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Pulse current electrodeposition of Al from an $AlCl_3$-EMIC ionic liquid

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ABSTRACT

Electrodeposition of aluminum from an $AlCl_3$-EMIC ionic liquid with or without the addition of saturated $LaCl_3$ was carried out by both direct- and pulse-current plating methods. The effects of various parameters, including current density, pulse frequency, current on/off duration (t_{on} and t_{off}), and temperature, on deposit morphology and crystal size were investigated. Deposits prepared by pulse-current plating gave a brighter and flatter surface than those prepared by direct-current plating at appropriate pulse current parameters. Temperature and pulse–current frequency (t_{off}) were shown to significantly affect deposit morphology. Coalescence of grains during t_{off} periods in the pulse current plating was observed, especially at temperatures above 60 °C. Increasing the temperature from 25 to 90 °C caused an increase in deposit grain size and resulted in a change of grain shapes from a small sphere-like form to a feather-like form. As a result, the adhesion of the deposited aluminum to the substrate was lowered. Smaller grain sizes and well-adhered deposits were achieved at lower temperatures. For example, deposition at 25 °C resulted in the smallest crystal size of about 0.3 μm under the conditions of $t_{on} = 80$ ms, $t_{off} = 20$ ms, and $i = 8$ mA/cm^2. Furthermore, the addition of $LaCl_3$ to the melt at 60 °C effectively reduced the porosity and improved compactness of deposits.

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1. Introduction

Room temperature ionic liquids have been employed as media for the electrodeposition of aluminum and its alloys, e.g., Al–La, Al–Mo, Al–Zr, AlInSb [1–19]. In particular, the $AlCl_3$-ethyl-3-methyl imidazolium chloride (EMIC) system has been considered the most promising electrolyte due to its excellent physicochemical properties. As previously reported [16,20–22], direct-current plating can be used to electrodeposit Al coatings from an $AlCl_3$-[EMIC] melt. However, the current density is limited to a range of 5–70 mA/cm^2 at a temperature range of 20–90 °C [21,22]. Higher current densities result in a gradually decreasing concentration gradient of reactant species caused by both a relatively low ion-diffusion rate and a gradually increasing diffusion-layer thickness. Of note, the morphology, grain size and compactness of the deposits are usually dependent on electroplating parameters such as current density and overpotential. Specifically, a larger current density or larger overpotential will help to form a smaller-size deposit.

According to the literature [23], in pulse plating with short pulse durations, two distinct cathodic diffusion layers exists between the cathode and the solution, including the pulsating diffusion layer and the stationary diffusion layer. The concentration gradient in the pulsating diffusion layer can be very high, allowing the pulse current density to reach extremely high values. Therefore, pulse current can also be used to electrodeposit Al in order to reduce the grain size of deposits. For example, when employing a square-wave pulse current, which changes current with time, current density can be maintained at a high value during the on-current period by keeping a high instantaneous concentration gradient of reactant species. During the off-current period, the concentration gradient for the reactant species immediately disappears, eliminating the possibility of forming a smaller concentration gradient over a long-duration electrodeposition. These processes are repeated continuously during the entire electrodeposition to ensure a larger current density or overpotential, which consequently increases the nucleation rate of electrodeposition and reduces the grain-size of deposits [24]. Literature reports have shown that pulsed currents greatly improve surface morphology [25]. The objectives of this study were to employ a square-wave pulse current-plating method to electrodeposit an aluminum coating from an $AlCl_3$-EMIC ionic liquid with or without the addition of $LaCl_3$ and to study the effects of pulse current parameters and temperature on deposit morphology and crystalline size.

