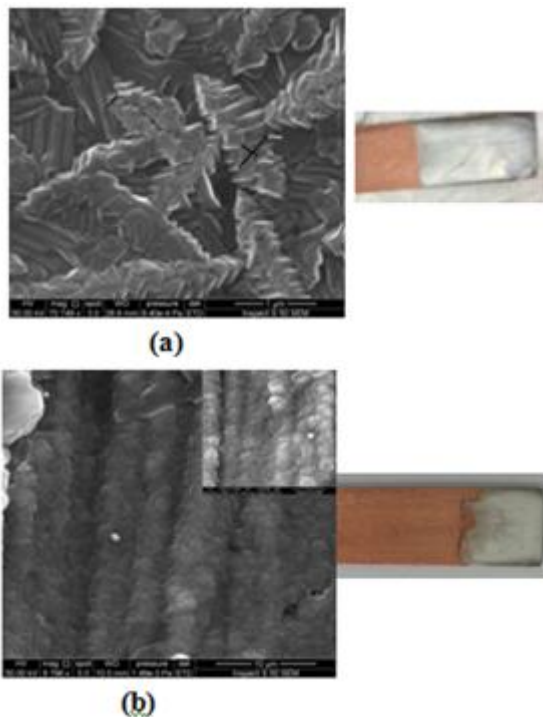
### 2.2 Measurements

The surface morphology of specimens of aluminium coatings on copper substrate was investigated with a high-resolution field emission scanning electron microscopy (INSPECT S50), the surface topography of samples were analyzed by atomic force microscopy (AFM) (AA2000, Angstrom Advanced Inc.) contact mode. The (X Flash 6110) Bruker EADX was used in conjunction with SEM. This was used for determination of the composition of samples surface and the (OLYMPUS BX 51-P POLARIZING MICROSCOPE) was used for visual observation. The (Thurlby 15V-4A, England) power supply was used to control the current and the potential of electrodeposition process.

## 3. Results and Discussion

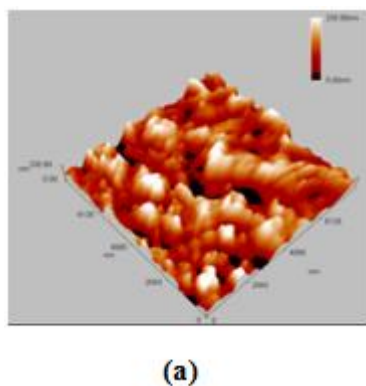
### 3.1 Effect of Mole Ratio of Electrolyte on Morphology

The content of  $\text{AlCl}_3$  in the electrolyte plays an important role in the electroplating process as it determines the properties of the electrolyte. For chloroaluminate, the molar ratio of the mixture changes the liquid nature thus can be classified as basic, neutral or acidic in sense of Lewis acidity. In the neutral 1: 1 melt Al present as  $\text{AlCl}_4^-$  ions which cannot be reduced whereas, in the 2: 1 melt it is present as  $\text{Al}_2\text{Cl}_7^-$ . In melts having a molar ratio between 1: 1 and 2: 1, both  $\text{Al}_2\text{Cl}_7^-$  and  $\text{AlCl}_4^-$  ions will be present.  $\text{Al}_2\text{Cl}_7^-$  are the only reducible species from which aluminium can be electrodeposited [26]. Ionic liquid of present work reported to contain the acidic species of the type  $[\text{AlCl}_2 \cdot n\text{Urea}]^+$  cation which is the active acidic species within the basic  $\text{AlCl}_4^-$ . This cation was reported to be present in the liquid phase of ionic liquid within the 1: 1 to 2: 1 mole ratios of  $\text{AlCl}_3$ : Urea respectively. Hence, ionic liquid of the mole ratio of 1.6: 1 and 2: 1 was used for electrodeposition of aluminium metal on copper substrate. Both ratios were diluted with 35v% toluene to insure fast mobility and expected better coating [31]. The electrodeposition were conducted at -0.6V potential for 2 hours' at room temperature. In the 1.6: 1 mole ratio, the well adhered electrodeposited aluminium particles were larger than in 2: 1 mole ratio ranged from (600 nm-1  $\mu\text{m}$ ) in a chips shape arranged in line compared with(200-550) nm in a leaf dendritic shape. Current densities were found to follow the dilution as it was 6.6 mA/cm<sup>2</sup> in 1.6: 1 mole ratio while increased to 10 mA/cm<sup>2</sup> in 2: 1 mole ratio, due to the increase in the number of ions in the electrolyte [31].

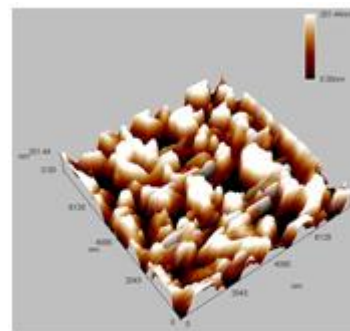


**Figure 1:** SEM images of aluminium deposited from (a) 2 AlCl<sub>3</sub>: 1Urea, (b) 1.6 AlCl<sub>3</sub>: 1Urea both diluted with 35v% of toluene at -0.6 V, 2 hours, room temperature and under statistic air. Each SEM image (left) is paired with the corresponding optical photograph of the same sample (right)

The appearance of coated aluminium on the cathode was silvery white as shown in the corresponding optical photograph of the same sample in Figure (1). On increasing the concentration, the cathodic polarization decreases due to the decrease in the thickness of the diffusion layer at the cathode. An increase in the concentration of ions at the cathode favors growth of the existing layer of the deposit and hence, resulting in the formation of larger amount of coated aluminium [32]. AFM images and data are presented in Figure 2(a) and (b) and Table 1 (A) respectively. It can be seen that both total grain and roughness are larger in 2: 1 mole ratio than 1.6: 1 mole ratio.



(a)



(b)

**Figure 2:** AFM images (contact mode) of aluminium deposited (SEM shown in Figure 1); (a) from 2: 1 mole ratio AlCl<sub>3</sub>: Urea ionic liquid, (b) from 1.6: 1 AlCl<sub>3</sub>: Urea ionic liquid

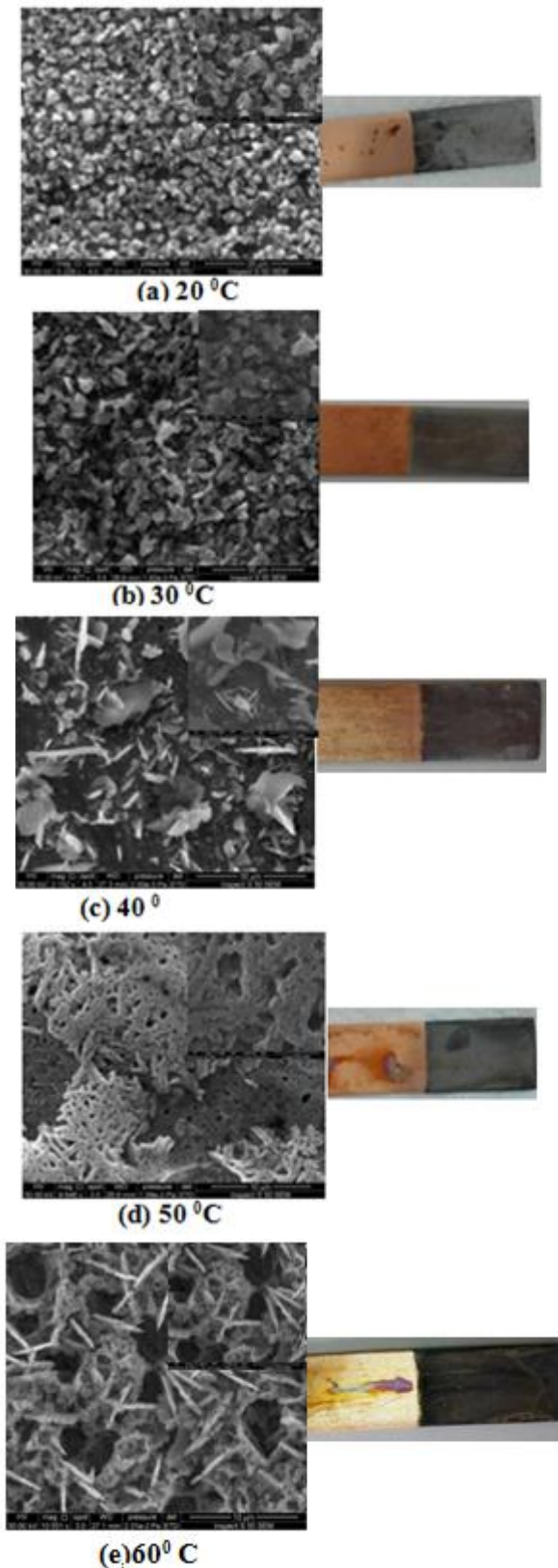
### 3.2 Effect of temperature on the morphology of deposited aluminium