2. Experimental

Anhydrous aluminum chloride was prepared as previously reported by sublimation of a two-phase molten salt consisting of 1 wt% NaCl and $AlCl_3$ (>99.0 wt%) with a small amount of high-purity Al flakes (99.999 wt%)[16,26]. Anhydrous lan-

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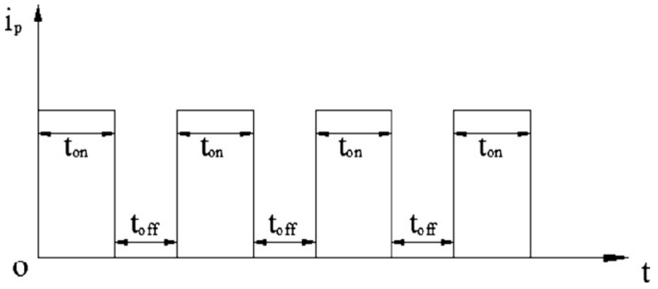

Fig. 1. Schematic for square-pulse train for electrodeposition of Al from the ionic liquid.

thanum chloride was prepared by gradually heating a solution of $LaCl_3 \cdot 7H_2O$ and NH_4Cl (1:8 molar ratio) to 120 °C, 200 °C and 340 °C and keeping for 3 h at each temperature. Upon completion of the dehydration, the anhydrous $AlCl_3$ and $LaCl_3$ were immediately transferred to a glove box until further use. Prior to the preparation of the $AlCl_3$-EMIC ionic liquid, EMIC (>97 wt%) was dried in phosphorus pentoxide (P_2O_5) in a glove box for 24 h. An acidic ionic liquid of $AlCl_3$-EMIC with a molar ratio of 2:1 was prepared as previously reported [26]. Finally, a $LaCl_3$-saturated $AlCl_3$-EMIC ionic liquid was obtained by adding anhydrous $LaCl_3$ to the above-prepared $AlCl_3$-EMIC ionic liquid while stirring for 12 h.

A tungsten wire served as a working electrode and two high-purity aluminum (99.999%) wires served as a counter electrode and a reference electrode, respectively. Cyclic voltammograms were carried out in a nitrogen-filled glove box in a three-electrode electrochemical cell using a Princeton Applied Research Corporation Model 2273 Potentiostat/Galvanostat. Direct- and pulse-current depositions were performed using a two-electrode setup (i.e., cathode and anode) with a pulse power (SMD-30 Digital Pulse Electroplating Power, China). A copper plate (>99%) was employed for the cathode substrate and a high-purity aluminum (99.999%) wire was used for the anode. Both electrodes were pretreated according to the procedure described previously [27].

After electrodeposition, all the samples were thoroughly cleaned with deionized water and dried in air. The morphology of the deposits was visualized using scanning electron microscopy (SEM, JSM-6360LV) and the chemical compositions were monitored using an auxiliary X-ray energy dispersive spectroscopy (EDS). Phase compositions were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and X-ray diffraction (XRD).

3. Results and discussion

Electrodeposition of aluminum was conducted on a copper substrate from the 2:1 molar ratio $AlCl_3$-EMIC melt by direct- and pulse-current plating. The square-pulse current train that was used is shown in Fig. 1, where t_{on} and t_{off} are current on and off durations in ms and i_p is the pulse current density in A/cm^2. XRD and EDS analyses showed that the deposits were composed of Al when using either pulse-current plating (Fig. 2) or by direct-plating (data not shown). The deposits prepared under 20 mA/cm^2 by direct-current plating at 60 °C were composed of ∼10 μm, strip-like grains (Fig. 3a) and showed a more compact surface than those prepared under 5 mA/cm^2 with ∼20 μm, sheet-like grains (Fig. 3b). These results indicated that a higher current density (or overpotential) could improve deposit compactness and reduce grain size. However, upon further increasing the current density to 30 mA/cm^2, the deposits become darker and were composed of dispersed Al_2O_3 granules (as determined by EDS). As a result, the deposits exhibited a lowered coherence to the copper substrate. This phenomenon was also observed in the $AlCl_3$-TMPAC melt [21] and may be due to the ability to deposit small-size aluminum grains (e.g., nano-aluminum grains) at a higher current density; these grains exhibited a higher activity and could react with oxygen to form Al_2O_3.