Temperature is expected to have an impact on the surface morphology of aluminium coatings [33], so it was useful to study the temperature effect on electrodeposition of aluminium in this ionic liquid. The effect of a temperature range from 20-60 °C on surface morphology was investigated using 1.3: 1 mole ratio AlCl<sub>3</sub>/Urea net ionic liquid covered with Decan. All experiment was carried out for 1.5 hour at -0.6 V under statistic air. Figure (5) shows the variation in current density as a function of temperature, which increases with increasing temperature. Temperatures would influence physical properties of the electrolyte, such as conductivity, as electrical conductivity increase with increasing the temperature due to lowering the viscosity of the electrolyte and hence the mobility of the ions increases and would cause an increase in rate of reaction [33]. SEM examinations of coated aluminium at different temperatures are presented in Figure (3). At 20 °C the shape of particles is sand like Figure 3(a), while at 30 °C the shape was flak Figure 3(b), both were metallic coating and well adhered to copper substrate. Aluminium was shaped as needles and flak at 40 °C Figure 3 (c) while a net of needles was formed at 50 °C Figure 3 (d) and a sponge with needles at 60 °C Figure 3 (e). The non-completely removed ionic liquid from substrate caused a variation in visual appearance of the coated aluminium on copper. Yet, reflection of light as more dense and smaller particles of coating would be brighter (samples at 20 °C and 30 °C) while with less dense having hole spaces have dull appearance (samples at 40, 50 and 60 °C) with poor adherence at 60 °C. AFM images and data are presented in Figure (4) and Table 1. Sec(b) respectively. The data were inconsistent with temperature (total grain and roughness) except the average height of the coated particles increase with temperature from 123 nm to 152 nm from 20°C to 60°C respectively. The amount of adhered coating of aluminium on copper increased from 20 °C to 50 °C as shown in Table 1 (B) except at 60 °C when the percentage of aluminium dropped from 91% to 82% at 60 °C.

It was found that the appearance of coated aluminium was silvery white at 20 °C, silver at 30 °C, silvery gray at 40 °C, gray at 50 °C and was darker gray at 60 °C. This was,

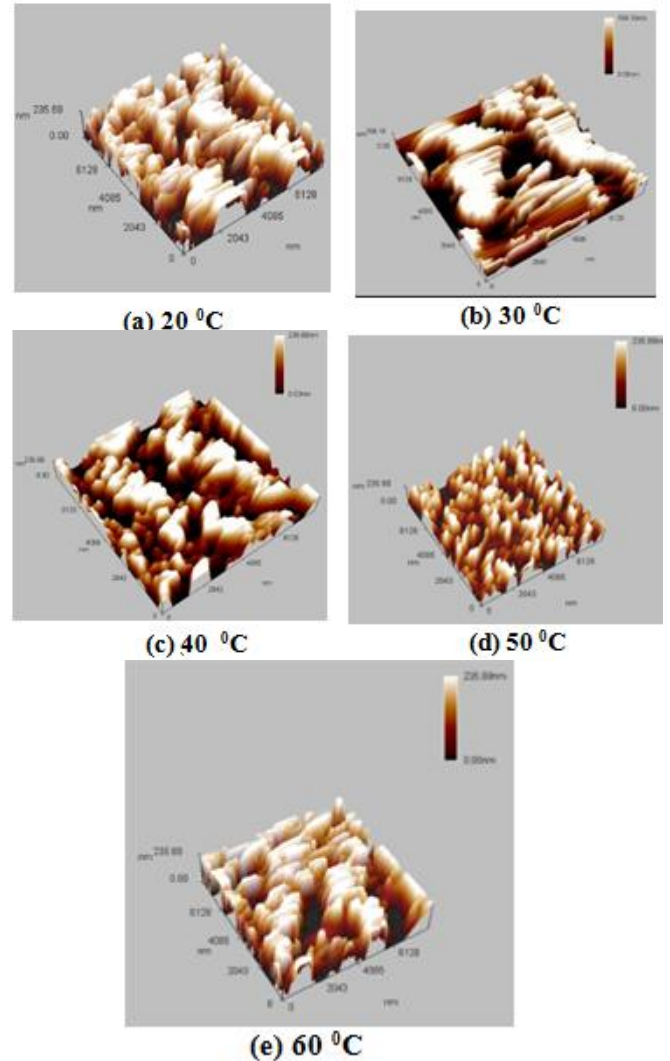


in addition to the presence of ionic liquid, also associated with changes in the shape of particles Figure (3). Manual measurement show the size of particles ranging from (600-900 nm) at 20 °C, (500-700 nm) at 30 °C, (450-650 nm) at 40 °C, (250-500nm) at 50 °C and (400-600nm) at 60 °C.

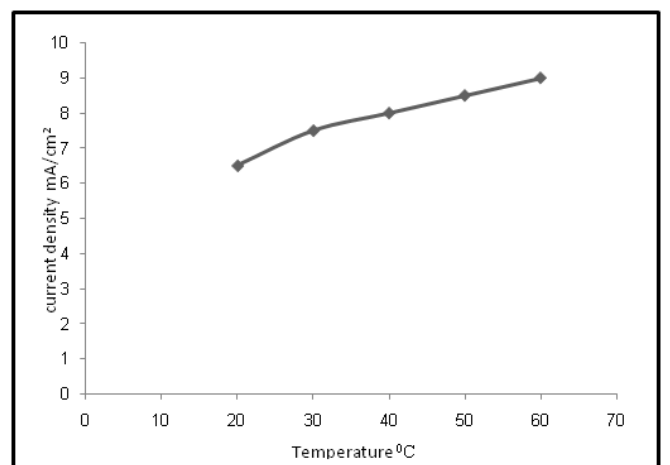


**Figure 3:** SEM images (left) of aluminium deposited from 1.3: 1 mole ratio  $\text{AlCl}_3$ : Urea ionic liquid for 90 minutes, -0.6V at different temperature under statistic air. Each

SEM image (left) is paired with the corresponding optical photograph of the same sample (right)