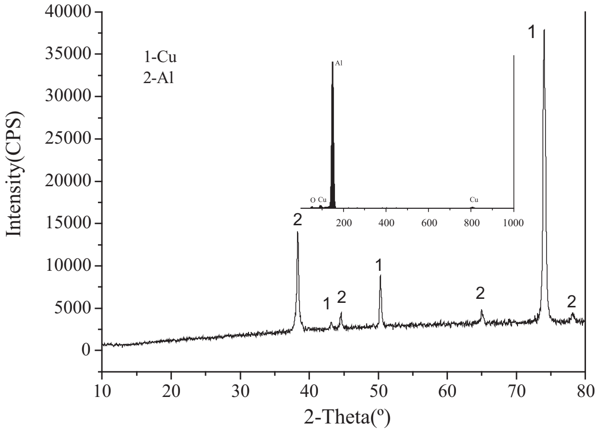

Fig. 2. X-ray diffraction pattern and EDS analysis (the inset) of deposit prepared under $i_m = 20\ mA/cm^2$; $t_{on} = 9$ ms; $t_{off} = 1$ ms; $T = 60$ °C and $t = 30$ min.

Pulse current plating was applied to electrodeposit aluminum at conditions of average current density of 5 mA/cm^2, $t_{on} = 9$ ms, and $t_{off} = 1$ ms (Fig. 3c). The deposits consisted of uniform and regular sphere grains of about ∼15 μm and gave a brighter and flatter surface than those deposited by direct-current plating at the same average current density (Fig. 3b).

The pulse-current parameters employed in this work, average current density (i_m), pulse current density (i_p), pulse frequency (f), on-current period (t_{on}) and off-current period (t_{off}), satisfy the relations in Eqs. (1) and (2),

$$i_m = \frac{i_p t_{on}}{t_{on} + t_{off}} \tag{1}$$

$$f = \frac{1}{t_{on} + t_{off}} \tag{2}$$

where i_m is average current density in A/cm^2, i_p is pulse current density in A/cm^2, t_{on} is the on-current period in ms, t_{off} is the off-current period in ms, and f is frequency in Hz.

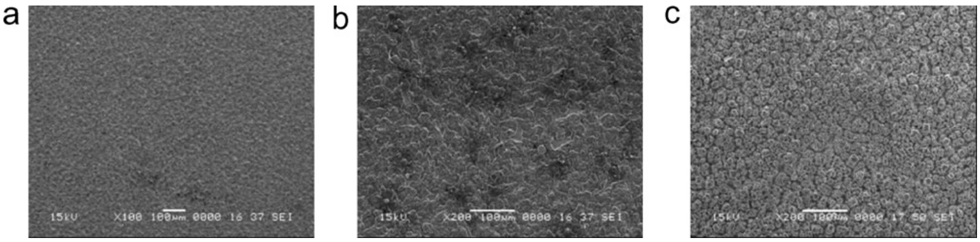

Fig. 3. SEM micrographs of deposits on Cu substrate of an $AlCl_3$-EMIC (2:1 molar ratio) at 60 °C for 30 min; (a) $i_m = 20\ mA/cm^2$; (b) $i_m = 5\ mA/cm^2$; (c) $i_m = 5\ mA/cm^2$; $t_{on} = 9$ ms; $t_{off} = 1$ ms.

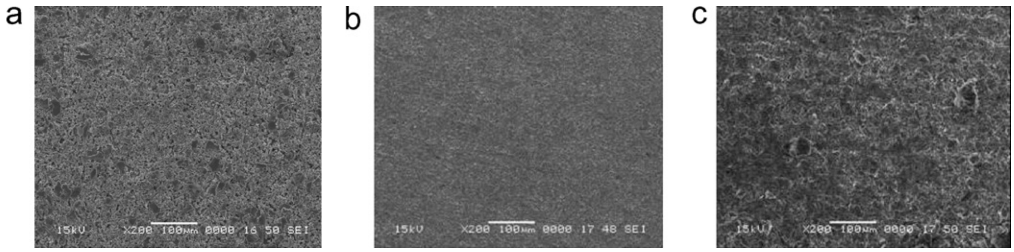

Fig. 4. Effects of pulse frequency on deposits of $AlCl_3$-EMIC (2:1 molar ratio) at 60 °C for 30 min at t_{on}/t_{off} = 9:1; i_m = 20 mA/cm^2 at (a) 10 Hz; (b) 100 Hz; (c) 500 Hz.