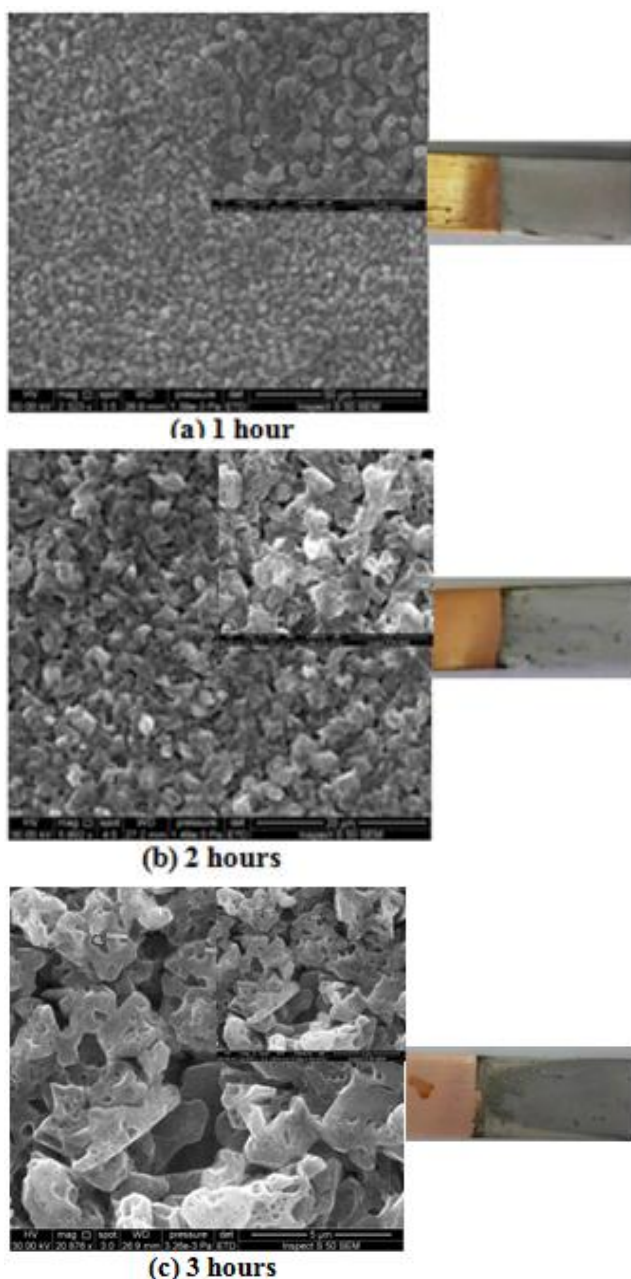
**Figure 4:** AFM images of the aluminium deposit obtained from 1.3: 1 mole ratio  $\text{AlCl}_3$ : Urea ionic liquid for 90 minutes, -0.6V at different temperature under statistic air



**Figure 5:** Relation between temperature and current density of aluminium deposited from 1.3: 1 mole ratio  $\text{AlCl}_3$ : Urea ionic liquid for 90 minutes, -0.6V at different temperature under statistic air

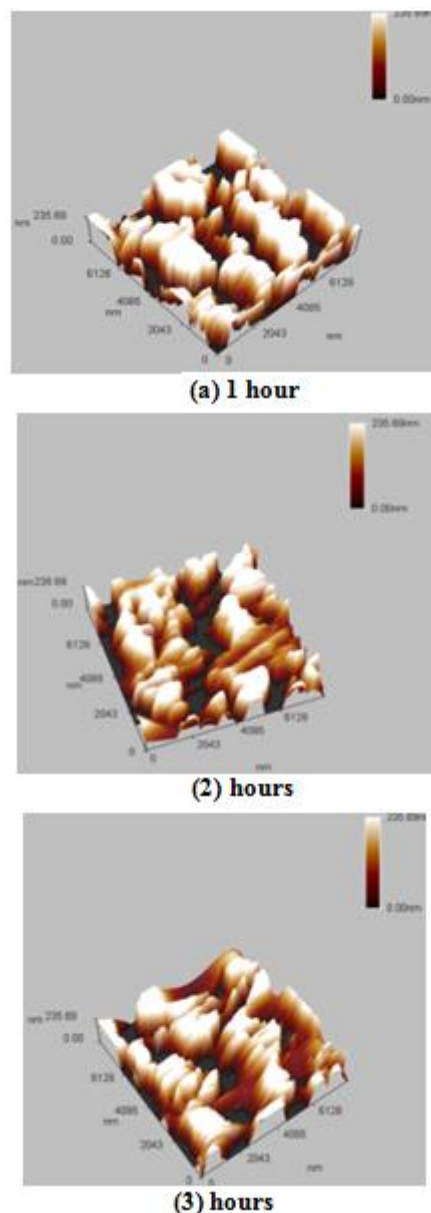
### 3.3 Effect of time on the morphology of deposited aluminium