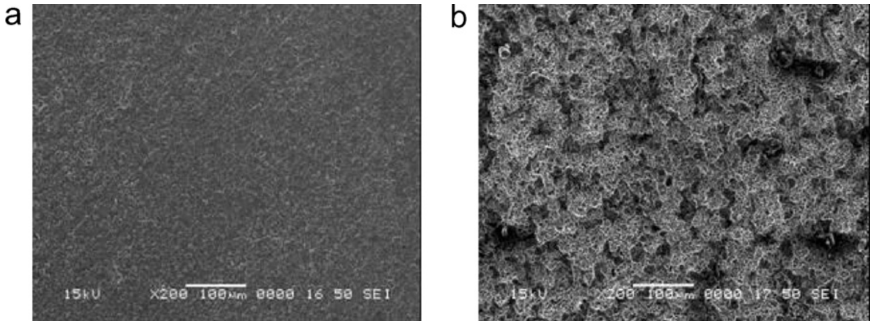

Fig. 5. Effects of t_{on} and t_{off} on deposits in $AlCl_3$-EMIC (2:1 molar ratio) melt i_m = 20 mA/cm^2, f = 100 Hz at 60 °C for 30 min at (a) t_{on} = 8 ms; t_{off} = 2 ms; (b) t_{on} = 5 ms; t_{off} = 5 ms.

In order to examine the effects of pulse frequency on the deposits, different pulse frequencies were applied to electrodeposit aluminum at a fixed ratio of t_{on}/t_{off} = 9:1 with an average current density of i_m = 20 mA/cm^2 at 60 °C, the results are shown in Fig. 4a–c. The corresponding pulse current density (i_p) was 22.2 mA/cm^2 as calculated from Eqs. (1) and (2). By comparison, the deposits in Fig. 4b showed a more compact and smooth surface with a grain-size of ~5 μm and lowered porosity. In contrast, the deposits prepared under 10 Hz (t_{off} = 10 ms and t_{on} = 90 ms) gave a flat surface with ~15 μm grain size and appeared more porous than others, which is likely due to H_2 evolution. In fact, even when prepared by normal methods, the EMIC ionic liquid invariably contains small quantities of water, providing a source of H_2 evolution during Al electrodeposition [28]. Pulse-current plating at a frequency of 500 Hz (t_{off} = 0.2 ms and t_{on} = 1.8 ms) gave deposits with the highest surface roughness with some island-like nodules and contained the biggest grains of about ~25 μm because they were nearly continuously plating (Fig. 4c).

The effects of t_{off} values on deposits were investigated in the same melt as above at the conditions of f = 100 Hz and i_m = 20 mA/cm^2 at 60 °C. The morphologies of the deposits as visualized with SEM are shown in Fig. 4b, 5a and b. When t_{off} = 5 ms (t_{on} = 5 ms), the deposits appeared black with thin, porous surfaces that were less adhered to the substrate (Fig. 5b). Although quality deposits were expected with a higher pulse current density, such as 40 mA/cm^2, these were not observed. The deposits shown in Figs.4b and 5a were prepared under current densities of 25 and 22 mA/cm^2, respectively, and were characterized by more compact and flat surfaces. The different t_{off} values of 5 ms, 2 ms and 1 ms may be responsible for these results, as the deposited grains would coalescence during the t_{off} period to form irregular and larger grains. From the above results, a t_{off} value of 1 ms was found to be most optimal in the $AlCl_3$-EMIC (2:1 molar ratio) melt with the conditions of f = 100 Hz and i_m = 20 mA/cm^2 at 60 °C.