Long coating time was expected to influence the thickness of deposited metal and effected the aggregation of particles and their compaction [34]. The effect of deposition time of aluminium ranging from 1 to 3 hours was investigated from 1.3: 1 mole ratio of  $\text{AlCl}_3$ : Urea net ionic liquid covered with Decan at  $-0.6\text{V}$  and  $25^\circ\text{C}$  under statistic air. Figure (6) show the SEM images for deposited aluminium appeared as silvery white as shown in the optical photograph of the sample in Figure (6), with bright, dense and homogeneous deposits. Manual measurement show the size of particles was  $(1-1.5\ \mu\text{m})$  at 1 hour,  $(1-1.7\ \mu\text{m})$  at 2 hours and  $(1.1-1.8\ \mu\text{m})$  at 3 hours.



**Figure 6:** SEM images (left) of aluminium deposited from 1.3: 1 mole ratio  $\text{AlCl}_3$ : Urea ionic liquid from different deposition time,  $-0.6\text{V}$  at room temperature  $25^\circ\text{C}$  under statistic air. Each SEM image (left) is paired with the corresponding optical photograph of the same sample (right).

AFM image presented in Figure (7) show the accumulation and the building up of particles that increased with increasing the deposition time. Table 1 (C) show the total grain, roughness, average size, average height and the % of aluminium coating that all increased with time.



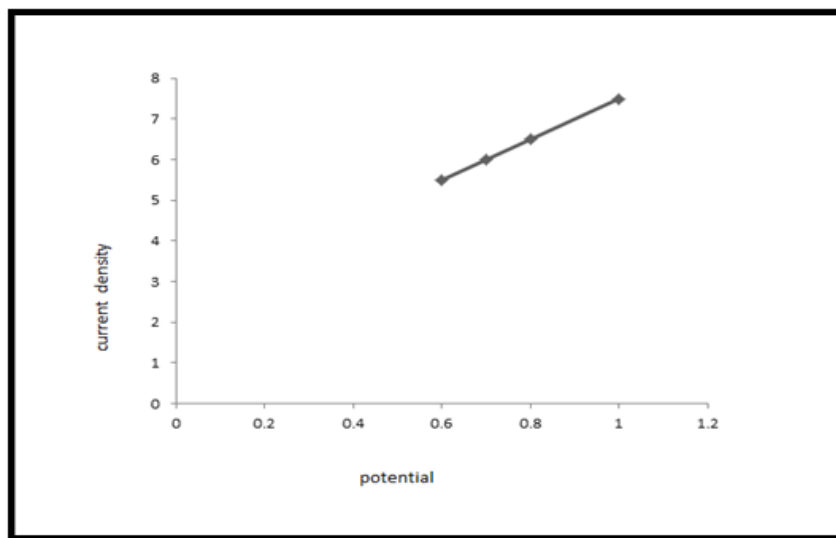
**Figure 7:** AFM images of the aluminium deposit obtained from 1.3: 1 mole ratio  $\text{AlCl}_3$ : Urea ionic liquid using different deposition time.