Temperature is also expected to have significant effects on the morphology and grains size of deposits. Electrodeposited aluminum from the same melt (2:1 molar ratio AlCl3-EMIC) at the conditions of t_{on}/t_{off} = 9:1, f = 100 Hz, and i_m = 20 mA/cm^2 for 30 min at 80 and 90 °C are shown in Fig. 6a and b. Both deposits were less compact and composed of grains larger than ~50 μm. The deposit prepared at 80 °C was composed of stone-like grains, while those deposited at 90 °C contained feather-like grains. These results indicate that increasing the temperature during pulsed-current electrodeposition not only results in an increase in the deposit grain size but also in a change in grain shape. Both deposits showed a lowered adhesion to the substrate, especially those prepared at 90 °C. Electrodepositions of aluminum by direct and pulse current plating were also carried out at 25 °C (Fig. 7a–c). As shown in Fig. 7a and b, the deposits by pulse-current plating under the conditions of 8 mA/cm^2, t_{on} = 80 ms, and t_{off} = 20 ms showed a more

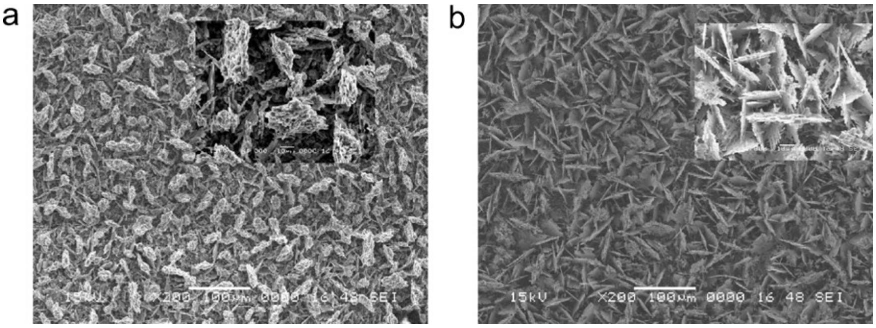

Fig. 6. Temperature effects on electrodeposits from $AlCl_3$-EMIC (2:1 molar ratio) melts; t_{on}/t_{off} = 9:1; f = 100 Hz; i_m = 20 mA/cm^2; t = 30 min at (a) 80 °C and (b) 90 °C.

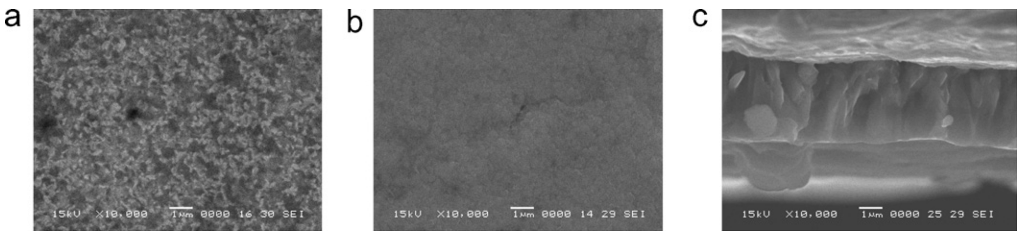

Fig. 7. Direct-current plating and pulse-current plating from an $AlCl_3$-EMIC melt at 25 °C for 30 min at (a) 10 mA/cm^2; (b) 8 mA/cm^2; t_{on} = 80 ms; t_{off} = 20 ms; (c)10 mA/cm^2; t_{on} = 80 ms; t_{off} = 30 ms.