### 3.3 Effect of the potential on the morphology of deposited aluminium

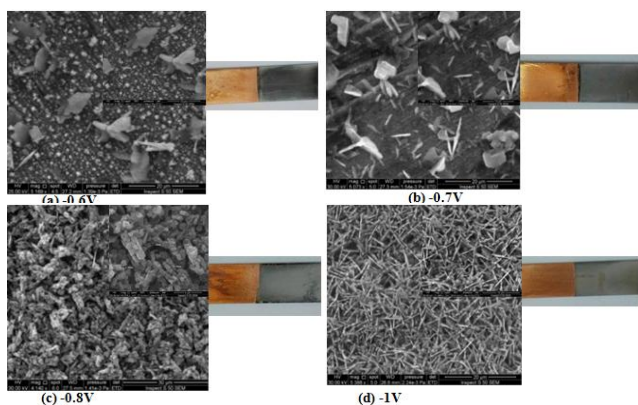
The effect of cell voltage on current density of the electrodeposition process of aluminium was studied in the range from  $(-0.6\text{V}$  to  $-1\text{V})$  at temperature of  $35^\circ\text{C}$  from 1.3: 1  $\text{AlCl}_3$ /Urea net ionic liquid covered with Decan under statistic air. Figure (8) shows the variation of current density with cell voltage. The current density was also found to increase linearly with increasing potential leading to an increase in the rate of reduction of aluminium at the cathode.

Figure (9) show the SEM images of deposited aluminium at different potential. It was clearly seen that deposited aluminium appearance is silvery as shown in the optical photograph of each sample Figure (9). The shape of particles at -0.6V and -0.7V were similar with two layers. The first layer was small while the second layer was larger, this different in size maybe due to the different in substrate. The first layer adherent on the copper substrate, while the second was adherent on the first layer of aluminium which adherent on the copper substrate. Manual measurement for particles at -0.6V shows that the

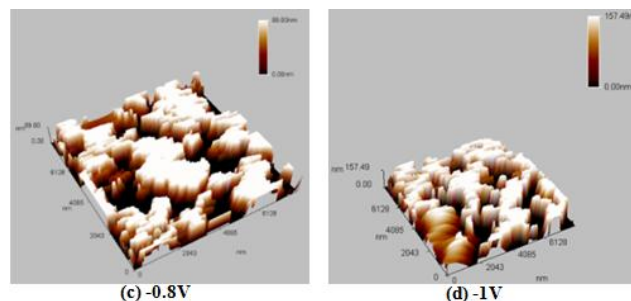
small particles nearly 200nm while the large particles nearly 600nm. At -0.7V the particles size was close to 250 nm for the first layer while the particles at the second layer was 400 nm. At -0.8V the particles was nearly (600-900nm) compacted together with prism shape. At 1V the shapes of particles like compact needles and the arrangement of particles in random orientation. Some are vertical and other are horizontally built on each other's ranging from (700-1200nm).



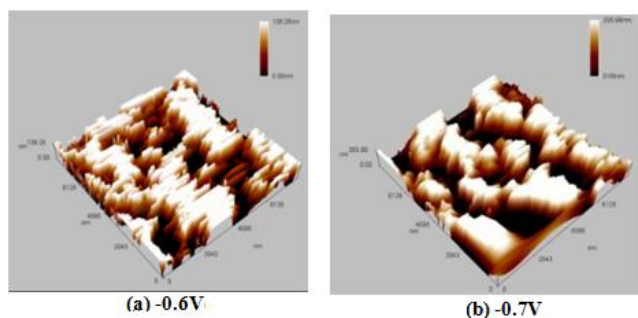
**Figure 8:** Relation between potential and current density of aluminium deposited from 1.3: 1 mole ratio  $\text{AlCl}_3$ : Urea ionic liquid from different potential,  $35^\circ\text{C}$  and 2 hours under statistic air.



**Figure 9:** SEM images (left) of aluminium deposited from 1.3: 1 mole ratio  $\text{AlCl}_3$ : Urea ionic liquid from different potential,  $35^\circ\text{C}$  and 2 hours under statistic air. Each SEM image (left) is paired with the corresponding optical photograph of the same sample (right)



**Figure 10:** AFM images of the aluminium deposit obtained from 1.3: 1 mole ratio  $\text{AlCl}_3$ : Urea ionic liquid using different potential



From Table (1) it can be seen that increasing the  $\text{AlCl}_3$  mole ratio would influence the amount of coated aluminium on copper (compare samples of A1,A2 with D1) which conducted at 2: 1, 1.6: 1 and 1.3: 1 mole ratio of  $\text{AlCl}_3$ -Urea, although the latter sample was at  $10^\circ\text{C}$  higher than the previous samples. Lowering the temperature to  $20^\circ\text{C}$  for sample B1 or increasing to  $35^\circ\text{C}$  for sample D1 did not give large difference in the amount of Al although the time for both samples were different too (1.5 and 2 hours respectively).