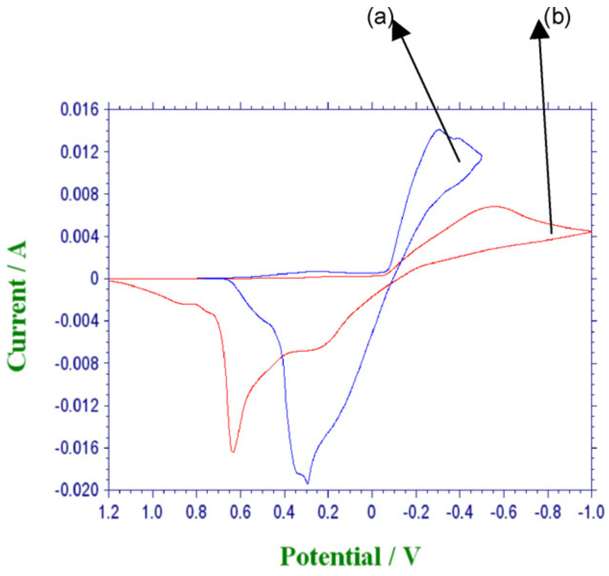

Fig. 8. Cyclic voltammograms recorded on a tungsten electrode in a 2:1 molar ratio $AlCl_3$-EMIC melt. WE, RE and CE: high-purity aluminum wires. WE area: 0.2512 cm^2. Scan rate: 100 mV/s. (a) 60 °C; (b) 25 °C.

compact and flatter surface than those deposited by direct-current plating at 10 mA/cm^2. Although the pulse current density was also 10 mA/cm^2, the same value as the direct current plating in Fig. 7a, the deposits by pulse current plating in Fig. 7b were composed of smaller, ~0.3 μm spherical grains. Furthermore, although t_{off} = 20 ms, it did not cause an increase in deposit grain size. These results imply that temperature has a significant effect on grain size and the morphology of the deposit in an $AlCl_3$-EMIC melt. Lower temperatures are favorable for obtaining deposits with smaller grain sizes. This finding can be explained by the cyclic voltammograms recorded on a tungsten electrode in the 2:1 molar ratio $AlCl_3$-EMIC melt at 25 °C and 60 °C (Fig. 8). The onset potential for aluminum ion reduction did not change with temperature, but the overpotential at 25 °C was much greater than that for 60 °C at the same current density. Overpotential η values influence the nucleation rate of deposited aluminum according to the relationship shown in Eq. (3). The greater overpotential η at 25 °C would result in a larger nucleus formation rate of deposited aluminum than that at 60 °C, resulting in a smaller grain size at 25 °C.

$$V = K_1 \exp\left(\frac{-K_2}{|\eta|}\right)\ \mathrm{s}^{-1}\,\mathrm{cm}^{-2} \tag{3}$$

At 25 °C, a distinct column crystal growth was observed along the cross-section of the pulse-plated deposits (Fig. 7c). In summary, we found that lower temperatures significantly reduce grain coalescence and decrease deposit porosity.

As previously reported [16,29], the addition of $LaCl_3$ to the $AlCl_3$-EMIC melt can improve the morphology of deposits. Indeed, upon the addition of $LaCl_3$, the deposits obtained by direct-current plating showed a regular face-centered cubic arrangement of Al as determined by XRD. The addition of $LaCl_3$ did not, however, change the way nucleus formation occurred in the deposits. The effects of direct- and pulsed-current parameters on deposits of $AlCl_3$-EMIC melts that were saturated with $LaCl_3$ were investigated. The resulting changes in surface morphology of deposits were shown in Figs. 9 and 10. As compared with the deposits without $LaCl_3$ (Fig. 3a), those with added $LaCl_3$ showed very compact and flat surface without any distinct porosity Obviously, $LaCl_3$ effectively improved the morphology of the deposit. But pulse-current plating did not exhibit significant effects (Figs. 9 and 10). The deposits were prepared under the conditions of i_m = 20 mA/cm^2, t = 20 min, t_{on} = 8 ms, t_{off} = 2 ms, and f = 100 Hz and were composed of Al with 0.1 wt% La content (as determined by ICP-AES analysis). These deposits gave nearly the same-size grain as those formed by direct-current plating. However, the pulse-current plating deposits exhibited a distinct coalescence between grains indicating that pulse-current plating does not result in deposits of better quality than the direct-current plating method when $LaCl_3$ is added to the ionic melt.