Nanoparticle size of electroplated aluminium on copper at different condition as summarized in Table (1), however, a micro size of aluminium particle also observed at



variable condition, yet it did not exceed 1.2  $\mu\text{m}$  as in samples C1 and D4.

**Table 1:** Grain number, roughness, average size, average height, % of Al coating and particle size of electrodeposited aluminium from  $\text{AlCl}_3/\text{Urea}$  ionic liquid at different conditions

Samples	No.	Potential (volt)	Mole ratio	Temperature $^{\circ}\text{C}$	Time (hour)	Total grain	Roughness [nm]	Avg. size [ $\text{nm}^2$ ]	Avg. height [nm]	% of Al from EDAX	Particle Size [nm]
A	1	-0.6	2: 1	25	2	224	46	147806	69	95	200-250
	2	$\neq$	1.6: 1	$\neq$	$\neq$	223	62	145975	80	72.2	600-1000
B	1	-0.6	1.3: 1	20	1.5	276	67	150883	123	55	600-900
	2	$\neq$	$\neq$	30	$\neq$	224	56	183420	121	76.1	500-700
	3	$\neq$	$\neq$	40	$\neq$	256	57.1	147806	133	80.1	450-650
	4	$\neq$	$\neq$	50	$\neq$	259	74	213961	139	91	250-500
	5	$\neq$	$\neq$	60	$\neq$	160	76.2	310630	152	82	400-600
C	1	-0.6	1.3: 1	25	1	85	62	420210	128	64.93	750-1200
	2	$\neq$	$\neq$	$\neq$	2	113	67	414175	129	68.16	500-950
	3	$\neq$	$\neq$	$\neq$	3	123	75	408693	137	76.86	00-1000
D	1	-0.6	1.3: 1	35	2	203	58	118166	100	61	200-600
	2	-0.7	$\neq$	$\neq$	$\neq$	136	41	313435	99	72	600-1000
	3	-0.8	$\neq$	$\neq$	$\neq$	116	40	106758	77	86.7	600-900
	4	-1	$\neq$	$\neq$	$\neq$	231	62	174695	108	88.2	700-1200

#### 4. Conclusions

The RTIL of aluminium chloride and urea have properties different from other ionic liquids based on quaternary ammonium cations or chloroaluminate ionic liquid. It was easy to prepare, less water sensitive and easy to handle by adding a layer of decan on the top of the liquid as protective top layer from air, so the electrodeposition process can be conducted under statistic air. Aluminium was deposited from different mole ratios of  $\text{AlCl}_3/\text{Urea}$  within the range of 2: 1-1: 1 respectively and the deposition adhered on copper cathode very well. The surface morphology of deposited aluminium on copper substrates from  $\text{AlCl}_3/\text{Urea}$  ionic liquids were affected by variations in temperature, mole ratio, potential and deposition time. Yet they were either in a nanoparticle size or larger but less than 1.3  $\mu\text{m}$ . It appears that the shape of deposits microstructure changed as a function of temperature and the morphology of deposits was also dependent on temperature. Similar results were obtained at different mole ratio of electrolyte, as the morphology and the shape of deposits changed with changing mole ratios of electrolyte. The deposition at different time showed linear relationship between time and the percentage of deposited aluminium giving the larger particle size at the 2<sup>nd</sup> layer. Changing electrodeposition potential resulted in changing in the shape and the morphology of deposited aluminium. At -0.6 and -0.7V the shape was relatively similar but at -0.8 and -1v the shape was compact, dense, and uniform. The current density increased with increasing potential, temperature and mole ratio.

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