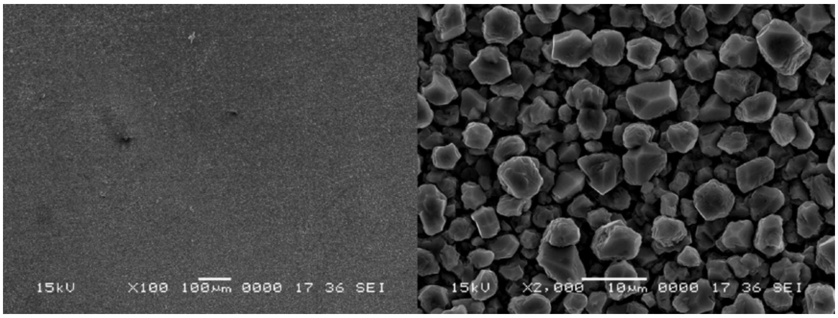

Fig. 9. Direct-current plating of an $AlCl_3$-EMIC-$LaCl_3$ melt at 60 °C at i_m = 20 mA/cm^2 and t = 30 min.

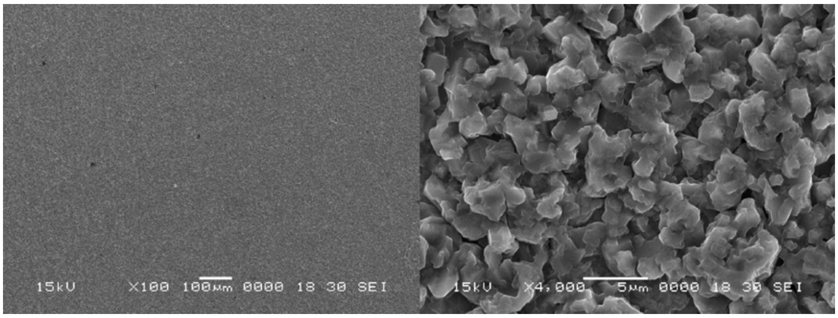

Fig. 10. Addition of $LaCl_3$ to a 2:1 molar ratio $AlCl_3$-EMIC melt at 60 °C at conditions of $i_m = 20\,mA/cm^2$; $t = 20$ min; $t_{on} = 8$ ms; $t_{off} = 2$ ms; $f = 100$ Hz.

4. Conclusions

Aluminum deposits were obtained from a 2:1 molar ratio $AlCl_3$-EMIC melt by both direct-current and pulse-current plating. At the appropriate conditions, the pulse-current plated deposits exhibited brighter and flatter surfaces compared to those obtained under the same average current density by direct-current plating. In addition to pulse-current density, other pulse parameters, including pulse frequency, t_{on} and t_{off} values, and temperature, were also found to play significant roles in deposit morphology. There was a distinct coalescence of grains during the t_{off} period in the 2:1 molar ratio $AlCl_3$-EMIC ionic liquid during pulse current electrodeposition, especially at temperature above 60 °C. The grain size of deposits increased significantly as the temperature was increased above 60 °C. Of note, the grain shape changed from spherical to stone-like and feather-like grains at 80 and 90 °C. Alternatively, pulsed current electrodeposition at 25 °C resulted in smaller crystal sizes of 0.3 μm under the conditions of $t_{on}:t_{off} = 8:2$; $f = 20$ Hz; and $i_m = 8\,mA/cm^2$. Addition of anhydrous $LaCl_3$ to the 2:1 molar ratio $AlCl_3$-EMIC melt at 60 °C was found to effectively reduce the porosity of deposits as well as improve the deposit compactness during direct-current plating. The addition of $LaCl_3$ was not found to influence pulse-current plated deposits. Mechanistic studies are currently under way to understand the effects of various pulse current parameters on the deposition kinetics.

Acknowledgement

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